JNC TN8400 99-079

Development of Thermodynamic Databases for Geochemical Calculations

September , 1999

Tokai Works

Japan Nuclear Cycle Development Institute

JNC TN8400 99－079
September,1999

Development of Thermodynamic Databases for Geochemical Calculations

Randolph C Arthur[1], Hiroshi Sasamoto[2], Masahiro Shibata[2]
Mikazu Yui[2], Atsushi Neyama[3]

Abstract

Two thermodynamic databases for geochemical calculations supporting research and development on geological disposal concepts for high level radioactive waste are described in this report. One, SPRONS.JNC, is compatible with thermodynamic relations comprising the SUPCRT model and software, which permits calculation of the standard molal and partial molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5000 bars and 0 to 1000℃. This database includes standard molal Gibbs free energies and enthalpies of formation, standard molal entropies and volumes, and Maier-Kelly heat capacity coefficients at the reference pressure (1 bar) and temperature (25℃) for 195 minerals and 16 gases. It also includes standard partial molal Gibbs free energies and enthalpies of formation, standard partial molal entropies, and Helgeson, Kirkham and Flowers (HKF) equation-of-state coefficients at the reference pressure and temperature for 1147 inorganic and organic aqueous ions and complexes. SPRONS.JNC extends similar databases described elsewhere by incorporating new and revised data published in the peer-reviewed literature since 1991.

The other database, PHREEQE.JNC, is compatible with the PHREEQE series of geochemical modeling codes. It includes equilibrium constants at 25℃ and 1 bar for mineral-dissolution, gas-solubility, aqueous-association and oxidation-reduction reactions. Reaction enthalpies, or coefficients in an empirical log *K(T)* function, are also included in this database, which permits calculation of equilibrium constants between 0 and 100℃ at 1 bar.

All equilibrium constants, reaction enthalpies, and log *K(T)* coefficients in PHREEQE.JNC are calculated using SUPCRT and SPRONS.JNC, which ensures that these two databases are mutually consistent. They are also internally consistent insofar as all the data are compatible with basic thermodynamic definitions and functional relations in the SUPCRT model, and because primary experimental and field observations that constrain these data are consistently evaluated

within this modeling framework. The accuracy of the data in SPRONS.JNC is evaluated in the present study and elsewhere by comparison of calculated equilibrium constants with their experimental counterparts at pressures and temperatures that span much of the subcritical and supercritical regions of H_2O stability. Additional experimental investigation of mineral solubilities and aqueous reactions, particularly between 0 and 100℃, are needed to further assess, and refine if necessary, the reliability of these databases. Field studies on phase equilibria in near-surface geological environments may be useful for this purpose because associated reaction times are greater than can be accommodated experimentally. The effects on mineral-solution equilibria of metastability and solid solution, and differences in the crystallinity and state of order/disorder in minerals, must be determined, however, before reliable thermodynamic properties can be retrieved from field investigations.

---

1) Monitor Scientific, L.L.C*., Denver, Colorado, USA*(*formerly QuantiSci Inc*)

2) Japan Nuclear Cycle Development Institute, Tokai Works, Japan

3) Computer Software Development Corp., Tokyo, Japan

JNC TN8400 99－079
１９９９年９月

地球化学計算のための熱力学データベースの開発
（研究報告）

Randolph C Arthur[1)], 笹本　広[2)], 柴田雅博[2)]
油井三和[2)], 根山敦史[3)]

要旨

本報告書では，高レベル放射性廃棄物地層処分の研究開発をサポートする地球化学計算のための２種類の熱力学データベースについて報告する。一つは，SPRONS.JNC であり，この熱力学データベースは，SUPCRT モデル・ソフトウェアの中で考慮されている熱力学的な関係式を基にしており，SUPCRT ソフトウェアを用いることで，広範囲にわたる圧力・温度条件（圧力：１～5000 bars，温度：０～1000℃）下での鉱物，ガスおよび水溶液化学種の標準モル熱力学特性・部分モル熱力学特性を計算することができる。SPRONS.JNC は，195 種類の鉱物・16 種類のガスについて，25℃，１bar の条件下での生成標準モルギブス自由エネルギー，生成標準モルエンタルピー，標準モルエントロピーおよび体積に関するデータを含むと共に，Maier-Kelly 式による熱容量の温度依存式を適用した場合の各係数についても整備している。また SPRONS.JNC は，1147 種類におよぶ無機・有機イオンや錯体について，25℃，１bar の条件下での生成標準モルギブス自由エネルギー，生成標準モルエンタルピー，標準部分モルエントロピーおよび Helgeson-Kirkham-Flowers（HKF）式による温度依存に係わる係数も整備している。SPRONS.JNC は，1991 年以降に公開された新たなデータや改訂されたデータを取り入れたものであり，他の同様な熱力学データベースの拡張版である。

もう一つのデータベースは，PHREEQE.JNC であり，これは，地球化学計算コードである「PHREEQE」で用いることができる熱力学データベースである。PHREEQE.JNC は，鉱物の溶解反応，ガスの溶解反応，水溶液化学種を含む反応，酸化還元反応について，25℃，１bar の条件下での平衡定数を整備している。また PHREEQE.JNC では，０～100℃，１bar の条件下での平衡定数を算出できる様に反応エンタルピーあるいは平衡定数（log K）の温度依存に係わる各係数についても整備している。

PHREEQE.JNC に含まれる平衡定数，反応エンタルピーおよび平衡定数の温度依存に係わる係数の全ては，SUPCRT ソフトウェアおよび SPRONS.JNC を用いて計算されているので，PHREEQE.JNC と SPRONS.JNC は，同一の熱力学データベースである。またこれらの熱力学データベースに含まれる全てのデータは，基本的な熱力学の定義や SUPCRT モデルで用い

られている数式に適合し，さらに，基礎的な実験データやフィールドでの観察結果をもとに整合性がとられているという点では，これらの熱力学データベースは，内部整合性がとれたデータベースであると言える。SPRONS.JNC に含まれるデータの精度に関しては，本報告書の中でも確証されており，また他の研究者らによる，水の臨界領域付近まで温度・圧力条件をパラメータとした実験で求められた平衡定数と計算値との比較等からも確証されている。今後は，特に 0 ～100℃の条件下における鉱物の溶解度や溶液化学種の反応に関する実験的研究が必要であり，また必要に応じて，これらデータベースの信頼性を向上させていく必要がある。但し，これらのデータを実験的に研究するには，比較的長い期間を要するため，浅地中環境下での相平衡に関するフィールド調査が有効であるかもしれない。しかしながら，信頼性のある熱力学的特性がフィールド調査からもたらされる前に，準安定，固溶体，結晶度による違い，鉱物における秩序－無秩序（転移）が鉱物－溶液間の平衡に与える影響について把握しておく必要がある。

---

1) Monitor Scientific, L.L.C*., Denver, Colorado USA *(formerly QuantiSci Inc)*

2) 核燃料サイクル開発機構　東海事業所

3) コンピュータソフト開発株式会社

TABLE OF CONTENTS

1 Introduction

The Japanese repository concept for permanent disposal of high-level nuclear wastes is based on an integrated system of natural and engineered barriers to radionuclide migration. A crystalline or sedimentary host rock (into which the wastes will be emplaced at depths of 1000 m, or 500 m, respectively) will function as the natural barrier. Engineered barriers will include a bentonite buffer, steel canister and vitrified-glass waste form. The natural and engineered barriers will act in concert, such that the wastes are isolated from the geosphere for long periods of time (e.g., 1000 years), and subsequent releases of radionuclides to the biosphere are below levels that would pose an unacceptable risk to the public's health.

The Japan Nuclear Cycle Development Institute (JNC) is carrying out an applied R&D program to evaluate the feasibility of this concept[1]. The program is broad in scope, and includes field studies of various geological environments (Tono, Kamaishi and Mobara sites), laboratory investigations of chemical and transport phenomena (ENTRY and QUALITY facilities), and modeling-based assessments of repository performance (PNC, 1992). A number of these studies deal specifically with geochemical and chemical engineering issues, including:

- the stability of engineered barriers in the disposal environment over time scales of thousands to millions of years,
- the solubility, aqueous-speciation and sorption behavior of radioelements and non-radioactive elements, and
- general and site-specific geochemical processes controlling groundwater evolution.

These issues can be resolved with the aid of thermodynamic models, which are routinely used by JNC and others to interpret the results of experimental and field studies (Sasamoto *et al.*, 1999a, b, c; Iwatsuki and Yoshida, 1999; Oda *et al.*, 1996; Sasaki *et al.*, 1995), to predict the long-term chemical evolution of natural and engineered-barrier systems (Oda *et al.*, 1999; Yui *et al.*, 1999; PNC, 1992, Yui *et al.*, 1992b), and to evaluate associated impacts on repository performance (Azuma *et al.*, 1999; PNC, 1992; Yui *et al.*, 1992a).

Thermodynamic models require basic thermodynamic data over an appropriate range of temperatures and pressures. It is essential that the basic data are reliable, because, as stated by Silva *et al.* (1995), "*.. the quality of the models cannot be better than the quality of the data they are based on*". Although the validity of

[1] JNC was established in 1998, and is responsible for many of the repository R&D functions formerly assigned to the Power Reactor and Nuclear Fuel Development Corporation (PNC).

this statement is beyond dispute, it is useful to clarify what the terms "reliable" and "quality" mean in the context of thermodynamic databases. Here we adopt a pragmatic definition of both terms that is consistent with concepts underlying recent advances in the development and management of thermodynamic databases (Helgeson *et al.*, 1978; Berman, 1988, Holland and Powell, 1990; Engi, 1992; Grenthe *et al.*, 1992; Silva *et al.*, 1995; Gottschalk, 1997). Thus, a database is considered reliable (or to be of high quality) if the following conditions are met, or are approximated as closely as possible:

- *internal consistency* - internal consistency is established among all the data, and is maintained as the database is updated and revised (the concept of internal consistency is discussed further in Section 3),

- *experimental basis* - selected values of thermodynamic parameters are based on evaluations of all available types of relevant experimental (and field) studies, not just on subsets of preferred experimental technique, or over arbitrary ranges of temperature and pressure,

- *documentation* - all procedures in the evaluations are documented such that selected data are *traceable* to original experimental sources, and that these sources are *scientifically defensible* and *reproducible*, and

- *verification of accuracy* - the accuracy of data retrieved from the evaluations is verified by comparison of calculated thermodynamic quantities with their experimental counterparts.

Unfortunately, most published compilations of thermodynamic data are not internally consistent, have not been evaluated on the basis of all (or even most) available types of experimental and field studies, and are poorly documented with respect to data sources and reasons for data selection or rejection (Engi, 1992; Nordstrom and Munoz, 1985; - important exceptions are summarized in Section 3, however). For this reason, PNC[1] commissioned a two-year project beginning in 1996 to develop a thermodynamic database that adheres as closely as possible to the conditions stated above. The project was limited in scope to data for minerals, gases and aqueous species characteristic of geologic systems, and some engineered barriers (e.g., bentonite "clays" and corrosion products of the steel canister). The project was also intended to complement, and to be consistent with, similar efforts carried out by PNC to obtain reliable thermodynamic data for actinide and fission-product elements (Yui *et al.*, 1992a).

The results of the project are summarized in this report, where two new databases, SPRONS.JNC and PHREEQE.JNC, are described, and where the basic philosophy and associated procedures used to generate them are documented. The report is organized as follows. General comments addressing the objectives of this study in relation to JNC's overall R&D program are summarized in Section 2. A survey of existing, reliable thermodynamic databases appropriate for geologic systems is summarized in Section 3. The

results of the survey are used to define a general modeling-based strategy for database development and management. The model, SUPCRT[2] (Johnson *et al.*, 1991; Johnson *et al.*, 1992) is consistent with SPRONS.JNC, and is briefly described in Section 4. The SPRONS.JNC and PHREEQE.JNC databases are described in Section 5, and listings of these databases are provided in Appendices A and B, respectively. The accuracy of these databases is assessed in Section 6 by comparison of experimental and calculated equilibrium constants for selected heterogeneous reactions (mineral and gas solubilities, Appendix C) and aqueous-speciation reactions (Appendix D).

2- SUPCRT is an abbreviation of "supercritical"; SPRONS stands for Sequential-access (ASCII) file of PROperties of Natural Substances

2 Objectives

As noted by Johnson *et al.* (1991), thermodynamic databases are never completed, only abandoned. There is always a need to uncover and correct any errors in the data (not all of which are merely typographical), and to update and revise the database as the results of new experimental and field studies become available. The present study is therefore considered to be an initial effort to implement a general strategy for managing thermodynamic data within a complex and evolving R&D program. SPRONS.JNC and PHREEQE.JNC are the first products of this strategy, but it is reasonable to expect that these databases, and others, will be refined and improved by JNC in the future.

With this in mind, the objective of the study is to develop a thermodynamic database that is both *reliable* and *relevant* for conditions considered in the Japanese repository concept. The range of temperatures *(T)*, pressures *(P)* and fluid- and solid-phase compositions embraced by this concept are bounded by:

- temperatures between 0 and 100°C, but also higher temperatures that may be considered in alternative scenarios of repository evolution (e.g., the so-called volcanism scenario),
- a total (fluid) pressure between 1 bar and hydrostatic pressures at the depth of the repository (≈ 50 to 100 bars), and
- minerals, gases and aqueous species characteristic of geologic environments and engineered barriers (essentially all components of the barriers that are not radioactive).

As noted in the introduction, however, the study is also based on the premise that a reliable thermodynamic database must be compatible with all relevant types of experimental studies (e.g., calorimetry, phase equilibrium, solubility, electrochemical, etc.) over as broad a range of temperatures and pressures as possible. For this reason, the first two conditions noted above are expanded in scope to consideration of P-T-ρ (where ρ refers to density) regions of stability of fluid phases of H_2O that include both subcritical and supercritical domains. This includes high-temperature (≈ 200 - 1000°C) and high-pressure (≈ 1 - 50 kb) conditions considered in hydrothermal and phase-equilibrium experiments.

Two databases are developed in this study to best accommodate this objective. One is adopted as a *primary* database. It is a *type S* database in the sense defined by Engi (1992), and therefore includes standard molal and partial molal properties of minerals, gases and aqueous species at the reference temperature and pressure, and empirical coefficients enabling calculation of corresponding thermodynamic properties at other temperatures and pressures. These data are obtained from a number of literature sources (Section 5), where procedures to retrieve the data from the results of experimental or field studies (see Section

4.3), or by various estimation techniques (see Section 4.4), are documented. The accuracy of these data is assessed in the present study by comparing calculated equilibrium constants with corresponding values determined experimentally, or by inferences drawn from observations of mineral stability relations in natural systems (Section 6). These comparisons are often at conditions of temperature and pressure that lie considerably outside the range of conditions nominally considered in the Japanese repository concept. Thus the primary database, and SUPCRT, are used to

- assess the accuracy of basic thermodynamic data over a broad range of experimental temperatures and pressures, and
- calculate thermodynamic properties of relevant reactions at temperatures and pressures considered in the repository concept.

These dual uses of the primary database address the requirements of reliability and relevance, respectively, which underlie the main objective of this project.

SPRONS.JNC is the primary database developed in this study. For minerals and gases, it includes standard molal Gibbs free energies and enthalpies of formation, and standard molal entropies and volumes, at a reference pressure of 1 bar and reference temperature of 25°C. Empirical coefficients enabling calculation of standard molal heat capacities and associated thermodynamic quantities at other temperatures and pressures are also documented. For aqueous species, standard partial molal Gibbs free energies and enthalpies of formation, and standard partial molal entropies at the reference temperature and pressure are reported, as are equation-of-state parameters for calculation of standard partial molal volumes and heat capacities, and associated standard partial molal properties as functions of temperature and pressure. The thermodynamic properties of reactions, including equilibrium constants and reaction enthalpies, are calculated using SUPCRT and SPRONS.JNC over a range of temperatures and pressures that encompass the subcritical and supercritical regions of H_2O stability (Section 4).

The other database is considered an *applications* database, or *type K* database according to Engi's classification (Engi, 1992). Thermodynamic data are in the form of equilibrium constants (*K*) for hydrolysis and aqueous-association reactions, and the temperature dependence of the equilibrium constant is calculated using either the van't Hoff equation (requiring the reaction enthalpy at the reference temperature and pressure; e.g., Langmuir, 1997) or an empirical equation representing log *K(T)*. The application database directly supports geochemical models that are used in safety assessments based on JNC's reference scenario. Repository temperatures in this scenario are determined only by the geothermal gradient and a relatively short-lived thermal excursion due to radiogenic heating. A temperature range of 0 to 100°C fully brackets expected repository temperatures in this scenario. The corresponding pressures of interest

will, as noted earlier, be in the range of 1 bar to that determined by the hydrostatic pressure at the depth of the repository (50 - 100 bars). Because such low pressures have negligible effects on most heterogeneous and homogeneous reactions, however, a pressure of 1 bar is considered adequate for these conditions.

PHREEQE.JNC is the applications database developed in this project. It supports the PHREEQE series of geochemical modeling codes (Parkhurst *et al.*, 1980), and therefore consists of equilibrium constants and reaction enthalpies at the reference pressure and temperature, or empirical coefficients that can be used in a polynomial equation to calculate equilibrium constants between 0 and 100°C at 1 bar.

All thermodynamic data in PHREEQE.JNC are calculated using SUPCRT and SPRONS.JNC. Consistency between the primary and applications databases is therefore ensured. This level of consistency among these type S and type K databases can be extended to other modeling software, which is advantageous because several geochemical modeling codes, including EQ3/6 (Wolery, 1992), the Geochemist's Workbench (GWB; Bethke, 1996) and several of the PHREEQE series of codes (PHREEQE, PHREEQE-60 and PHREEQC), will be used by JNC in specialized research areas. Consistency among thermodynamic data in the primary database and other databases used by JNC (i.e., data for minerals, gases and aqueous species of radioelements) are assessed by comparison of data that are common among the databases to determine if they are compatible (i.e., values are identical within stated uncertainty limits). Results are discussed in Section 5.2.6.

3 Status of Thermodynamic Databases

Four databases have been developed over the past twenty years that fulfill to varying degrees the conditions noted in the introduction that we have adopted as standards for a reliable database. Some remarks on these conditions are summarized below. This is followed by a brief description of the four databases. Supplementary comments on other thermodynamic databases are also included for completeness. We then outline the general strategy used to develop SPRONS.JNC and PHREEQE.JNC.

3.1 Database Requirements

3.1.1 Internal consistency

Internal consistency ensures that there are no sources of ambiguity in the database. Such ambiguities are revealed when mathematical manipulation of the data in various ways results in two (or more) different values for a given thermodynamic property. The two values are mutually incompatible, and therefore internally inconsistent with respect to the data used to calculate them. If, on the other hand, a database is internally consistent, and all such discrepancies are therefore resolved, then data that are in conflict with experimental observations can be attributed unequivocally to errors in the data, or to errors in the experimental results. Internal consistency is thus a conditional requirement, which must be met before the accuracy of a database can be unambiguously assessed.

Engi (1992) suggests that the internal consistency of a database is best evaluated in terms of a level of increasingly stringent conditions:

- all the data are compatible with basic thermodynamic definitions, and basic functional relations used to retrieve thermodynamic data from experimental results,
- a single set of reference values (e.g., reference temperature and pressure) and constants (e.g., gas constant, atomic weights, etc.) is adhered to,
- the interdependence of the data is minimized by simultaneous evaluation of experimental results for multiple reactions,
- parameter values are constrained by all relevant experimental (and field) data, except those that are rejected (or uncertainties "relaxed") on the basis of experimental procedures employed.

Thermodynamic databases are then classified as:

- *formally* consistent if only the first two conditions are satisfied,

- *partially* consistent if the third condition is also satisfied, and
- *fully* consistent if all four conditions are satisfied.

According to this definition, the databases described in Sections 3.2 and 3.3 are *at least* partially consistent because parameter values are determined by simultaneous evaluations of experimental data for many reactions (see Section 4.3.4.3). The databases are not fully consistent in the strictest sense, however, because statistical techniques to identify discordant experimental data, and reasons for ultimately rejecting such data, are inadequately documented. The need for brevity in scientific journals, where all these databases are described, accounts for this general lack of full and complete documentation.

The definition of internal consistency given above is useful because it includes the concept of "levels-of-attainment". A fully consistent database is thus an ideal standard, which may be extremely difficult to achieve in practice, and to maintain as the database is inevitably updated and revised. It is important to emphasize here that the level of internal consistency does not necessarily correlate in any meaningful way with the accuracy of the data (Section 3.5). Thus, thermodynamic data in an uncritical data compilation may still be accurate.

3.1.2 Experimental basis

We adopt the premise of Berman (1988) that "... *it is only possible to evaluate the validity of thermodynamic properties by comparison with all available data, because subsets of preferred experimental data are never sufficiently precise to define fully all thermodynamic properties*". This view is based in part on the work of Helgeson *et al.* (1978), who realized that enthalpies of formation had not generally been determined calorimetrically with the accuracy needed to reproduce the results of high temperature and high pressure phase-equilibrium experiments [see also Berman and Brown (1985)]. Internally consistent databases developed since 1978 (Sections 3.2 and 3.3) are therefore constrained by both phase-equilibrium data and a limited amount of reference, or "anchor", calorimetric values. Berman's premise is further supported by more recent investigations, which show that thermodynamic properties retrieved from solubility and mineral-stability experiments at relatively low-temperatures and pressures are in some cases inconsistent with corresponding data retrieved from both calorimetric and phase-equilibrium studies (Sverjensky *et al.*, 1991; Pokrovskii and Helgeson, 1995; 1997b). This suggests that reliable thermodynamic data for minerals, gases and aqueous species must be properly constrained by all available types of experimental (and field) data spanning as broad a range of temperatures and pressures as possible.

Nordstrom *et al.* (1990) apparently contravene these views, however, with the reasonable argument that because reversible solubilities for many minerals have

never been convincingly demonstrated at low temperatures and pressures, equilibrium constants for corresponding reactions should not be included in a thermodynamic database appropriate for such conditions. We agree with this, but believe such considerations should be exercised when the data are applied to a particular problem, not when the database itself is being developed. There is always some level of interdependence among thermodynamic data, and valuable constraints on the thermodynamic properties of minerals that exhibit reversible equilibrium at low temperatures can therefore be extracted from the results of high-temperature and high-pressure experiments involving minerals that do not exhibit such behavior.

3.1.3 Documentation

Quality assurance is an important component of any applied R&D program, and particularly that being carried out by JNC for the permanent disposal of high-level nuclear wastes. A quality-assured thermodynamic database is sufficiently well documented that results of any calculation using the data can be traced back to original data sources. This requirement is addressed in the present study by documenting appropriate references, compiling a library of the referenced studies, and documenting assessments of the accuracy of selected values.

In addition to quality-assurance issues, it is also important that data analysis procedures used to retrieve thermodynamic parameters from experimental and field studies are adequately documented. This is because independent retrievals may lead to recommended values of thermodynamic properties that are in conflict with accepted values in the database. To resolve these conflicts, it is essential to understand the thermodynamic framework and assumptions supporting the procedures used to retrieve the database values, as well as the statistical/mathematical basis for selecting, and rejecting, experimental observations. Also, it is necessary that the database should be updated and revised as results of new experimental or field studies become available. This also requires familiarity with the details of the data analysis procedures supporting the database.

3.1.4 Verification of accuracy

Verifying the accuracy of thermodynamic data is necessary to build confidence in inferences drawn from the results of geochemical calculations that are based on the data. An essential step in assessing the accuracy of a database is to compare calculated values of thermodynamic parameters (e.g., standard Gibbs free energies of reaction, or corresponding equilibrium constants) with their experimental counterparts over as broad a range of temperatures and pressures as possible. Such comparisons are effectively documented in the form of diagrams, in which the reported uncertainty of each experimental value is also portrayed. A more rigorous test of the accuracy of the data is to compare calculated results

with constraints derived from geologic observations, particularly if these constraints refer to conditions of temperature, pressure and time that have not been simulated experimentally. Activity diagrams are especially useful in this regard because calculated equilibrium relations among minerals, gases and aqueous solutions in various chemical subsystems can be simultaneously correlated with the observed compositions of natural waters. Inconsistencies revealed by such correlations are common at relatively low temperatures and pressures, however, and result from the effects of metastability and from uncertainties in the state of crystallinity and degree of order/disorder in the minerals considered (e.g., Helgeson *et al.*, 1978).

3.2 Internally Consistent Databases for Minerals, Gases and Aqueous Species

Databases that partially fulfill the requirements discussed in Section 3.1, and which also include data for minerals, gases and aqueous species, have evolved more-or-less continuously since 1974 through the combined efforts of researchers affiliated with the Laboratory of Theoretical Geochemistry at the University of California, Berkeley. For convenience, the results of this collective effort are referred to here as the SUPCRT model, and its associated databases.

3.2.1 SUPCRT

An internally consistent thermodynamic database developed primarily on the basis of calorimetric and phase-equilibrium data was first developed by Helgeson et. al. (1978). It includes standard thermodynamic properties for 83 minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Several of these minerals exhibit considerable non-stoichiometry and complications due to temperature-dependent disordering and phase transitions. This study also pioneered the use of equations of state for aqueous species [Na^+, K^+, $O_2(aq)$ and $SiO_2(aq)$: Helgeson and Kirkham (1974 a,b; 1976), Walther and Helgeson (1977) and Delany and Helgeson (1978)] to retrieve Gibbs free energies of formation of minerals from the results of solubility and mineral-stability experiments. The accuracy of the data is verified for more than 130 reactions in the form of diagrams, where experimental solution compositions, or phase-equilibrium reversal temperatures (see Section 4.3.1.1), are compared with calculated equilibrium constants, or univariant/divariant equilibrium curves.

Johnson *et al.* (1991) utilized subsequent improvements to theoretical models giving more accurate representation of the thermodynamic and dielectric properties of H_2O at subcritical and supercritical temperatures and pressures (see Section 4) to add data for 294 aqueous species, and an additional 96 minerals[3] ,

[3] Many of the data for minerals are from Table 9 of Helgeson *et al.* (1978), which are based solely on calorimetric data from several different sources. The reliability of these data was not assessed by Helgeson *et al.* (1978), nor by Johnson *et al.* (1991).

to the original Helgeson *et al.* (1978) database. The revised database is referred to as SPRONS92.DAT, and is included in the SUPCRT software package described by Johnson *et al.* (1991).

Oelkers *et al.* (1995) discuss results of calculations using SUPCRT and a modified version of SPRONS92.DAT, which includes revisions to thermodynamic data for minerals and aqueous species in the system Al_2O_3-H_2O-NaCl (Pokrovskii and Helgeson, 1995), and unpublished revisions to data for minerals and aqueous species in the system Na_2O-Al_2O_3-SiO_2-HCl. Standard Gibbs free energies of formation are the only data documented by these authors, however, (the complete database will be described in a future report; E. H. Oelkers, *pers. comm.*).

Revisions and additions of new data to SPRONS92.DAT are also available from the Lawrence Livermore National Laboratory (LLNL), Livermore, California. The revised database (SPRONS96) can be obtained from LLNL at ftp://s122.es.llnl.gov. Databases supporting EQ3/6 and the Geochemist's Workbench, which incorporate data in SPRONS96, can also be obtained at this site.

3.3 Internally Consistent Databases for Minerals

Three databases that partially fulfill the requirements discussed in Section 3.1 have been developed for minerals. All these databases also consider the thermodynamic properties of H_2O and simple H_2O-CO_2 mixtures. None of the databases include data for other aqueous solutes, however, and they are therefore less comprehensive in this regard than the databases discussed in Section 3.2.

3.3.1 Berman (1988)

Berman (1988) derived an internally consistent database constrained primarily by the results of phase-equilibrium studies and a limited number of calorimetric reference values for 67 minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. The minerals considered are those for which phase-equilibrium data were available, and for which complications due to solid-solution behavior are minimal. Retrieved values of standard molal Gibbs free energies and enthalpies of formation, and standard molal heat capacities and volumes are reported. Coefficients in an empirical heat capacity equation given by Berman and Brown (1985) are provided, as are coefficients in an empirical equation for calculation of standard molal volumes over an appropriate range of pressures and temperatures. Berman (1988) also lists empirical equations and coefficients to calculate the effects of temperature-dependent phase transitions on the standard molal heat capacity and associated thermodynamic properties of akermanite, alpha cristobalite, hematite, magnetite, alpha quartz and low tridymite, and similar effects of disordering on the standard molal heat capacity and associated thermodynamic properties of dolomite, gehlenite and K-feldspar.

Phase equilibrium data [approximately 1200 experimental results involving 180 equilibria] are used to retrieve values of the thermodynamic parameters using a mathematical programming technique (Berman *et al.*, 1986). The results of calculations using the retrieved data are compared with experimental phase-equilibrium results (44 figures). Good agreement overall is obtained. Less than 1% of the experimental data are discordant with calculated values.

3.3.2 Holland and Powell (1990)

Holland and Powell (1990) derived an internally consistent database on the basis of phase-equilibrium studies and a limited number of calorimetric reference values for 123 minerals in the system Na_2O-K_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Values of standard molal enthalpies of formation, and standard molal entropies and volumes retrieved from experimental phase-equilibrium studies utilizing calorimetric enthalpies of formation of 23 reference minerals are reported. Coefficients in an empirical heat capacity equation are provided, as are coefficients of thermal expansion and compressibility. Retrieval of standard molal enthalpies of formation is carried out using a least-squares regression technique. Results are documented in a tabular format for several reactions. Good agreement is achieved overall with respect to both the experimental database, and data retrieved by Berman (1988).

3.3.3 Gottschalk (1997)

Gottschalk (1997) derived an internally consistent database constrained primarily by the results of phase-equilibrium studies and a limited number of calorimetric reference values for 94 minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Retrieved values of standard molal enthalpies of formation, and standard molal entropies are reported. Standard molal volumes and coefficients of thermal expansion and compressibilities from various sources are used in the retrievals. Coefficients in an empirical heat capacity equation from Haas and Fisher (1976) are provided. Gottschalk also lists coefficients in an empirical heat capacity equation from Berman and Brown (1985) to extrapolate values beyond the upper temperature range constrained by the calorimetric data. Phase equilibrium data (approximately 5300 experimental results involving 253 equilibria) are used to retrieve values of the thermodynamic parameters using an iterative regression technique. An advantage of this approach is that all available experimental results are considered in the regression procedure, whether they are consistent with other data in the set or conflicting. The results of calculations using the retrieved data are compared with experimental phase-equilibrium results [all figures and references to experimental data are available at http://www.gfz-potsdam.de/ - navigate to "major projects", then "thermodynamische daten für gesteinbildende minerale (thermodynamic data for rock-forming minerals)]. Good agreement overall is obtained, reproducing 92% of the available phase-equilibrium results reported in the literature.

3.4 Other Internally Consistent Databases, and Data Compilations

Other internally consistent databases for minerals that are derived on the basis of phase-equilibrium and calorimetric data are described by Robinson *et al.* (1983), Halbach and Chatterjee (1984), Holland and Powell (1985), Berman *et al.* (1986), Saxena *et al.* (1993) and Berman and Aranovich (1996). These databases pertain to minerals in relatively small chemical subsystems, however, and are therefore of limited use for general geochemical calculations. Although they are not considered here for this reason, these studies are important additional sources of reliable thermodynamic data, which can in some cases be merged with other internally consistent databases with little, if any, conflict (Saxena, 1997).

Robie *et al.* (1978) and Hemingway *et al.* (1982) describe databases for a large number of minerals, and a limited number of gases and aqueous species. These databases are internally consistent, but reported values are evaluated exclusively on the basis of calorimetric investigations carried out by the U.S. Geological Survey. These calorimetric databases have been superseded by the databases described in Sections 3.2 and 3.3 for reasons discussed in Section 3.1.2. The calorimetric data reported by Robie *et al.* (1978) and Hemingway *et al.* (1982) nevertheless provide important constraints on evaluations of phase equilibrium data, and are used to varying degrees in all the databases described in Sections 3.2 and 3.3.

Numerous databases, including most that support geochemical modeling codes such as PHREEQE and EQ3/6, are compilations of log K values obtained from many different sources. These data have not been evaluated simultaneously, nor are they necessarily compatible with all available calorimetric, phase-equilibrium and other experimental constraints. These data compilations are *at best* only formally consistent, and are not considered further here.

There are numerous compilations of thermodynamic data for geochemical calculations that are also, at best, only formally consistent. Nordstrom and Munoz (1985), for example, cite 206 literature sources of thermodynamic data for minerals, gases and aqueous species that are appropriate for geologic systems, and 40 sources on the thermodynamic properties of H_2O.

3.5 Comparison of Reliable Thermodynamic Data for Minerals

Arthur *et al.* (1997) compared standard molal volumes and entropies, and standard molal Gibbs free energies and enthalpies of formation, of minerals that are common to the Helgeson *et al.* (1978), Berman (1988), Holland and Powell (1990), Johnson *et al.* (1991) and Oelkers *et al.* (1995) databases at 25°C and 1 bar [the Gottschalk (1997) database had not been published at the time this comparison was carried out]. Comparisons among any two of these databases are of interest because discrepancies in reported values for a given mineral

indicate that at least one of the values must be in error. The comparisons do not provide a basis for deciding which value, if either, is actually correct, however.

The results are summarized in Figs. 3.5_1 - 3.5_4 where, for convenience, the abbreviations 78HEL, 88BER, 90HOL, 91JOH and 95OEL refer to Helgeson *et al.* (1978), Berman (1988) Holland and Powell (1990), Johnson *et al.* (1991), and Oelkers *et al.* (1995), respectively. Mineral names are abbreviated in the figures as:

- *elements* - gph (graphite), iron (elemental Fe),
- *oxides* - bcri (beta cristobalite), coe (coesite), cor (corundum), hem (hematite), ilm (ilmenite), lime [CaO*(c)*], mt (magnetite), mang (manganosite), per (periclase), q (quartz), bq (beta quartz), ru (rutile), sp (spinel),
- *hydroxides* - br (brucite), dia (diaspore),
- *carbonates* - arag (aragonite), cc (calcite), dol (dolomite), fdol (Fe-dolomite) mag (magnesite), rhc (rhodocrosite), sid (siderite), and
- *silicates* - acm (acmite), ak (akermanite), ab (albite), abh (albite-high), abl (albite-low), alm (almandine), and (andalusite), andr (andradite), ann (annite), an (anorthite), ant (antigorite), anth (anthophyllite), cap (Ca-Al pyroxene), cel (celadonite), chr (chrysotile), clin (clinochlore), cz (clinozoisite), crd (cordierite), cumm (cummingtonite), di (diopside), ed (edenite), ep (epidote), fa (fayalite), fo (forsterite), fs (ferrosilite), geh (gehlenite), gl (glaucophane), gr (grossular), grun (grunerite), hed (hedenbergite), jd (jadeite), kao (kaolinite), ksp (K-feldspar), kals (kalsilite), ky (kyanite), law (lawsonite), ma (margarite), me (meionite), merw (merwinite), mont (monticellite), mu (muscovite), ne (nepheline), pa (paragonite), parg (pargasite), phl (phlogopite), pre (prehnite), pswo (pseudo-wollastonite), py (pyrope), pyhl (pyrophyllite), san (sanidine), sill (sillimanite), sph (sphene), ta (talc), tr (tremolite) and wo (wollastonite).

A notation in the figures, such as 90HOL - 78HEL, signifies that the indicated parameter in one database (i.e., from Helgeson *et al.*, 1978) is subtracted from that of another (i.e., Holland and Powell, 1990).

Differences among standard molal volumes retrieved by Holland and Powell (1990) and those determined by Helgeson *et al.* (1978), Johnson *et al.* (1991) and Berman (1988) are shown in Fig. 3.5_1. As can be seen, there is little discrepancy among these data. This is because molar volume data are calculated on the basis of X-ray cell refinements, which are routinely determined with small standard errors, in the range of 0.1-0.2%. Molar volumes in the 91JOH database for celadonite, cummingtonite, glaucophane, grunerite, merwinite, and nepheline differ significantly compared with corresponding values in the 90HOL and 88BER databases, however.

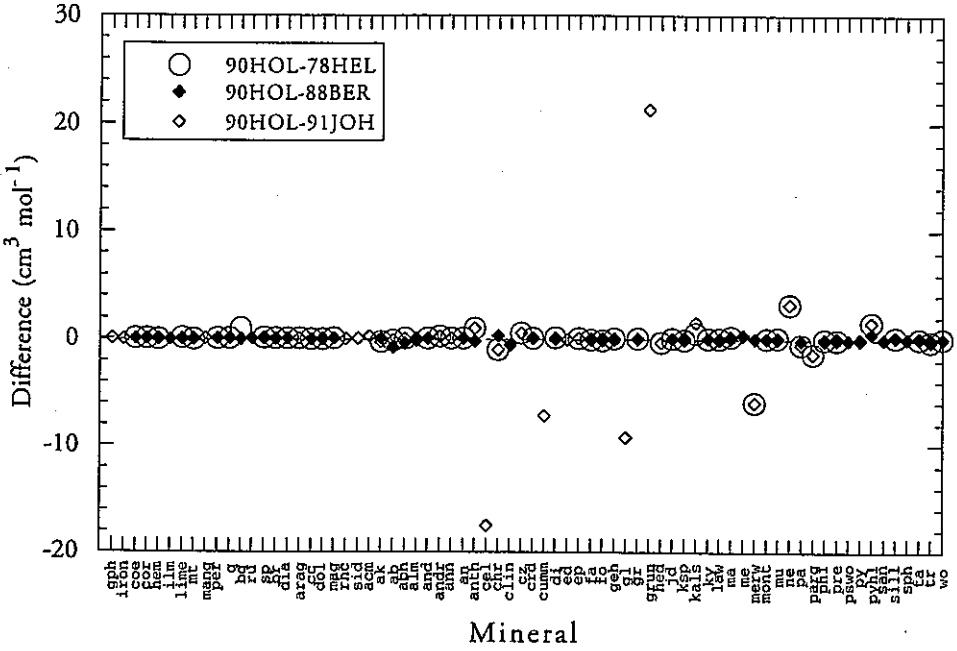


Figure 3.5_1. Differences in standard volumes of minerals between the 90HOL and 78HEL, 88BER and 91JOH databases.

A plot similar to Fig. 3.5_1 is shown for standard entropies in Fig. 3.5_2, where it can be seen that the entropies determined by Holland and Powell (1990) and Berman (1988) agree in most cases, but discrepancies exist for albite, clinochlore, cordierite, gehlenite and phlogopite. Berman (1988) assigns entropy values for

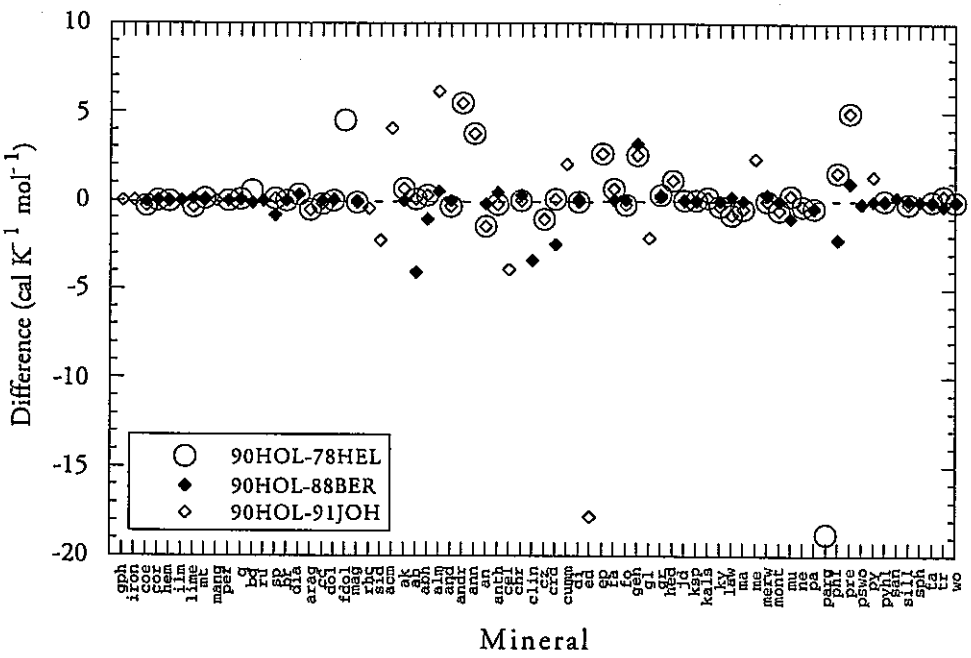


Figure 3.5_2. Differences in standard entropies of minerals between the 90HOL and 78HEL, 88BER and 91JOH databases.

"high" albite to albite, whereas Holland and Powell (1990), Helgeson *et al.* (1978) and Johnson *et al.* (1991), attribute values for "low" albite to this phase. Significant discrepancies (e.g., greater than ± 2 cal K^{-1} mol^{-1}) exist between the 90HOL and 78HEL and 91JOH databases for ferrous dolomite, siderite, acmite (aegerine), almandine, andradite, annite, celadonite, edenite, epidote, gehlenite, glaucophane, nepheline, pargasite and prehnite.

A plot similar to Fig. 3.5_1 is shown for standard enthalpies in Fig. 3.5_3. The 90HOL and 88BER data agree reasonably well, but data for albite, high albite, clinochlore, cordierite, and meionite differ significantly (e.g., greater than ± 2 kcal mol^{-1}). The discrepancy for albite may be more apparent than real for reasons noted above. A number of such discrepancies also exist between the 90HOL and 78HEL and 91JOH databases, i.e., for corundum, spinel, akermanite, high albite, andalusite, andradite, anorthite, anthophyllite, clinozoisite, cordierite, grossular, jadeite, kalsilite, kyanite, lawsonite, margarite, merwinite, monticellite, muscovite, nepheline, paragonite, phlogopite, pyrophyllite, sillimanite and tremolite. Many of these minerals are aluminous phases, and the discrepancies could therefore reflect a systematic error in the 78HEL and 91JOH databases (Section 4.3.4.3).

Differences among standard Gibbs free energies of formation retrieved by Berman (1988) and those of Helgeson *et al.* (1978) and Johnson *et al.* (1991) are shown in Fig. 3.5_4 [the 90HOL database does not include free energy values]. Data from Oelkers *et al.* (1995), which, as noted earlier, include several revisions to the 78HEL database, are also shown in the figure for comparison. Significant

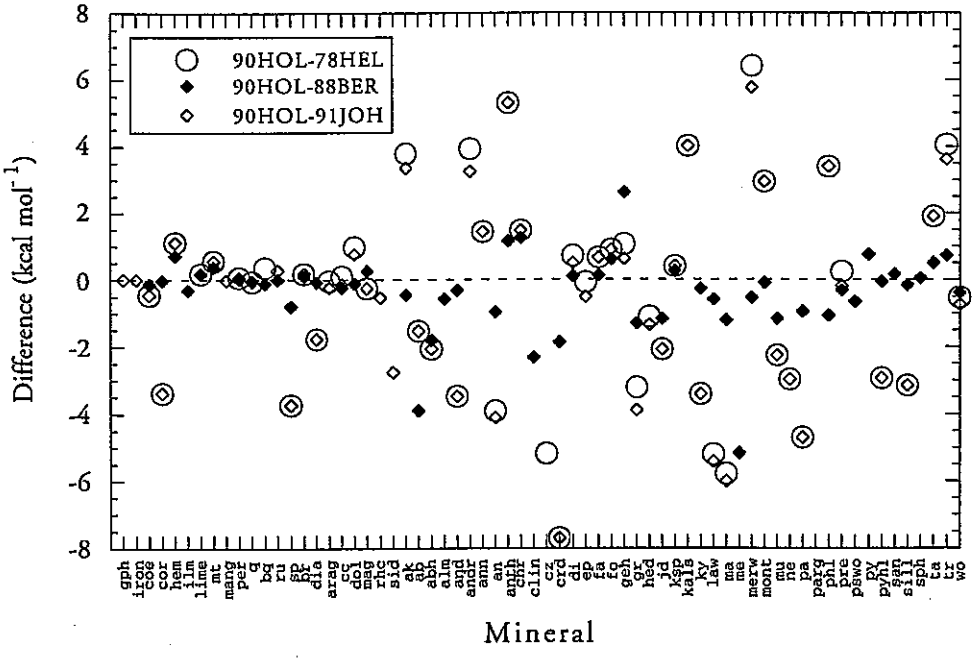


Figure 3.5_3. Differences in standard enthalpies of formation of minerals between the 90HOL and 78HEL, 88BER and 91JOH databases.

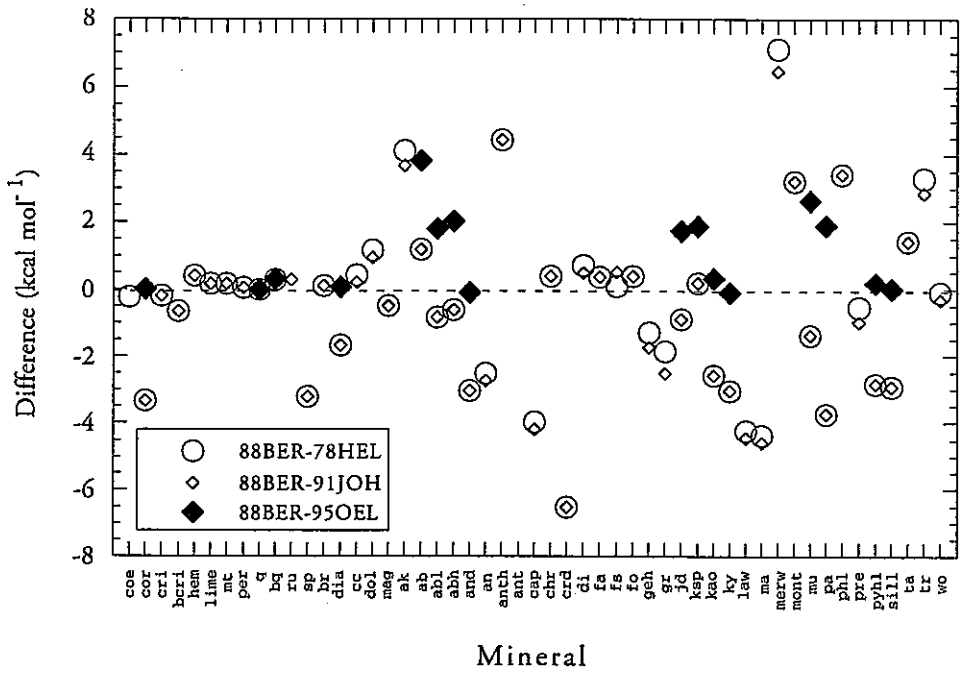


Figure 3.5_4. Differences in standard Gibbs free energies of formation of minerals between the 88BER and 78HEL, 91JOH and 95OEL databases.

discrepancies (e.g., exceeding ± 2 kcal mol^{-1}) are apparent between the 88BER and 78HEL and 91JOH databases for corundum, spinel, akermanite, andalusite, anorthite, anthophyllite, Ca-Al pyroxene, cordierite, grossular, kaolinite, kyanite, lawsonite, margarite, merwinite, monticellite, paragonite, phlogopite, pyrophyllite, sillimanite and tremolite. Revisions incorporated into the 95OEL database, however, agree substantially better with the 88BER data. This improvement includes revised data for corundum, diaspore, andalusite, kaolinite, kyanite, paragonite, pyrophyllite and sillimanite. Moreover, major discrepancies (> ± 2 kcal mol^{-1}) remain only for albite and muscovite. The discrepancy involving albite is probably due to differences between the 88BER and other databases in assigning the properties of either low, or high, albite to albite.

Figures 3.5_1 - 3.5_4 reveal generally good agreement among all the databases with regard to standard molal volumes and entropies, but rather poor agreement with regard to standard enthalpies and Gibbs free energies of formation. This may seem surprising because all the databases are internally consistent and are constrained by similar, and in some cases identical, calorimetric and phase-equilibrium data. Discrepant values could result for a number of reasons, including differences among the databases in adopted calorimetric reference data, and uncertainties that are inherent in extrapolating data that are retrieved from high-temperature, high-pressure experiments to the much lower reference pressure and temperature (Engi, 1992). The 88BER and 90HOL databases generally agree better with each other than they do with either of the 78HEL and 91JOH databases. It is encouraging, however, that

recent revisions incorporated by Oelkers *et al.* (1995) bring a number of formerly discrepant values in the 78HEL and 91JOH databases into significantly better agreement with those of 88BER and 90HOL. The evolution of these databases therefore appears to be on a convergent path. Incorporation of constraints derived from solubility and mineral-stability experiments at relatively low temperatures and pressures may be needed to resolve remaining discrepancies.

3.6 Reliable Databases for Geochemical Calculations

3.6.1 Recommended databases

The databases described in Sections 3.2 and 3.3 are considered the *most reliable* available. Each is internally consistent, and selected values of thermodynamic properties are based on evaluations of at least calorimetric and phase-equilibrium data. Moreover, the accuracy of the selected values is documented in the form of diagrams comparing calculated and experimental values of equilibrium constants, or calculated and experimentally observed pressure-temperature coordinates of univariant or divariant equilibria. Future revisions and expansions of the databases described by Berman (1988), Holland and Powell (1990), Johnson *et al.* (1991) and Gottschalk (1997) are expected.

Of these preferred databases, the SUPCRT model and associated databases, such as that described partially by Oelkers *et al.* (1995), are the *most relevant* to JNC's R&D program. This is because the database includes the thermodynamic properties of minerals, gases and aqueous species, all of which are needed to evaluate mineral-water equilibria at the relatively low temperatures and pressures of primary interest. The databases published by Berman (1988), Holland and Powell (1990) and Gottschalk (1997) are less useful, because they do not include data for aqueous species, and consider only the thermodynamic properties of pure fluid phases of H_2O, and H_2O-CO_2 mixtures.

3.6.2 Databases not recommended

The other databases noted in Section 3.4 are not recommended because:

- they are derived primarily or entirely from calorimetric data (see Section 3.1.2), and/or
- they are uncritical compilations, for which the internal consistency among reported values is highly questionable.

The latter compilations also suffer in many cases from inadequate documentation, and little or no evidence is given that the accuracy of the data has been verified by direct comparison with all available experimental results.

3.6.3 Development strategy

The review of thermodynamic databases summarized above is the foundation of a strategy to develop reliable thermodynamic databases appropriate for JNC's geochemical calculations (Arthur *et al.*, 1997). This strategy includes the following steps:

1. adopt the thermodynamic model and database (SPRONS92.DAT) comprising the SUPCRT software package (Johnson *et al.*, 1991),

2. update SPRONS92.DAT with revised and new data for minerals, gases and aqueous species reported in the literature since 1991,

3. verify the accuracy of the revised database by comparison of calculated and experimental equilibrium constants for important heterogeneous reactions (mineral and gas solubilities), and important aqueous-speciation reactions,

4. revise equilibrium constants and reaction enthalpies at 25°C and 1 bar in the PHREEQE databases, using SUPCRT and SPRONS.JNC, and

5. calculate the values of coefficients in a polynomial expression used by PHREEQE to account for the temperature dependence of equilibrium constants by regression of corresponding values of equilibrium constants calculated using SUPCRT and SPRONS.JNC.

Implementation of this strategy is the subject of the remainder of this report. Section 4 provides background information on the thermodynamic framework of the SUPCRT model. Steps 2, 4 and 5 are discussed in Section 5, and documented in Appendices A and B. The results of Step 3 are discussed in Section 6, with reference to figures in Appendices C and D.

4 Thermodynamic Framework

The SUPCRT model includes:

- an equation of state for H_2O (Levelt-Sengers *et al.*, 1983; Haar *et al.*, 1984),
- equations enabling calculation of the dielectric properties of the solvent as functions of temperature and pressure (Johnson and Norton, 1991),
- the revised HKF (Helgeson-Kirkham-Flowers; Helgeson *et al.*, 1981) equations of state for aqueous species, and equations to calculate their apparent standard partial molal thermodynamic properties as functions of temperature and pressure (Tanger and Helgeson, 1988), and
- equations of state for minerals and gases, and equations to calculate their apparent standard molal thermodynamic properties as functions of temperature and pressure (Helgeson *et al.*, 1978).

The thermodynamic framework represented by these equations as a whole, and their temperature, pressure and solvent-density (ρ_{H_2O}) regions of validity, has evolved more or less continuously since 1974 (Helgeson and Kirkham, 1974a,b; Helgeson and Kirkham, 1976; Helgeson *et al.*, 1978; Helgeson *et al.*, 1981; Shock and Helgeson, 1988; Tanger and Helgeson, 1988; Johnson *et al.*, 1991 (see also Johnson *et al.*, 1992); Shock *et al.*, 1992; Sassani and Shock, 1992; Shock and Koretsky, 1995; Haas *et al.*, 1995; Shock *et al.*, 1997a,b; Sverjensky *et al.*, 1997). The SUPCRT model permits calculation of the apparent standard molal thermodynamic properties of minerals and gases from 1 to 10000 bars and from 0°C to a maximum value consistent with the Maier-Kelly (Maier and Kelly, 1932) heat-capacity coefficients for the mineral or gas of interest (see below). For charged aqueous species, calculation of the apparent standard partial molal Gibbs free energy of formation is restricted to $\rho_{H_2O} \geq 0.35$ g-cm^3, and to $T \leq 350$°C, or $T \geq 400$°C at $P < 500$ bars. Calculation of the standard partial molal enthalpy of formation of charged species and their standard partial molal entropy, heat capacity and volume is limited to $\rho_{H_2O} \geq 0.35$ g-cm^3 and $T \leq 350$°C at $P < 1000$ bars.

Thermodynamic relations in the SUPCRT model are briefly summarized in this section with the objective of identifying the primary data needed to calculate the thermodynamic properties of minerals, gases, aqueous species and reactions as functions of P and T (see Sections 4.2.1.1 and 4.2.2.5). These data comprise the primary database (SPRONS.JNC) described in Section 5. In-depth descriptions of the SUPCRT model are included in the references noted above.

4.1 Standard-State and Other Conventions

The standard state for thermodynamic components that are stoichiometrically

equivalent to minerals calls for unit activity of the pure component at all pressures and temperatures. For liquids, including $H_2O(l)$, the standard state corresponds to unit activity of the pure solvent at any pressure and temperature. The standard state for gases is unit fugacity of the hypothetical ideal gas at 1 bar and any temperature. For aqueous species other than H_2O, the standard state is unit activity in a hypothetical ideal one molal solution referenced to infinite dilution at any pressure and temperature.

Standard molal Gibbs free energies and enthalpies of formation of minerals, gases and aqueous species are calculated in terms of their *apparent* standard molal counterparts[4]. The apparent standard molal Gibbs free energy and enthalpy of formation ($\Delta G^\circ_{P,T}$ and $\Delta H^\circ_{P,T}$, respectively) are defined at a given pressure and temperature by:

$$\Delta G^\circ_{P,T} \equiv \Delta G^\circ_f + (G^\circ_{P,T} - G^\circ_{P_r,T_r}) \qquad (4.1\_1)$$

and

$$\Delta H^\circ_{P,T} \equiv \Delta H^\circ_f + (H^\circ_{P,T} - H^\circ_{P_r,T_r}), \qquad (4.1\_2)$$

where ΔG°_f and ΔH°_f represent the standard molal Gibbs free energy and enthalpy of formation from the elements in their stable phase at the reference pressure (P_r = 1 bar) and temperature (T_r = 25°C). The parenthetical terms in these equations refer to differences in the absolute standard Gibbs free energy *(G°)* and absolute standard enthalpy *(H°)* caused by changes in pressure ($P - P_r$) and temperature ($T - T_r$).

The thermodynamic properties of aqueous ionic species refer to two half-cell reactions: one involving formation of the ion from its element and the other, by convention, formation of H^+ from $H_2(g)$. The reactions are always written such that the mass of electrons is balanced when the two half-cell reactions are combined. The number of electrons produced in the combined reaction is thus equal to the number consumed, and it is therefore unnecessary to specify their thermodynamic properties explicitly (e.g., Garrels and Christ, 1965). The standard molal properties of ions derived in this manner are referred to as *conventional* properties[5]. The conventional standard molal properties of aqueous ionic species are related to their *absolute* counterparts by:

4- Apparent standard molal quantities are defined as a matter of convenience to avoid the necessity of accounting for changes in the stable phase of the elements with changes in temperature and pressure (e.g., Anderson and Crerar, 1993). It is unnecessary to account for these changes because the thermodynamic properties of the elements always cancel in any balanced chemical reaction.

5- Conventional standard molal properties of aqueous solutes are equivalent to their conventional standard *partial* molal analogs (Helgeson *et al.*,1981). These two terms are used interchangeably in the following discussion.

$$\Delta\Xi^{\circ}_{j,P,T} \equiv \Delta\Xi^{\circ,abs}_{j,P,T} - Z_j\Delta\Xi^{\circ,abs}_{H^+,P,T}, \quad (4.1\_3)$$

and

$$\Xi^{\circ}_{j,P,T} \equiv \Xi^{\circ,abs}_{j,P,T} - Z_j\Xi^{\circ,abs}_{H^+,P,T}, \quad (4.1\_4)$$

where $\Delta\Xi^{\circ}_{j,P,T}$ and $\Delta\Xi^{\circ,abs}_{j,P,T}$ denote the conventional and absolute standard molal Gibbs free energy or enthalpy of formation of the j-th ionic species, $\Xi^{\circ}_{j,P,T}$ and $\Xi^{\circ,abs}_{j,P,T}$ stand for the conventional and absolute standard molal entropy, heat capacity or volume of the j-th ion, and Z_j represents the ion's charge. The quantity $\Delta\Xi^{\circ,abs}_{H^+,P,T}$ stands for the absolute standard molal Gibbs free energy or enthalpy of H^+ formation, and $\Xi^{\circ,abs}_{H^+,P,T}$ represents the hydrogen ion's absolute standard molal entropy, heat capacity or volume. All conventional standard molal properties of the hydrogen ion are thus equal to zero at any temperature and pressure.

Although the thermodynamic properties of the aqueous electron, *e-*, are not considered explicitly in SUPCRT, it is convenient to define these properties in a conventional sense that maintains consistency with the basic thermodynamic framework in this model. This enables the results of calculations using SUPCRT to be directly incorporated into databases that support certain geochemical modeling codes, such as PHREEQE, in which oxidation-reduction reactions are written in terms of *e-*. Although the thermodynamic properties of the aqueous electron are in fact unknown (Hostetler, 1984), its conventional thermodynamic properties can nevertheless be defined by assuming that the reaction for formation of the hydrogen ion,

$$1/2H_2(g) \rightleftharpoons H^+ + e^-,$$

also refers to "formation" of *e-* (e.g., Drever, 1982). Thus,

$$\Delta\Xi^{\circ,abs}_{e^-,P,T} = \Delta\Xi^{\circ,abs}_{H^+,P,T}, \quad (4.1\_5)$$

$$\Xi^{\circ,abs}_{e^-,P,T} = \Xi^{\circ,abs}_{H^+,P,T}, \quad (4.1\_6)$$

and, as follows from Eqns. (4.1_3) and (4.1_4),

$$\Delta\Xi^{\circ}_{e^-,P,T} = \Xi^{\circ}_{e^-,P,T} = 0. \quad (4.1\_7)$$

Thus, as for H^+, all *conventional* standard molal properties of *e-* are equal to zero at any temperature and pressure. An additional assumption, often made in electrochemical studies, that

$$\Delta\Xi^{\circ,abs}_{H^+,P,T} = \left(\Xi^{\circ,abs}_{H^+,P,T} + \Xi^{\circ,abs}_{e^-,P,T} - 1/2\Xi^{\circ,abs}_{H_2(g),P,T}\right) = 0$$

(i.e., the so-called "hydrogen-ion convention"; Denbigh, 1971; Puigdomenech *et al.*, 1997) is not adopted here, because it results in only a slight simplification of notation, and is otherwise unnecessary (Anderson and Crerar, 1993).

Conventional standard molal properties of an aqueous electrolyte are related to the corresponding conventional properties of its constituent ions by additivity constraints (Shock *et al.*, 1992):

$$\Delta\Xi^{\circ}_{k,P,T} = \sum_{j} \nu_{j,k}\, \Delta\Xi^{\circ}_{j,P,T}, \tag{4.1_8}$$

and

$$\Xi^{\circ}_{k,P,T} = \sum_{j} \nu_{j,k}\Xi^{\circ}_{j,P,T} \tag{4.1_9}$$

where subscripts k and j refer to the electrolyte and ion, respectively, and $\nu_{j,k}$ stands for the number of moles of the j-th ion in one mole of the k-th electrolyte. Equations (4.1_3), (4.1_4), (4.1_8) and (4.1_9) imply that the standard molal thermodynamic properties of aqueous anions are equivalent to those of the corresponding fully associated acid electrolyte, and that the standard molal thermodynamic properties of an aqueous electrolyte are equal to the stoichiometric sum of the corresponding properties of the cation and anion.

The units of thermodynamic quantities considered in the SUPCRT model are temperature in Kelvins (°K), pressure in bars, energy in calories (cal), mass in moles (mol) and volume in cubic centimeters (cm^3). We retain these units in favor of SI standards to avoid confusion.

4.2 Thermodynamic Relations

The parenthetical terms in Eqns. (4.1_1) and (4.1_2) are evaluated using equations of state for pure minerals and gases, and equations of state for aqueous species that account for changes in both the thermodynamic and dielectric properties of fluid phases of H_2O as functions of temperature and pressure. Thermodynamic functions relate equation-of-state parameters characterizing the standard molal volume to corresponding values of the isobaric heat capacity, entropy, and Gibbs free energy and enthalpy of formation. The functions contain adjustable coefficients determined either by evaluation of experimental data (Section 4.3) or by estimation techniques based on empirical correlations among known values of standard molal or partial molal quantities (Section 4.4).

4.2.1 Minerals and Gases

The equation of state for minerals adopted in the SUPCRT model is given by (Helgeson *et al.*, 1978):

$$V^{\circ}_{P,T} = V^{\circ}_{Pr,Tr} + \sum_{i=1}^{\phi_{PT}} \Delta V^{\circ}_{t,i}, \qquad (4.2.1\_1)$$

where V° refers to the standard molal volume of the mineral and $\Delta V^{\circ}_{t,i}$ stands for the change in the standard molal volume caused by the i-th of ϕ_{PT} phase transitions that occur between P_r, T_r and P, T. Although the effects of variations in temperature and pressure on the standard molal volume are not considered in this equation-of-state, this simplifying approximation is appropriate for most minerals over a broad range of pressures and temperatures. This is because the effects of thermal expansion and compression cause opposing changes in V° on the order of 3% or less at temperatures less than 800°C at 1 bar, and pressures less than 20 kb at 25°C (Helgeson *et al.*, 1978; Berman *et al.*, 1986). Evaluation of mineral compressibilities and expansivities may be important, however, for low-entropy (e.g., solid-solid) reactions and reactions involving highly contrasting volumetric properties (Berman, 1988; Holland and Powell, 1990; Gottschalk, 1997). The equation of state for minerals is also used for gases, in which case $\phi_{PT} = 0$, and $V^{\circ}_{P,T} = V^{\circ}_{Pr,Tr}$.

The apparent standard molal Gibbs free energy and enthalpy of formation of a mineral or gas is calculated using Eqns. (4.1_1), (4.1_2) and (4.2.1_1), and the following equations from Helgeson *et al.* (1978) for the parenthetical terms in Eqn. (4.1_1) and (4.1_2):

$$G^{\circ}_{P,T} - G^{\circ}_{Pr,Tr} = -S^{\circ}_{Pr,Tr}(T - T_r) + \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C^{\circ}_{Pr,i}\, dT - T \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C^{\circ}_{Pr,i}\, d\ln T + \int_{P_r}^{P} V^{\circ}_{Pr,T}\, dP - \sum_{i=1}^{\phi_P} \int_{P_{t,i}T}^{P} \Delta V^{\circ}_{t,i}\, dP - \sum_{i=1}^{\phi_T} \frac{\Delta H^{\circ}_{t,i}}{T_{t,i}} (T - T_{t,i}), \qquad (4.2.1\_2)$$

and

$$H^{\circ}_{P,T} - H^{\circ}_{Pr,Tr} = \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C^{\circ}_{Pr,i}\, dT + \int_{P_r}^{P} V^{\circ}_{Pr,T}\, dP - \sum_{i=1}^{\phi_P} \int_{P_{t,i}T}^{P} \Delta V^{\circ}_{t,i}\, dP + \sum_{i=1}^{\phi_T} \Delta H^{\circ}_{t,i}. \qquad (4.2.1\_3)$$

An expression for the standard molal entropy consistent with Eqns. (4.2.1_2) and (4.2.1_3) is given by:

$$S^{\circ}_{P,T} = S^{\circ}_{Pr,Tr} + \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C^{\circ}_{Pr,i}\, d\ln T + \sum_{i=1}^{\phi_T} \frac{\Delta H^{\circ}_{t,i}}{T_{t,i}} \qquad (4.2.1\_4)$$

In Eqns. (4.2.1_2) - (4.2.1_4), ϕ_T refers to the number of phase transitions from P_r, T_r to P_r, T (where $T_1 = T_r$); ϕ_P stands for the number of phase transitions from P_r, T to P, T; $P_{t,i,T}$ represents the pressure of the i-th phase transition at T, and $\Delta H^{\circ}_{t,i}$ denotes the change in the standard molal enthalpy of the i-th phase transition. The isobaric heat capacity, $C^{\circ}_{Pr,i}$, is expressed in terms of the Maier-Kelly power function (Maier and Kelly, 1932):

$$C^{\circ}_{Pr,i} = a_i + b_i T + c_i T^{-2}, \tag{4.2.1_5}$$

where a_i, b_i, and c_i stand for regression coefficients valid over the temperature range T_i to T_{i+1}.

Substitution of Eqn. (4.2.1_5) into Eqns. (4.2.1_2), (4.2.1_3) and (4.2.1_4) leads to (Helgeson *et al.*, 1978; Johnson *et al.*, 1991):

$$\begin{aligned} G^{\circ}_{P,T} - G^{\circ}_{Pr,Tr} = & -S^{\circ}_{Pr,Tr}(T - T_r) + \sum_{i=1}^{1+\phi_T} a_i \left\{ T_{i+1} - T_i - T_{i+1} \ln\left(\frac{T_{i+1}}{T_i}\right) \right\} \\ & + \sum_{i=1}^{1+\phi_T} \left\{ \frac{(-c_i - b_i T_{i+1} T_i^2)(T_{i+1} - T_i)^2}{2 T_{i+1} T_i^2} \right\} + V^{\circ}_{Pr,T}(P - P_r) \\ & - \sum_{i=1}^{\phi_P} \int_{P_{t,i,T}}^{P} \Delta V^{\circ}_{t,i}\, dP - \sum_{i=1}^{\phi_T} \frac{\Delta H^{\circ}_{t,i}}{T_{t,i}} (T - T_{t,i}); \end{aligned} \tag{4.2.1_6}$$

$$\begin{aligned} H^{\circ}_{P,T} - H^{\circ}_{Pr,Tr} = & \sum_{i=1}^{1+\phi_T} \left\{ a_i (T_{i+1} - T_i) + \frac{b_i}{2}(T_{i+1}^2 - T_i^2) - c_i \left(\frac{1}{T_{i+1}} - \frac{1}{T_i} \right) \right\} \\ & + V^{\circ}_{Pr,T}(P - P_r) - \sum_{i=1}^{\phi_P} \int_{P_{t,i,T}}^{P} \Delta V^{\circ}_{t,i}\, dP + \sum_{i=1}^{\phi_T} \Delta H^{\circ}_{t,i}; \end{aligned} \tag{4.2.1_7}$$

and,

$$S^{\circ}_{P,T} = S^{\circ}_{Pr,Tr} + \sum_{i=1}^{1+\phi_T} \left\{ a_i \ln\left(\frac{T_{i+1}}{T_i}\right) + b_i (T_{i+1} - T_i) - \frac{c_i}{2} \left(\frac{1}{T_{i+1}^2} - \frac{1}{T_i^2} \right) \right\} + \sum_{i=1}^{\phi_T} \frac{\Delta H^{\circ}_{t,i}}{T_{t,i}} \tag{4.2.1_8}$$

Equations (4.1_1), (4.1_2) and (4.2.1_6) - (4.2.1_8) are the fundamental equations in SUPCRT that are used to calculate thermodynamic properties of minerals and gases over a wide range of pressures and temperatures.

4.2.1.1 Primary thermodynamic data for minerals and gases. Inspection of Eqns. (4.1_1), (4.1_2) and (4.2.1_6) - (4.2.1_8) indicates that for gases and minerals that do not undergo phase transitions, the following data are needed to calculate their apparent standard molal thermodynamic properties at a given temperature and pressure: ΔG_f°, ΔH_f°, $S^\circ_{Pr,Tr}$, $V^\circ_{Pr,Tr}$, a_i, b_i, c_i and T_{max} (where T_{max} refers to the upper temperature limit of validity of the Maier-Kelly coefficients). These data are also required for minerals that experience phase transitions, in addition to the enthalpy and volume change at each transition temperature, and Maier-Kelly coefficients for each transitional phase and the upper temperature limits of their validity. In practice, the only first-order phase transitions[6] that have been considered in this framework are those for which the Clapeyron slope is positive (Helgeson *et al.*, 1978). Lambda transitions have also been evaluated to account for the effects of substitutional order/disorder in albite, dolomite, K-feldspar and epidote (Helgeson *et al.*, 1978).

4.2.2 Aqueous species: Summary of the revised HKF model

The structure of the revised Helgeson, Kirkham and Flowers (HKF) model is represented by the total differential of the partial molal Gibbs free energy of the j-th ion (or neutral species) in a hypothetical ideal one molal solution corresponding to the standard state at any temperature and pressure:

$$d\bar{G}_j^\circ = -\bar{S}_j^\circ dT + \bar{V}_j^\circ dP.$$

Changes in $\bar{G}_j^\circ$ caused by variations in temperature and pressure are evaluated by integrating this equation from reference conditions to the temperature and pressure of interest:

$$\int_{Pr,\,Tr}^{P,\,T} d\bar{G}_j^\circ = -\int_{Tr}^{T} \bar{S}^\circ_{j,Pr}\, dT + \int_{Pr}^{P} \bar{V}^\circ_{j,T}\, dP.$$

The HKF model provides a framework for evaluating this equation using semi-empirical equations-of-state for $\bar{V}_j^\circ$, and associated equations for the isobaric standard partial molal heat capacity, $\bar{C}^\circ_{P_j}$ (which are needed to evaluate the first term on the right hand side of this equation). The equations-of-state are semi-empirical in the sense that they account for both solvation (non-empirical) and non-solvation (empirical) contributions to the standard partial molal volume and heat capacity. The equation of state for aqueous ions and neutral species at any

6 First-order phase transitions are characterized by discontinuities in the temperature dependence of the entropy, enthalpy, volume, heat capacity, expansivity and compressibility of a mineral. In contrast, lambda transitions result from continuous infinitesimal changes in the internal structure of the mineral, or its distribution of atoms, with variations in pressure and/or temperature. The dependence on temperature of the heat capacity, expansivity and compressibility of a mineral undergoing a lambda transition differ significantly before and after the transition, in contrast to the behavior of first-order transitions (Helgeson *et al.*, 1978) .

temperature and pressure[7] is given by (Tanger and Helgeson, 1988):

$$\bar{V}^{\circ} = \Delta\bar{V}^{\circ}_{s} + \Delta\bar{V}^{\circ}_{n} =$$

$$\hat{C}\left\{a_1 + \frac{a_2}{\Psi + P} + \frac{a_3}{T-\Theta} + \frac{a_4}{(\Psi+P)(T-\Theta)} - \omega Q + \left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial \omega}{\partial P}\right)_T\right\}, \qquad (4.2.2\_1)$$

where $\bar{V}^{\circ}$ stands for the standard partial molal volume of the j-th ion. The solvation contribution ($\Delta\bar{V}^{\circ}_{s}$) is represented by terms containing the a_i equation-of-state coefficients, which are pressure- and temperature-independent and unique to the j-th species. The non-solvation contribution ($\Delta\bar{V}^{\circ}_{n}$) is represented by remaining terms, which contain the conventional Born coefficient, ω (see below). The parameter $\hat{C}$ is a conversion factor equal to 41.84 bar cm^3 cal^{-1}.

Comments on the solvation and non-solvation contributions to this equation of state, and associated equations for the isobaric heat capacity, are summarized in Sections 4.2.2.1 - 4.2.2.3. The comments address how various parameters that appear in expressions for the standard partial molal thermodynamic properties of aqueous solutes (Section 4.2.2.4) are related to the solute's partial molal volume and heat capacity.

4.2.2.1 Solvation contribution to $\bar{V}^{\circ}_{P,T}$. The solvation contribution to the standard partial molal volume arises from the change in free energy involved in moving an ion of radius r_e and charge, Z, from a vacuum and placing it in H_2O *(l)* of dielectric constant ε (Born, 1920):

$$\Delta\bar{G}^{\circ}_{s} = \frac{N_a (Z e)^2}{2 r_e}\left(\frac{1}{\varepsilon} - 1\right), \qquad (4.2.2\_2)$$

where $\Delta\bar{G}^{\circ}_{s}$ denotes the standard partial molal Gibbs free energy of ion solvation, or *Born function* for the j-th ion, N_a stands for Avogadro's number (6.02252 x 10^{23} mol^{-1}), and e represents the absolute electronic charge (4.80298 x 10^{-10} cm$^{3/2}$ g$^{1/2}$ s^{-1}). This equation, based only on theoretical consideration of coulombic forces, has been shown to predict enthalpies of hydration that are usually within an order of magnitude of values determined experimentally (e.g., Shock and Helgeson, 1988).

[7] To simplify notation in the following, all properties are taken to apply to the j-th ion at a given temperature and pressure.

The *effective* ionic radius of the j-th aqueous ion[8], r_e, is related to its corresponding crystallographic ionic radius (r_x) by

$$\begin{aligned} r_e &= r_x + |Z|\,g \text{ (anions), or} \\ r_e &= r_x + |Z|\,(0.94 + g) \text{ (cations),} \end{aligned} \qquad (4.2.2\_3)$$

where the "g" function is introduced in the revised HKF model to account for the effects on r_e of variations in T and P. Tanger and Helgeson (1988) derive an empirical function for g:

$$g = a_g(1-\hat{\rho})^{b_g} - f,$$

in which $\hat{\rho}$ is a dimensionless variable (equal to ρ_{H_2O}/1 g-cm^3), a_g and b_g denote regression coefficients (Shock *et al.*, 1992) and f stands for a pressure- and temperature-dependent difference function. Values of f are given for H_2O by Shock *et al.* (1992). Values of g have been retrieved from regressions of experimental data over a wide range of temperatures and pressures on the standard partial molal volumes and heat capacities of NaCl(*aq*) (Tanger and Helgeson, 1988; Shock *et al.*, 1992). The results indicate g = 0 when T < 150°C, or when P > 2000 bars.

The Born function [Eqn. (4.2.2_2)] refers to the properties of individual ions, which cannot be determined experimentally (i.e., only the thermodynamic properties of electrolytes containing the ion of interest are experimentally accessible). For this reason, a *conventional* electrostatic Born "coefficient" consistent with Eqn. (4.1_4) is defined:

$$\omega_j \equiv \omega_j^{abs} - Z_j\omega_{H^+}^{abs} = \frac{N_a(Z_j e)^2}{2r_{e,j}} - Z_j\left(\frac{N_a(Z_{H^+}e)^2}{2r_{e,H^+}}\right), \qquad (4.2.2\_4)$$

and the corresponding *conventional* Born function is then given by:

$$\Delta\bar{G}^{\circ}_{s,j} = \omega_j\left(\frac{1}{\varepsilon} - 1\right). \qquad (4.2.2\_5)$$

The solvation contribution to the partial molal volume is derived from the conventional Born function, i.e., (Tanger and Helgeson, 1988; Shock and Helgeson, 1988):

---

8 The effective radius of neutral aqueous species and polyatomic ionic species cannot be assessed unambiguously because it is not possible in these cases to compute r_x. Alternative approaches described by Shock *et al.* (1989) and Shock and Helgeson (1988), respectively, are used to estimate effective radii for these species.

$$\Delta \bar{V}_s^\circ = \left(\frac{\partial \Delta \bar{G}_s^\circ}{\partial P}\right)_T = -\omega Q + \left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial \omega}{\partial P}\right)_T, \qquad (4.2.2\_6)$$

where Q refers to a *solvent Born function* defined by (Helgeson and Kirkham, 1974a; Helgeson *et al.*, 1981)

$$Q \equiv \frac{1}{\varepsilon^2}\left(\frac{\partial \varepsilon}{\partial P}\right)_T. \qquad (4.2.2\_7)$$

The magnitude of the solvation contribution is thus a function of both the conventional Born coefficient, ω [and therefore of the charge and effective electrostatic radius of the j-th species, Eqn. (4.2.2_4)], and of the dielectric constant of the solvent and its associated pressure derivatives (Section 4.2.2.3).

4.2.2.2 Non-solvation contribution to $\bar{V}^\circ_{P,T}$. The revised HKF model assumes that any discrepancies in comparisons of experimental values of $\bar{V}^\circ$ with $\Delta \bar{V}_s^\circ$, which is calculated using the conventional Born function [Eqn. (4.2.2_5)] and the first identity in Eqn. (4.2.2_6), can be attributed to non-solvation contributions, and that the discrepancies can be accounted for with equations of the form (e.g., Shock and Helgeson, 1988):

$$\Delta \bar{V}_n^\circ = a_1 + \frac{a_2}{\Psi + P} + \frac{a_3}{T - \Theta} + \frac{a_4}{(\Psi + P)(T - \Theta)}. \qquad (4.2.2\_8)$$

where Ψ and Θ denote temperature- and pressure-independent constants equal to 2600 bars and 228°K, respectively and $a_{1..4}$ denote empirical pressure- and temperature-independent coefficients unique to the j-th aqueous solute. The non-solvation contributions are due to other interactions involved in the hydration process, primarily the energetics associated with disrupting the water structure near the hydrated ion. The values of the coefficients $a_{1..4}$ are obtained by regression of experimental data on the partial molal volumes of electrolytes containing the ion of interest (Section 4.3), or by estimation techniques based on correlations among standard partial molal thermodynamic properties (Section 4.4). Regression strategies are described by Shock and Helgeson (1988), Shock *et al.* (1989; 1997a) and Sverjensky *et al.*, (1997).

4.2.2.3 Heat capacities of aqueous solutes. Conventional standard partial molal heat capacities (at constant pressure) of aqueous ions are considered in terms of solvation and non-solvation contributions, in a manner analogous to that discussed above for conventional standard partial molal volumes, i.e.,

$$\bar{C}_P^\circ = \Delta \bar{C}^\circ_{P,s} + \Delta \bar{C}^\circ_{P,n}. \qquad (4.2.2\_9)$$

The solvation contribution to $\bar{C}_P^\circ$ is related to the conventional Born function [Eqn. (4.2.2_5)] by (Tanger and Helgeson, 1988; Shock and Helgeson, 1988):

$$\Delta\bar{S}_s^\circ = -\left(\frac{\partial \Delta\bar{G}_s^\circ}{\partial T}\right)_P, \tag{4.2.2_10}$$

and

$$\Delta\bar{C}_{P_s}^\circ = T\left(\frac{\partial \Delta\bar{S}_s^\circ}{\partial T}\right)_P$$

$$= \omega TX + 2TY\left(\frac{\partial \omega}{\partial T}\right)_P - T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P, \tag{4.2.2_11}$$

where the parameters X and Y denote additional solvent Born functions given by:

$$Y = \frac{1}{\varepsilon^2}\left(\frac{\partial \varepsilon}{\partial T}\right)_P, \text{ and } X = \frac{1}{\varepsilon^2}\left(\frac{\partial^2 \varepsilon}{\partial T^2}\right)_P - 2\varepsilon Y^2.$$

Discrepancies in comparisons of experimental values of $\bar{C}_P^\circ$ and $\Delta\bar{C}_{P_s}^\circ$ are similarly attributed to non-solvation contributions, and are accounted for when $P = P_r$ with equations of the form (e.g., Shock and Helgeson, 1988):

$$\Delta\bar{C}_{P_n}^\circ = c_1 + \frac{c_2}{(T-\Theta)^2} \tag{4.2.2_12}$$

where c_1 and c_2 refer to empirical pressure- and temperature-independent coefficients unique to the j-th ion. Regression of experimental data using strategies such as described by Shock *et al.* (1989) permits values for these coefficients to be retrieved. They are estimated if experimental data are unavailable (Section 4.4).

A relation describing the dependence of $\bar{C}_P^\circ$ on pressure is derived in terms of the partial molal volume, consistent with the identity:

$$\left(\frac{\partial \bar{C}_P^\circ}{\partial P}\right) = -T\left(\frac{\partial^2 \bar{V}^\circ}{\partial T^2}\right), \tag{4.2.2_13}$$

or,

$$\bar{C}_{P_{P,T}}^\circ = \bar{C}_{P_{P_r,T}}^\circ + \int_{P_r}^{P} -T\left(\frac{\partial^2 \bar{V}^\circ}{\partial T^2}\right) dP. \tag{4.2.2_14}$$

Integration yields (Tanger and Helgeson, 1988):

$$\bar{C}^{\circ}_{P_{n,T}} = c_1 + \frac{c_2}{(T-\Theta)^2} - \left[\frac{2T}{(T-\Theta)^3}\right]\left[a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]$$
$$+ \omega TX + 2TY\left(\frac{\partial \omega}{\partial T}\right)_P - T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P . \qquad (4.2.2\_15)$$

The pressure and temperature partial derivatives of the conventional Born coefficients in this equation [see also Eqn. (4.2.2_6)] are given by (Tanger and Helgeson, 1988):

$$\left(\frac{\partial \omega}{\partial P}\right)_T = -\eta\left\{\frac{|Z|^3}{r_e^2} - \frac{Z}{(3.082+g)^2}\right\}\left(\frac{\partial g}{\partial P}\right)_T , \qquad (4.2.2\_16)$$

$$\left(\frac{\partial \omega}{\partial T}\right)_P = -\eta\left\{\frac{|Z|^3}{r_e^2} - \frac{Z}{(3.082+g)^2}\right\}\left(\frac{\partial g}{\partial T}\right)_P , \qquad (4.2.2\_17)$$

and

$$\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P = 2\eta\left\{\frac{Z^4}{r_e^3} - \frac{Z}{(3.082+g)^3}\right\}\left(\frac{\partial g}{\partial T}\right)_P^2 - \eta\left\{\frac{|Z|^3}{r_e^2} - \frac{Z}{(3.082+g)^2}\right\}\left(\frac{\partial^2 g}{\partial T^2}\right)_P$$
(4.2.2_18)

where the partial derivatives of the g function for H_2O are given by Shock *et al.* (1992), and η represents a constant equal to 1.66027 x 10^5 Å cal mol^{-1}.

4.2.2.4 Apparent standard partial molal thermodynamic properties of aqueous ions and neutral species. The apparent standard partial molal Gibbs free energy and enthalpy of formation of aqueous species are calculated using Eqns. (4.1_1) and (4.1_2), equations analogous to Eqns. (4.2.1_2) and (4.2.1_3) for aqueous species (Tanger and Helgeson, 1988; Shock and Helgeson, 1988), and Eqns. (4.2.2_1) and (4.2.2_11):

$$\bar{G}^{\circ}_{P,T} - \bar{G}^{\circ}_{P_r,T_r} = -\bar{S}^{\circ}_{P_r,T_r}(T-T_r) - c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(P-P_r) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)$$
$$- c_2\left\{\left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right]\left[\frac{\Theta-T}{\Theta}\right] - \frac{T}{\Theta^2}\ln\left[\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right]\right\}$$
$$+ \left(\frac{1}{T-\Theta}\right)\left[a_3(P-P_r) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right] + \omega\left(\frac{1}{\varepsilon}-1\right) - \omega_{P_r,T_r}\left(\frac{1}{\varepsilon_{P_r,T_r}}-1\right)$$
$$+ \omega_{P_r,T_r} Y_{P_r,T_r}(T-T_r), \qquad (4.2.2\_20)$$

and,

$$\bar{H}^{\circ}_{P,T}-\bar{H}^{\circ}_{Pr,Tr}=c_1(T-T_r)-c_2\left[\left(\frac{1}{T-\Theta}\right)-\left(\frac{1}{T_r-\Theta}\right)\right]+a_1(P-P_r)+a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)$$
$$+\left[\frac{2T-\Theta}{(T-\Theta)^2}\right]\left[a_3(P-P_r)+a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]+\omega\left(\frac{1}{\varepsilon}-1\right)+\omega TY$$
$$-T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_P-\omega_{Pr,Tr}\left(\frac{1}{\varepsilon_{Pr,Tr}}-1\right)-\omega_{Pr,Tr}T_rY_{Pr,Tr}. \quad (4.2.2\_21)$$

The corresponding expression for $\bar{S}^{\circ}_{j,P,T}$ is given by:

$$\bar{S}^{\circ}_{P,T}=\bar{S}^{\circ}_{Pr,Tr}+c_1\ln\left(\frac{T}{T_r}\right)-\frac{c_2}{\Theta}\left\{\left[\frac{1}{T-\Theta}\right]-\left[\frac{1}{T_r-\Theta}\right]+\frac{1}{\Theta}\ln\left[\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right]\right\}$$
$$+\left(\frac{1}{T-\Theta}\right)^2\left[a_3(P-P_r)+a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]+\omega Y-\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_P-\omega_{Pr,Tr}Y_{Pr,Tr} \quad (4.2.2\_22)$$

Equations (4.1_1), (4.1_2) and (4.2.2_20) - (4.2.2_22) represent the HKF model as it is incorporated into SUPCRT.

4.2.2.5 Primary thermodynamic data for aqueous species. Inspection of Eqns. (4.1_1), (4.1_2) and (4.2.2_20) - (4.2.2_22) indicates that the following data are needed for the j-th aqueous solute to calculate its corresponding apparent standard molal thermodynamic properties at a given temperature and pressure: $\Delta\bar{G}^{\circ}_f$, $\Delta\bar{H}^{\circ}_f$, $\bar{S}^{\circ}_{Pr,Tr}$, $a_{1...4}$, $c_{1...2}$, $\omega_{Pr,Tr}$ and Z. Species that have been considered within this framework include aqueous ions and electrolytes (Shock and Helgeson, 1988; Tanger and Helgeson, 1988, Shock *et al.*, 1997a) inorganic neutral species (Shock *et al.*, 1989), organic species (Shock and Helgeson, 1990), and inorganic and organic metal complexes (Sverjensky *et al.*, 1997).

4.2.3 Reactions among minerals, gases and aqueous species

The change in the apparent standard molal Gibbs free energy or enthalpy of a reaction is given by

$$\Delta\Xi^{\circ}_{r,P,T}=\sum_{i=1}^{I}\nu_i\Delta\Xi^{\circ}_{i,P,T}+\sum_{j=1}^{J}\nu_j\Delta\Xi^{\circ}_{j,P,T}+\nu_{H_2O}\Delta\Xi^{\circ}_{H_2O,P,T}, \quad (4.2.3\_1)$$

where $\Delta\Xi$ refers to ΔG or ΔH, ν_i denotes stoichiometric reaction coefficients of minerals (and/or gases), ν_j stands for those of aqueous species, and ν_{H2O} refers to that of fluid H_2O under subcritical (liquid or gaseous) or supercritical conditions. The corresponding equilibrium constant ($K_{r,P,T}$) is given by:

$$\ln K_{n,P,T} = \frac{-\Delta G_{n,P,T}}{RT} \qquad (4.2.3\_2)$$

where R stands for the gas constant. The equilibrium constant can be calculated at any P and T using Eqns. (4.2.3_2), (4.2.3_1), (4.1_1) and (4.1_2), and

- Eqn. (4.2.1_6) for minerals and gases,
- Eqn. (4.2.2_20) for aqueous species, and Eqn. (4.2.2_4) for the conventional Born coefficient and its associated pressure and temperature derivatives [Eqns. (4.2.2_16) - (4.2.2_18] plus associated values of the g function given by Tanger and Helgeson (1988) and Shock et al. (1992), and
- equations summarized by Johnson and Norton (1991) and Johnson *et al.* (1991) for calculation of the thermodynamic properties of H_2O as a function of temperature and pressure.

All these equations are incorporated into the SUPCRT software package (Johnson *et al.*, 1991), which, with appropriate thermodynamic data (Sections 4.2.1.1 and 4.2.2.5), permits calculation of equilibrium constants and other reaction properties over the range of temperatures and pressures noted in the introductory paragraph of Section 4.

4.3 Retrieval of Thermodynamic Properties from Experimental Data

Experimental data are evaluated using thermodynamic relations summarized in Section 4.2 to retrieve values of the thermodynamic parameters identified in Sections 4.2.1.1 and 4.2.2.5. The evaluation approach is summarized below for several types of experimental methods that have been used to derive much of the data in SPRONS.JNC. This is followed by a brief description of statistical/ mathematical techniques to analyze experimental results, and to retrieve an internally consistent set of thermodynamic properties. Alternative methods described in Section 4.4 are used to estimate the data identified in Sections 4.2.1.1 and 4.2.2.5 if appropriate experimental results are unavailable.

4.3.1 Reaction data

Reaction equilibria among minerals and a fluid phase are studied using a variety of experimental techniques. Two alternative statements of Eqn. (4.2.3_1) are appropriate for such experiments, depending on whether the fluid is pure H_2O, or an aqueous solution, i.e.,:

$$\Delta\Xi^{\circ}_{n,P,T} = \sum_{i=1}^{I} \nu_i \Delta\Xi^{\circ}_{i,P,T} + \nu_{H_2O}\Delta\Xi^{\circ}_{H_2O,P,T}, \text{ or} \qquad (4.3.1\_1)$$

$$\Delta\Xi^{\circ}_{n,P,T} = \sum_{i=1}^{I} \nu_i \Delta\Xi^{\circ}_{i,P,T} + \sum_{j=1}^{J} \nu_j \Delta\Xi^{\circ}_{j,P,T} + \nu_{H_2O}\Delta\Xi^{\circ}_{H_2O,P,T}, \qquad (4.3.1\_2)$$

respectively. *Phase-equilibrium* experiments are evaluated using Eqn. (4.3.1_1). Although experiments evaluated using Eqn. (4.3.1_2) are also phase-equilibrium experiments in a strict sense, we refer to them as *solubility* experiments to emphasize the difference between Eqns. (4.3.1_2) and (4.3.1_1).

4.3.1.1 Phase-equilibrium experiments. These experiments characterize reversals in the relative stabilities of reactant and product mineral assemblages (Gordon, 1973; Carmichael, 1977; Newton 1987; Navrotsky, 1987; Wood, 1987; Kerrick, 1987; Lofgren, 1987). The reversals are determined by holding an initial reactant assemblage at fixed *P-T* conditions for a specified period of time. The pressure and temperature are then rapidly reduced and the reaction products, if any, identified. A new pressure and/or temperature are then selected, and the experiment repeated using a fresh set of reactants. Ideally, a number of such experiments will closely approximate equilibrium conditions, which are bounded by the experimentally determined set of *P-T* coordinates, or "half brackets", over a range of temperatures and pressures. The exact equilibrium temperature and pressure are rarely determined in phase-equilibrium studies, however.

Each phase-equilibrium experiment defines a specific *P-T* coordinate at which $\Delta G^{\circ}_{r,P,T} > 0$ (reactants stable), or $\Delta G^{\circ}_{r,P,T} < 0$ (products stable). This constitutes an inequality constraint on the standard molal Gibbs free energy of reaction, i.e.,:

$$\Delta G^{\circ}_{r,P,T} = \sum_{i=1}^{I} \nu_i \Delta G^{\circ}_{i,P,T} + \nu_{H_2O} \Delta G^{\circ}_{H_2O,P,T} \begin{pmatrix} > \\ < \end{pmatrix} 0, \qquad (4.3.1.1\_1)$$

which can be expanded such that all thermodynamic variables are written in terms of fitting parameters and standard molal properties. For example, simplifying the discussion in Section 4.2.1 by assuming no first-order or lambda transitions, Eqn. (4.3.1.1_1) can be written as:

$$\Delta G^{\circ}_{r,P,T} \begin{pmatrix} > \\ < \end{pmatrix} \sum_{i}^{I} \nu_i \left\{ \begin{array}{l} \Delta G^{\circ}_{f,i} - S^{\circ}_{i,P_r,T_r}(T-T_r) + a_i\left[T - T_r - T\ln\left(\frac{T}{T_r}\right)\right] \\ + \frac{\left(-c_i - b_i T T_r^2\right)\left(T-T_r\right)^2}{2TT_r^2} + V^{\circ}_{P_r,T}(P-P_r) \end{array} \right\} + \nu_{H_2O} \Delta G^{\circ}_{H_2O,P,T}. \qquad (4.3.1.1\_2)$$

To evaluate this equation, one or more sets of phase-equilibrium data are plotted on a *P-T diagram* (e.g., Fig. 4.3.1.1_1). Equilibrium conditions, where $\Delta G^{\circ}_{r,P,T} = 0$, are then estimated by calculating the best-fit curve through all the *P-T* half brackets, such that the curve, representing univariant equilibrium, passes between half-brackets where reactants are stable and those where products are stable. Regression techniques applied to the experimental dataset with respect to Eqn. (4.3.1.1_2) and the condition $\Delta G^{\circ}_{r,P,T} = 0$ are then used to retrieve values of

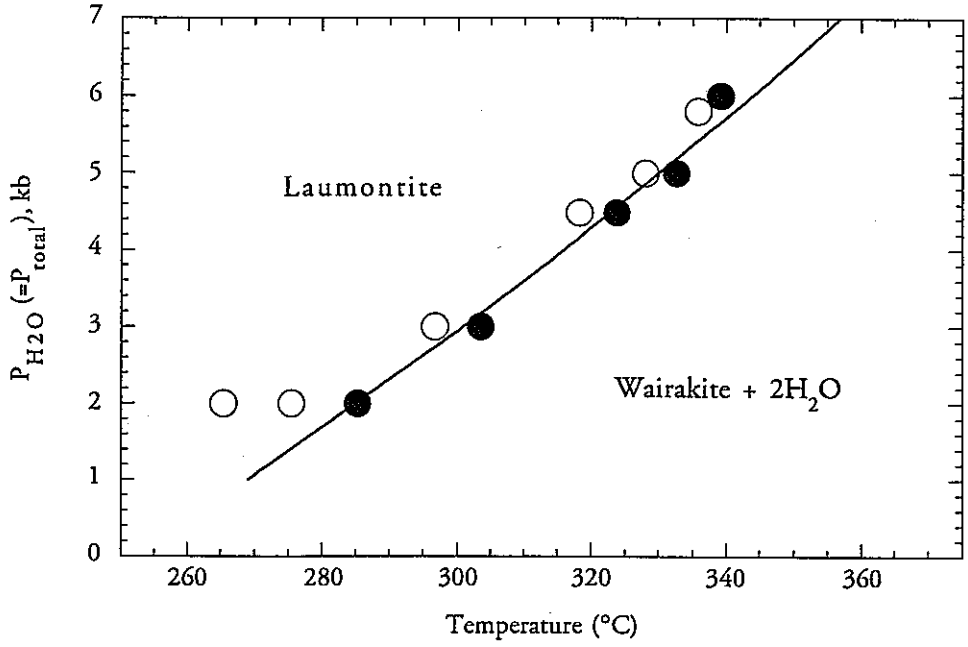


Figure 4.3.1_1. *P-T* diagram showing calculated and experimental equilibrium conditions for the reaction laumontite ⇌ wairakite + 2 H_2O. The curve is calculated using SUPCRT and SPRONS.JNC. Experimental data are from Liou (1971). Half brackets where the zeolite laumontite is the stable phase are indicated by open symbols; half brackets where the zeolite wairakite is stable are indicated by filled symbols (see Helgeson *et al.*, 1978, Fig. 91b). The calculated curve is consistent with all the experimental data, except the point indicating that wairakite is stable at 340°C and 6 kb.

unknown properties (e.g., $\Delta G^{\circ}_{f,i}$). In practice, additional constraints on a few of the parameters in this equation (e.g., the a_i Maier-Kelly coefficients) are usually required to adequately constrain the regression calculations. These independent constraints are obtained using other experimental techniques, such as calorimetry (Section 4.3.2.1).

Alternative approaches to that described above have been used to evaluate phase-equilibrium data. Berman (1988) evaluates inequalities in equations similar to Eqn. (4.3.1.1_2) explicitly using a linear programming technique (Gordon, 1973; Berman *et al.*, 1986). The other internally consistent databases described in Section 3.3 are derived using alternative regression-based methods unique to each database. Differences in the regression methods deal mainly with the problem of locating true equilibrium temperatures and pressures between the experimentally determined *P-T* half brackets (Engi, 1992). The strengths and limitations of regression and linear programming techniques are discussed by Berman *et al.* (1986) and Kolassa (1990).

Thermodynamic data for 83 minerals in SPRONS.JNC were originally retrieved by Helgeson *et al.* (1978) using the approach described above. The data added to this database by Johnson *et al.* (1991) to generate SPRONS92. DAT (Section 3.2) are from Table 9 of Helgeson *et al.* (1978). The added data are for selected elements, oxides, halides, sulfates, carbonates and sulfides, and

are retrieved solely from calorimetric investigations. Although the reliability of these calorimetric data is untested on the basis of experimental phase-equilibrium constraints, they appear to be more consistent with phase relations observed in geologic systems (Helgeson *et al.*, 1978) than values adopted in previous studies (Helgeson, 1969).

4.3.1.2 Solubility experiments. These experiments use a variety of techniques[9] to determine the equilibrium constants of reactions involving one or more minerals (and/or gases) and an aqueous solution. Attainment of equilibrium is thus the primary goal of these experiments, in contrast to phase-equilibrium studies, where it is only necessary to approximate equilibrium conditions in terms of bounding temperatures and pressures. This requires verification that the reaction is reversible, which can be demonstrated by approaching equilibrium from conditions of both undersaturation and supersaturation of the aqueous solution's composition with respect to the reaction of interest. Non-ideal behavior of the aqueous phase must also be accounted for to accurately calculate the activities of aqueous reactants and products that partially or completely determine the value of the equilibrium constant.

To retrieve thermodynamic properties from the results of solubility studies, the experimental equilibrium constants must first be converted into Gibbs free energies of reaction using Eqn. (4.2.3_2), and then cast into terms containing fitting parameters and standard molal properties using appropriate equations described in Sections 4.2.1 and 4.2.2.4. Unknown properties (e.g., ΔG_f°) are obtained by regression of the derived equations using the experimentally determined equilibrium constants as constraints over an appropriate range of temperatures and pressures. Additional independently determined parameters (e.g., Maier-Kelly coefficients) may be required to adequately constrain the regression calculations.

In practice, the results of solubility experiments have been used primarily to test and refine the accuracy of thermodynamic properties retrieved from phase-equilibrium and calorimetric data. An example of this use of solubility data is illustrated by comparison of Figs. 4.3.1.2_1 and 4.3.1.2_2 (see also Figs. 48a and 47a, respectively, in Helgeson *et al.*, 1978). Fig. 4.3.1.2_1 shows experimental phase-equilibrium data for the reaction:

$$\text{pyrophyllite} + H_2O \rightleftharpoons \text{kaolinite} + 2\ \text{quartz},$$

where the corresponding univariant equilibrium curve calculated using SUPCRT and SPRONS.JNC is also indicated for comparison. As can be seen, the calculated curve is poorly constrained by the limited amount of experimental data. The reliability of most of these data (Thompson, 1970) may also be

[9] References cited in Section 6 include detailed descriptions of these techniques. The book edited by Ulmer and Barnes (1987) describes associated experimental equipment.

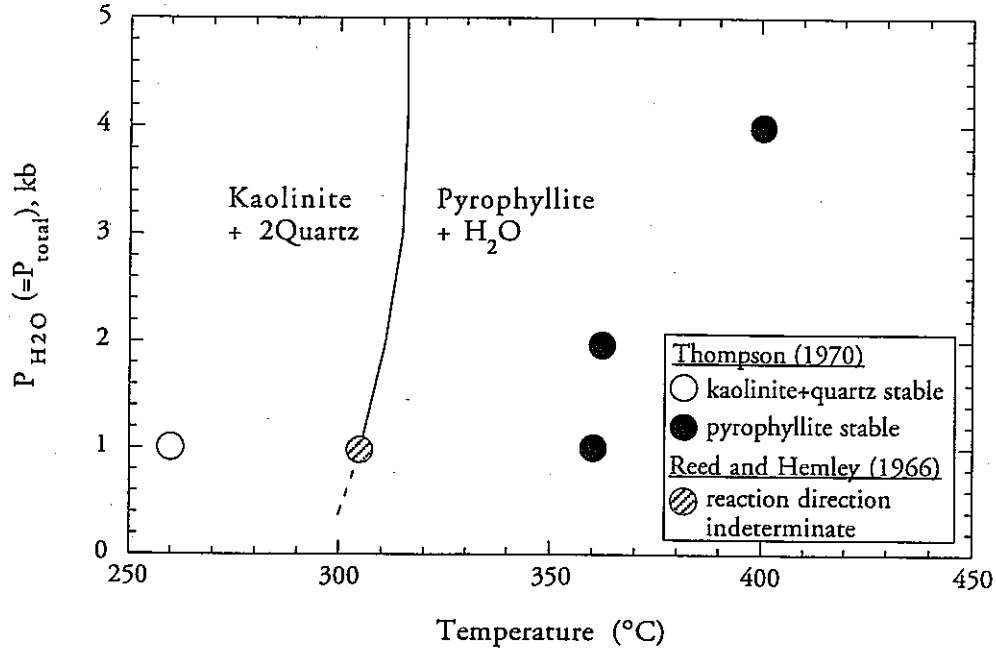


Figure 4.3.1.2_1. Calculated univariant equilibrium curve and experimental observations (symbols) of phase equilibria among kaolinite, quartz, pyrophyllite and H_2O.

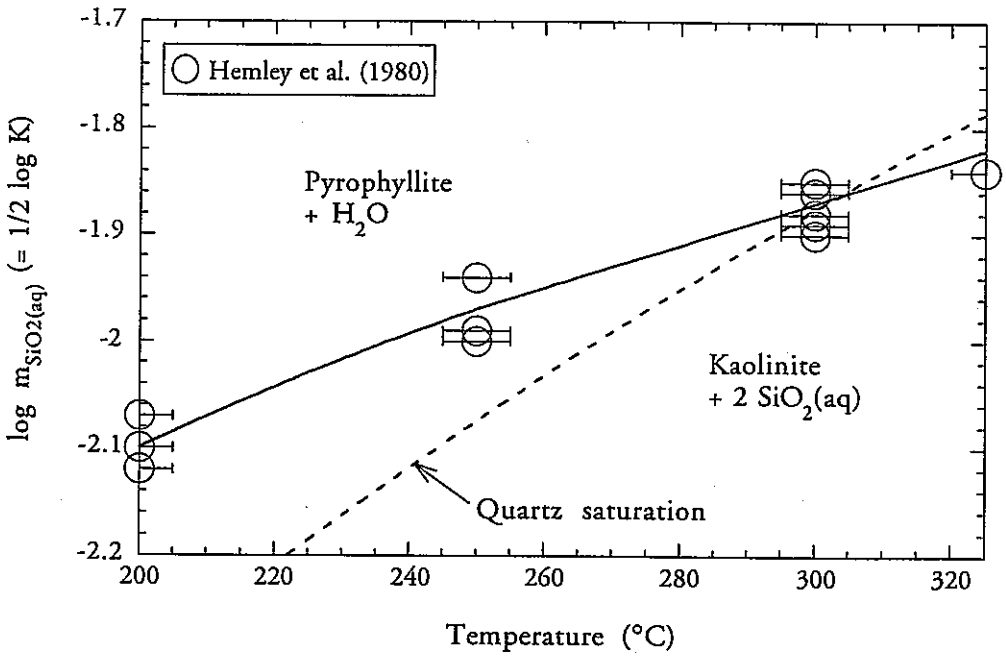


Figure 4.3.1.2_2. Calculated (solid curve) and experimental (symbols) equilibrium constants for the reaction pyrophyllite + H_2O ⇌ kaolinite + 2 $SiO_2(aq)$. The size of the symbols is greater than the analytical uncertainty assigned by Hemley *et al.* (1980) to $SiO_2(aq)$ measurements (±5% of the reported value). The uncertainty in temperature measurements is ± 5°C (Hemley *et al.*, 1980). Note that $m_{SiO2(aq)} \approx a_{SiO2(aq)}$ for these experimental conditions.

questionable (Section 4.3.4.2).

Fig. 4.3.1.2_2 shows experimental equilibrium constants at 1 kb, and their calculated counterparts (using SUPCRT and SPRONS.JNC), for the similar, solubility reaction:

pyrophyllite + H_2O ⇌ kaolinite + 2 $SiO_2(aq)$.

As can be seen, the calculated curve is in good agreement with the available experimental data, within stated uncertainty limits. Moreover, this curve intersects the dashed curve representing quartz saturation at approximately 303°C. This partially confirms results from the phase equilibrium experiments (Fig. 4.3.1.2_1), which indicate that pyrophyllite, kaolinite and quartz should equilibrate at 1 kb when T ≈ 305°C.

Similar uses of solubility data to test and refine thermodynamic properties retrieved from phase-equilibrium and calorimetric experiments are described by Helgeson *et al.* (1978) for various minerals in the systems: MgO-SiO_2-H_2O, CaO-MgO-SiO_2-CO_2-H_2O, Al_2O_3-SiO_2-H_2O, K_2O-Al_2O_3-SiO_2-HCl-H_2O, Na_2O-Al_2O_3-SiO_2-HCl-H_2O, Na_2O-K_2O-Al_2O_3-SiO_2-H_2O, CaO-FeO-Fe_2O_3-SiO_2-H_2O, and CaO-FeO-Fe_2O_3-Al_2O_3-SiO_2-CO_2-H_2O. The thermodynamic properties of these minerals (forsterite, talc, chrysotile, antigorite, wollastonite, anthophyllite, enstatite, quartz, sepiolite, calcite, dolomite, diopside, tremolite, gibbsite, boehmite, diaspore, corundum, kaolinite, pyrophyllite, andalusite, albite, low albite, high albite, K-feldspar, high sanidine, maximum microcline, analcime, paragonite, muscovite, anorthite, kalsilite, nepheline, epidote, andradite, hedenbergite, magnetite and hematite) are thus constrained by three different types of experimental data. Most of these data pertain to relatively high temperatures and pressures, however, which are far removed from conditions of primary interest in the Japanese repository concept (see Section 6). It is similarly noted that Johnson *et al.* (1991) revised Gibbs free energies and enthalpies of formation of several Ca-bearing minerals in the Helgeson *et al.* (1978) database to be consistent with updated values of Gibbs free energies of Ca^{2+} and CO_3^{2-} formation retrieved from experimental determinations of calcite and aragonite solubility reported by Plummer and Busenberg (1982).

As noted in Section 3.2, all the data for minerals from Helgeson *et al.* (1978), and the revisions incorporated by Johnson *et al.* (1991), are included in SPRONS.JNC. More recent uses of solubility data to test and refine thermodynamic properties retrieved from phase-equilibrium and calorimetric experiments are reported by Sverjensky *et al.* (1991) and Pokrovskii and Helgeson (1995; 1997b). The results of these studies are also incorporated in SPRONS.JNC (Section 5.2.2).

4.3.2 Mineral and gas data

The heat capacities and molar volumes of minerals and gases are independent of all other thermodynamic properties because they can be determined directly using calorimetric methods (heat capacity), or calculated from refinements of X-ray data on a mineral's unit-cell dimensions, or from the ideal gas law (molar volumes). Calorimetric experimental techniques and apparatus are summarized by McCullough and Scott (1968) and Robie (1987). Nordstrom and Munoz (1985) describe the procedure to calculate molar volumes from unit-cell data. The unit-cell dimensions (Bloss, 1971) of many rock-forming minerals are described by Deer et al. (1962-1963).

To evaluate these experimental data, various empirical expressions are assumed for the heat capacity as a function of temperature (i.e., Eqn. 4.2.1_5; see also Anderson and Crerar, 1993), or molar volume as a function of pressure and temperature (e.g., Berman, 1988; Holland and Powell, 1990; Gottschalk, 1997). The fitting parameters in these expressions are then determined by regression of one or more experimental datasets that span as broad a range of temperatures or pressures as possible.

4.3.2.1 Standard molal heat capacities. The empirical $a_{1...3}$ parameters in SPRONS.JNC used with Eqn. (4.2.1_5) to calculate isobaric heat capacities as a function to temperature are:

- from calorimetric investigations (e.g., Kelly, 1960; Pankratz, 1964a,b; Walther and Helgeson, 1977; King *et al.*, 1975; Pankratz and King, 1965, Pankratz and King, 1970; Pankratz and Kelley, 1964; Pankratz, 1968a,b; King and Weller, 1961; Mah *et al.*, 1967; Mills, 1974),

- generated by Helgeson *et al.* (1978) by calculation or regression of heat capacity data reported by others (Stull and Prophet, 1971; Holm *et al.*, 1967; Perkins *et al.*, 1977; Kiseleva *et al.*, 1972, 1974; Holm and Kleppa, 1966; Thompson *et al.*, 1974; Krupka *et al.*, 1977a,b; Kelley *et al.*, 1953; Robie and Hemingway, 1973), or

- estimated using equations described by Helgeson *et al.* (1978) and calorimetric data from King (1955) and King and Weller (1961).

The coefficients are valid from 25°C to an upper temperature limit corresponding to the maximum temperature investigated experimentally, or to the temperature of phase transitions (see Section 5 and Appendix A). Equation (4.2.1_5) yields fits of experimental heat capacities in this temperature range to within ± 0.1 cal mol^{-1} K^{-1}, or less (Helgeson *et al.*, 1978). Less accurate fits are obtained, however, in the case of minerals with high Debye temperatures (Denbigh, 1971; Berman and Brown, 1985). The effects of solid-state phase transitions, order/disorder, and vacancy defects on the heat capacity and other thermodynamic properties of minerals are evaluated by Helgeson *et al.* (1978),

Robie *et al.* (1978) and Berman and Brown (1985). These effects were accounted for in the original Helgeson *et al.* (1978) database, and are thus incorporated in SPRONS.JNC.

4.3.2.2 Standard molal volumes. The volumetric properties of minerals and gases in SPRONS.JNC are limited to standard molal volumes at the reference temperature and pressure. This is because the equation of state for minerals and gases adopted in SUPCRT (Section 4.2.1) does not consider the effects of variations in temperature and pressure on the standard molal volume. Associated data characterizing thermal expansivities and compressibilities of minerals are therefore unnecessary (Helgeson *et al.*, 1978). Standard molal volumes in SPRONS.JNC are:

- reported values (Robie and Waldbaum, 1968; Robie *et al.*, 1966; Fyfe *et al.*, 1958; Ernst, 1968; Chatterjee, 1970; Kunze, 1961, Helgeson and Kirkham, 1974a),
- computed by Helgeson *et al.* (1978) using published data on unit-cell dimensions (Donnay and Ondik, 1973; Burnham, 1965; Deer *et al.*, 1962-1963; Berry, 1974), or
- estimated using procedures described by Helgeson *et al.* (1978) and data from Sheppard and Gude (1970) and Steinfink (1958).

The reported values for minerals, and values computed by Helgeson *et al.*, (1978), are based on refinements of unit-cell data determined by X-ray diffraction. Standard volumes determined in this manner are generally accurate to within ±0.05 to ±0.25% (Nordstrom and Munoz, 1985). It is not uncommon, however, for several volume determinations to disagree by more than the limits of reported uncertainties. This is often observed when the molar volumes of natural and synthetic samples of the same mineral are determined.

4.3.3 Electrolyte data

Equation-of-state parameters ($a_{1...4}$, c_1 and c_2, see Section 4.2.2.4) for aqueous solutes are retrieved from experimental measurements of the *apparent* molal volumes and heat capacities of electrolytes over a range of temperatures and electrolyte concentrations. For a single electrolyte solution, apparent molal properties (ϕ_Ξ) are related to their partial molal analogs by:

$$\phi_\Xi = \frac{1}{m_k}\int_0^{m_k} \Xi_k \, dm_k, \qquad (4.3.3\_1)$$

where,

$$\Xi_k = \left(\frac{\partial \Xi}{\partial m_k}\right)_{P,T}, \qquad (4.3.3\_2)$$

and m_k stands for the molality of the k-th electrolyte (Helgeson, 1981). The retrieval procedure therefore involves:

- extrapolation of the apparent molal properties to reference-state conditions of infinite dilution, at which point the corresponding standard partial molal properties are defined,
- calculation of non-solvation contributions to the standard partial molal volume, or heat capacity,
- regression of the non-solvation volumes or heat capacities as a function of temperature and pressure to determine respective values of the empirical coefficients, $a_{1...4}$, or $c_{1...2}$, and
- calculation of corresponding equation-of-state parameters for the electrolyte's constituent ions.

An approach to carry out the first of these tasks is described in Section 4.3.3.1. Regression strategies that address the three latter tasks are discussed in Section 4.3.3.2. Calorimetric methods for experimental determination of apparent molal heat capacities are described by Robie (1987) and Chen *et al.* (1994). Experimental methods for determination of apparent molal volumes are described by Hepler *et al.* (1965), Ellis (1968) and Barta and Hepler (1986).

4.3.3.1 Partial molal volumes and heat capacities of aqueous electrolytes. An approach to extrapolate experimental apparent molal properties to infinite dilution is described by Helgeson *et al.* (1981) and Helgeson (1981). The approach is based on calculation of differences between experimental apparent molal volumes or heat capacities and values of these properties that are estimated using a version of the extended Debye-Hückel equation described by Helgeson *et al.* (1981). These so-called *difference functions* are defined by (Helgeson, 1981; Shock and Helgeson, 1988):

$$\rho^{*}_{V,k} \equiv \bar{V}^{\circ}_{k} + \frac{\nu_k \, b_{V,k} I}{4} \text{ , and} \qquad (4.3.3.1\_1)$$

$$\rho^{*}_{J,k} \equiv \bar{C}^{\circ}_{P,k} - \frac{\nu_k \, b_{J,k} I}{4} \qquad (4.3.3.1\_2)$$

where $\rho^{*}_{V,k}$ and $\rho^{*}_{J,k}$ denote difference functions for the partial molal volume and heat capacity of the k-th electrolyte, respectively, $b_{V,k}$ and $b_{J,k}$ are terms that can be calculated from temperature and pressure derivatives of the extended term of the Debye-Hückel equation (Helgeson, 1981), I represents the *effective* ionic strength,

$$I = 1/2 \sum_{j} Z_j^2 m_j \text{ ,} \qquad (4.3.3.1\_3)$$

where Z stands for the ion's charge and m represents its molality, and ν_k is given by

$$\nu_k = \sum_j \nu_{j,k}, \qquad (4.3.3.1\_4)$$

where $\nu_{j,k}$ refers to the number of moles of the j-th ion in the electrolyte.

Helgeson (1981) notes that for completely dissociated electrolytes, the effective and *stoichiometric* ionic strength,

$$I \equiv 1/2 \sum_j \nu_{j,k} Z_j^2 m_k, \qquad (4.3.3.1\_5)$$

are equivalent, and that a plot of Eqn. (4.3.3.1._1) or (4.3.3.1_2) versus I at a given temperature and pressure should therefore be linear. Extrapolation of the linear curve in such plots to the intercept, I = 0, will then yield $\bar{V}_k^\circ$ or $\bar{C}_{Pk}^\circ$, respectively. This behavior is confirmed for a large number of electrolytes in relatively dilute solutions, but deviations from linear behavior are often observed at higher ionic strengths (Helgeson *et al.* 1981; Shock and Helgeson, 1988[10]). Representative results are shown in Figs. 4.3.3.1_1 and 4.3.3.1_2, for example. The deviations are caused by the effects of ion-association, which become more pronounced with increasing ionic strength and increasing temperature.

Shock and Helgeson (1988) and Shock *et al.* (1997a) employ this approach to determine standard partial molal volumes of 75 electrolytes, and standard partial molal heat capacities of 80 electrolytes. These data serve as primary constraints in the regression strategies described below to determine standard partial molal properties of the corresponding ions. Correlations among the retrieved ionic properties enable estimates to be made of standard partial molal properties of other ions and complexes, for which experimental data are unavailable (Section 4.4).

4.3.3.2. Equation-of-state parameters for aqueous ions. These parameters are obtained by regression of non-solvation contributions to the standard partial molal volumes and heat capacities of corresponding electrolytes. The non-solvation parameters are determined by rearranging Eqns. (4.2.2_1) and (4.2.2_9), i.e.,

$$\Delta\bar{V}_{n\,k}^\circ = \bar{V}_k^\circ - \Delta\bar{V}_{s\,k}^\circ, \text{ and}$$

$$\Delta\bar{C}_{Pn,k}^\circ = \bar{C}_{Pk}^\circ - \Delta\bar{C}_{Ps,k}^\circ,$$

and thus by subtracting the respective solvation contributions calculated using

10. The appendix to this reference contains 37 pages of supplemental data supporting this conclusion, and is available in microfiche form from the National Auxiliary Publication Service (document No. 04597), P.O. Box 3513, Grand Central Station, New York, NY 10163-3513.

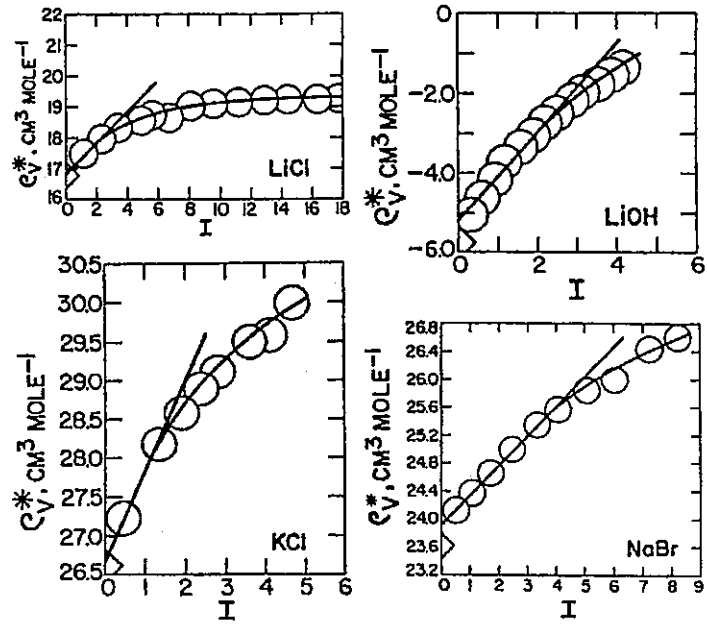


Figure 4.3.3.1_1. Calculated values (symbols) of the difference function [Eqn. (4.3.3.1_1)] for the apparent molal volumes of various electrolytes at 25°C and 1 bar (from Helgeson , 1981; Fig 7.20). Extrapolation to conditions of zero ionic strength, indicated by the linear portion of the curves, defines the standard partial molal volume. Similar plots by Helgeson (1981), Helgeson *et al.* (1981) and Shock and Helgeson (1988), document sources of experimental data.

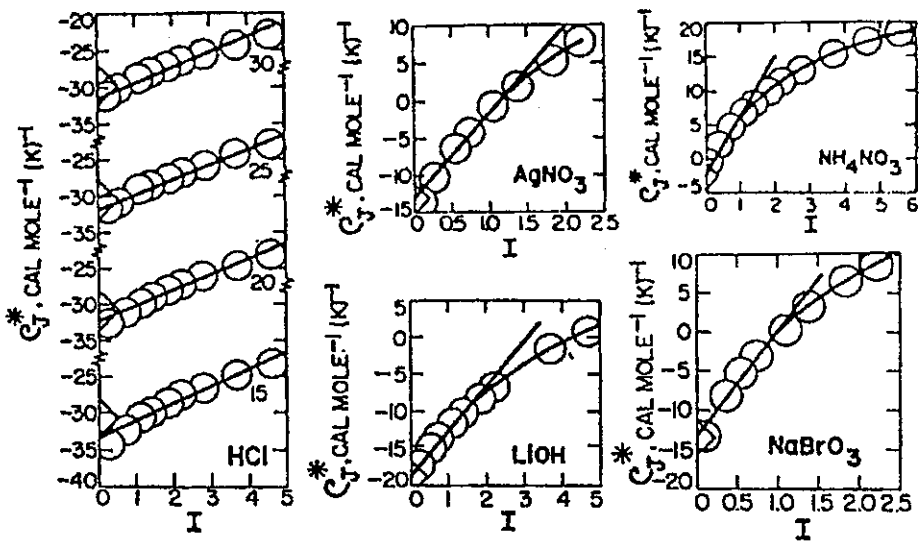


Figure 4.3.3.1_2. Calculated values (symbols) of the difference function [Eqn. (4.3.3.1_2)] for the apparent molal heat capacities of various electrolytes at 1 bar and temperatures between 15 and 30°C (from Helgeson, 1981; Fig 7.19). Extrapolation to conditions of zero ionic strength, indicated by the linear portion of the curves, defines the standard partial molal heat capacity. Similar plots by Helgeson (1981), Helgeson *et al.* (1981) and Shock and Helgeson (1988), document sources of experimental data.

Eqns. (4.2.2_6) or (4.2.2_11) from the experimentally constrained values of the standard partial molal volume or heat capacity (i.e., Section 4.3.3_1).

With the non-solvation parameters in hand, the regression strategy focusses on retrieving values for the empirical coefficients $a_{1...4}$, and $c_{1...2}$. One approach that has been used for this purpose (e.g., Shock and Helgeson, 1988; Shock *et al.*, 1997a) to retrieve all the equation-of-state parameters for aqueous solutes in SPRONS.JNC (Section 5.2.1) combines terms in Eqn. (4.2.2_8),

$$\sigma = a_1 + \frac{a_2}{\Psi + P}, \text{ and} \qquad (4.3.3.2\_1)$$

$$\xi = a_3 + \frac{a_4}{\Psi + P}, \qquad (4.3.3.2\_2)$$

such that the non-solvation volume is represented by a linear equation with respect to temperature given by,

$$\Delta \bar{V}^{\circ}_{n} = \sigma + \frac{\xi}{T - \Theta}. \qquad (4.3.3.2\_3)$$

The analogous equation for the non-solvation heat capacity is Eqn. (4.2.2_12):

$$\Delta \bar{C}^{\circ}_{Pn} = c_1 + \frac{c_2}{(T - \Theta)^2},$$

which is linear with respect to $(T - \Theta)^2$. Plots of $\Delta \bar{V}^{\circ}_{n,k}$ versus $1/(T - \Theta)$, or $\Delta \bar{C}^{\circ}_{Pn,k}$ versus $1/(T - \Theta)^2$, can thus be fit to experimentally constrained data on non-solvation volumes or heat capacities, respectively, to determine σ, or c_1, from the intercepts of the resultant linear curves (at T = 25°C), and ξ, or c_2, from their slopes. Plots of this kind are illustrated in Figs 4.3.3.2_1. Corresponding data for the ionic constituents of the electrolyte are determined using Eqn. (4.1_9).

Shock and Helgeson (1988) and Shock *et al.* (1989) demonstrated that equation -of-state parameters for aqueous species obtained by regression of experimental standard partial molal volumes and heat capacities in the manner described above correlate linearly with the standard partial molal volume or heat capacity of the species at 25°C and 1 bar. The derived correlations for ionic species are given by (Sverjensky *et al.*, 1997):

- $a_1 = (0.013684)\left\{\bar{V}^{\circ}_{Pr,Tr} + (41.84)\,\omega_{Pr,Tr} Q_{Pr,Tr}\right\} + 0.1765$ (4.3.3.2_4)
- $a_2 = (33.423)\left\{\bar{V}^{\circ}_{Pr,Tr} + (41.84)\,\omega_{Pr,Tr} Q_{Pr,Tr}\right\} - 347.23$ (4.3.3.2_5)
- $a_3 = -(0.1435)\left\{\bar{V}^{\circ}_{Pr,Tr} + (41.84)\,\omega_{Pr,Tr} Q_{Pr,Tr}\right\} + 7.0274$ (4.3.3.2_6)

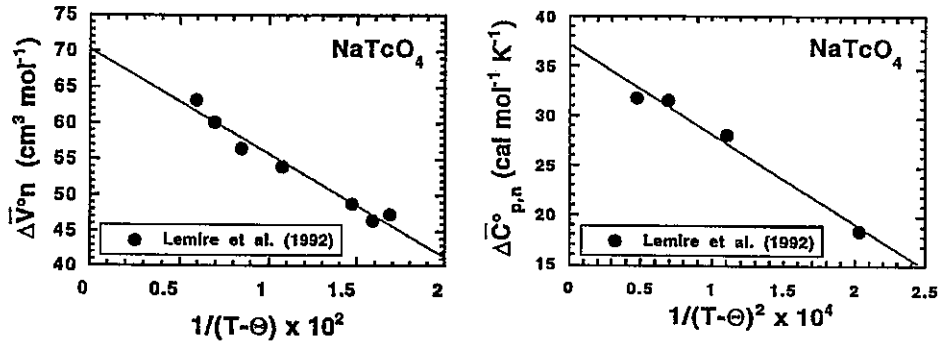


Figure 4.3.3.2_1. Non-solvation contributions to the standard partial molal volume and heat capacity of $NaTcO_4$ plotted versus temperature functions given by Eqns. (4.3.3.2_3) and (4.2.2_12), respectively (from Shock *et al.*, 1997a).

- $a_4 = -(138.17)\left\{\bar{V}^{\circ}_{Pr,Tr} + (41.84)\,\omega_{Pr,Tr} Q_{Pr,Tr}\right\} - 26355$ (4.3.3.2_7)

- $c_1 = (0.6087)\,\bar{C}^{\circ}_{PPr,Tr} + \omega_{Pr,Tr} T_r X_{Pr,Tr} + 5.85$ (4.3.3.2_8)

- $c_2 = (2037)\,\bar{C}^{\circ}_{PPr,Tr} - 30460$ (4.3.3.2_9)

where $Q_{Pr,Tr}$ and $X_{Pr,Tr}$ (see Sections 4.2.2.1 and Section 4.2.2.3, respectively) are equal to 5.903×10^{-7} (bar^{-1}) and -3.09×10^{-7} (K^{-2}), respectively, at T_r = 25°C and P_r = 1 bar, and $\omega_{Pr,Tr}$ is given by Eqn. (4.2.2_4). These correlations can be substituted into Eqns. (4.1_1), (4.1_2) and (4.2.2_20) - (4.2.2_22) to derive regression equations for the standard partial molal Gibbs free energy and enthalpy of formation, and the standard partial molal entropy, in which the regression parameters are only $\bar{V}^{\circ}_{Pr,Tr}$, $\bar{C}^{\circ}_{Pr,Tr}$, and $\omega_{Pr,Tr}$ (Sverjensky *et al.*, 1997).

4.3.4 Statistical/Mathematical analyses

Retrieval of thermodynamic properties from experimental data is carried out using statistical/ mathematical techniques on three levels:

- analysis of properties,
- analysis of reactions, and
- simultaneous evaluation of multiple reactions

The techniques applicable to each of these levels are briefly described below.

4.3.4.1 Properties. Regression techniques to evaluate standard molal heat capacities and volumes seek to minimize the *residual* function defined by:

$$R = \sum_{i=1}^{n} W_i (Q_i - q_i)^2, \qquad (4.3.4.1\_1)$$

where R stands for the residual among the set of $i...n$ determinations, q_i refers to parameter values used as estimators of the measured data, Q_i, and W_i denotes a weighting factor, which is usually taken as being inversely proportional to the measurement precision [i.e., the more precise (smaller in precision magnitude) data are accorded more weight in the regression] (e.g., Engi, 1992). For example, Q_i could represent measured values over a range of temperatures, q_i would then denote corresponding heat capacities calculated using Eqn. (4.2.1_5), and W_i would refer to the inverse of the precision of each measurement. The problem then becomes one of finding values for the temperature-independent linear fit parameters (a_i, b_i, c_i) in the Maier-Kelly equation that lead to a minimization of the residual function.

The next step in the analysis entails comparison of individual measurements to corresponding values of q_i, which, to continue with the example in the preceding paragraph, would be calculated using the Maier-Kelly equation and the optimized values for a_i, b_i, and c_i at the measurement temperature. Error plots are useful devices for visualizing such comparisons (Robinson *et al.*, 1983). The error is defined by:

$$\text{Error} = W_i(Q_i - q_i),$$

and a plot of values over the temperature range of the measurements provides a visual picture of the overall quality of the data set. An error plot is shown, for example, in Fig. 4.3.4.1_1 for a set of calorimetric measurements of anorthite's heat capacity reported by Krupka *et al.* (1979). Ideally, the errors should be centered about the zero axis, and should not exceed the precision of the measurement technique (two standard deviations are reported by Krupka *et al.*, 1979). As can be seen, all the data meet these requirements, and all are therefore considered consistent.

In similar experiments, some of the data may exceed two standard deviations from the weighted average among all the data in the set, however, and these data are then considered to be *discordant*. Rejection of discordant data is not automatic, and two approaches are taken for dealing with such data. First, the data may be rejected if an examination of experimental technique points to possible causes for the discrepancies. Potential sources of experimental error include inadequate compositional analyses of starting materials, lack of information concerning the ordering/disordering state of the reactants, and other errors or ambiguities, which can only be detected by thorough assessments of the experimental technique.

If errors in the experimental procedures cannot be identified, then the discordant data must be retained in the evaluation because there is no scientific basis for rejecting these data (i.e., rejection criteria are not based solely on statistical evaluations). In such cases, the influence of discordant data on

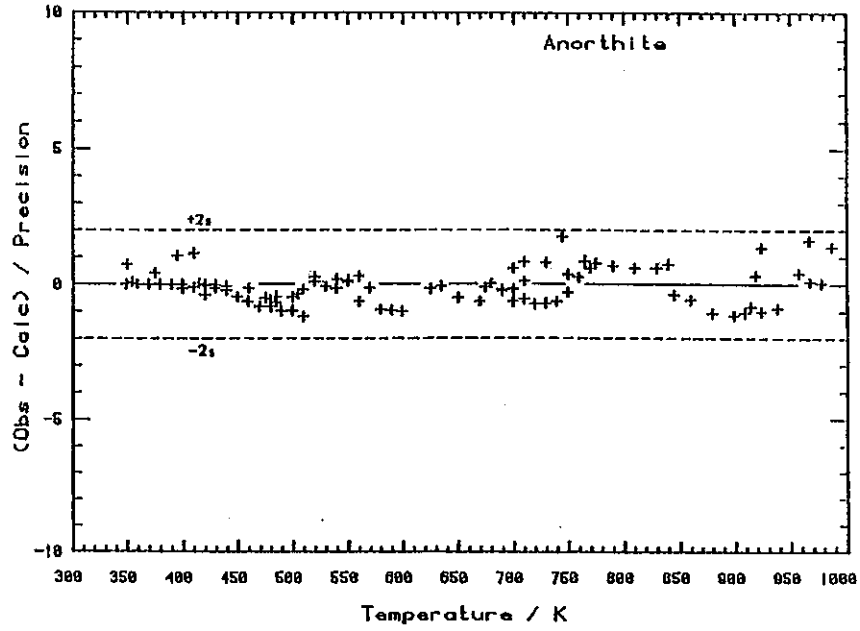


Figure 4.3.4.1_1. Error plot as a function of temperature (from Robinson *et al.*, 1983) for differential scanning calorimetry measurements of the heat capacity of anorthite reported by Krupka *et al.* (1979).

regression parameters is minimized through adjustment of weighting parameters. Such adjustments may involve increasing the magnitude of the measurement precision (i.e., acknowledging greater uncertainty in these data) thus decreasing the weight accorded to the discrepant data and their influence on the residual function. Regression techniques for evaluation of thermodynamic data are described by Haas (1974), Haas and Fisher (1976), Robinson *et al.* (1983), and Nordstrom and Munoz (1985).

4.3.4.2 Reactions. Standard molal thermodynamic properties retrieved from experiments involving reactions are not independent because they are determined by the individual thermodynamic properties of all reactant and product phases and aqueous species. Reaction-based data that constrain the internally consistent databases described in Sections 3.2 and 3.3 are predominantly constrained by phase-equilibrium results.

Two statistical/mathematical approaches have been developed for evaluation of thermodynamic properties from phase-equilibrium studies (Berman *et al.*, 1986):

- mathematical (or linear) programming (MAP), and
- regression analysis.

The MAP approach translates each *P-T* half-bracket into an inequality relation [Eqn. (4.3.1.1_1)] and a corresponding inequality constraint equation given by the following *objective* function (Engi, 1992):

$$O_b = \sum_{i=1}^{n} W_i'(Q_i' - q_i')^2, \qquad (4.3.4.2\_1)$$

where the primed symbols are similar to those discussed above for the residual function evaluated in regression analyses, but differ in the sense that parameter values may be determined using both equality and inequality constraints. In this sense, MAP differs from regression methods because the objective function is capable of operating on individual half-brackets, rather than on pairs of half-brackets and associated assumptions about the true location of the equilibrium point, and more generally about the probability distribution of the equilibrium position between half-brackets. The merits and deficiencies of both approaches are considered by Berman *et al.* (1986), Holland and Powell (1990) and Kolassa (1990). Both approaches have been used successfully to evaluate thermodynamic data from phase-equilibrium studies using a minimum of additional calorimetric constraints.

The regression-based methods for data selection described earlier for individual properties are similar in principle to selection methods based on regression applied to individual reactions. Selection criteria derived from MAP evaluations are also basically determined by comparison of the weighted average of a set of thermodynamic properties with observed values. Discordant data are readily identified in such comparisons, and may be rejected if warranted by a subsequent review of experimental procedures.

Robinson *et al.* (1983), for example, used regression methods to evaluate solubility data from Hemley *et al.* (1980) and phase-equilibrium data reported by Thompson (1970) for the reaction (see Section 4.3.1.2):

$$\text{kaolinite} + 2\ SiO_2(aq) \rightleftharpoons \text{pyrophyllite} + H_2O.$$

The Gibbs free energy change for this reaction over a broad temperature range is shown in Fig. 4.3.4.2_1, where it can be seen that the Hemley *et al.* (1980) data are closely approximated by the weighted average of the full data set. The Thompson (1970) data, however, are consistently displaced upwards with respect to the weighted average.

An error plot for these data (Fig. 4.3.4.2_2) reveals that the solubility data all lie within one standard deviation of the weighted average (one standard deviation is the error of precision assigned to these data by Hemley *et al.*, 1980). In contrast, the Thompson (1970) data exceed two standard deviations of the weighted average [two standard deviations is the precision reported by Thompson (1970)]. These results suggest that the Thompson (1970) data are, at best, discordant. A review of the experimental technique used by Thompson (1970) suggests that the reason for the discordance could be due to the finely ground kaolinite used in the experiments and/or to the short duration of the

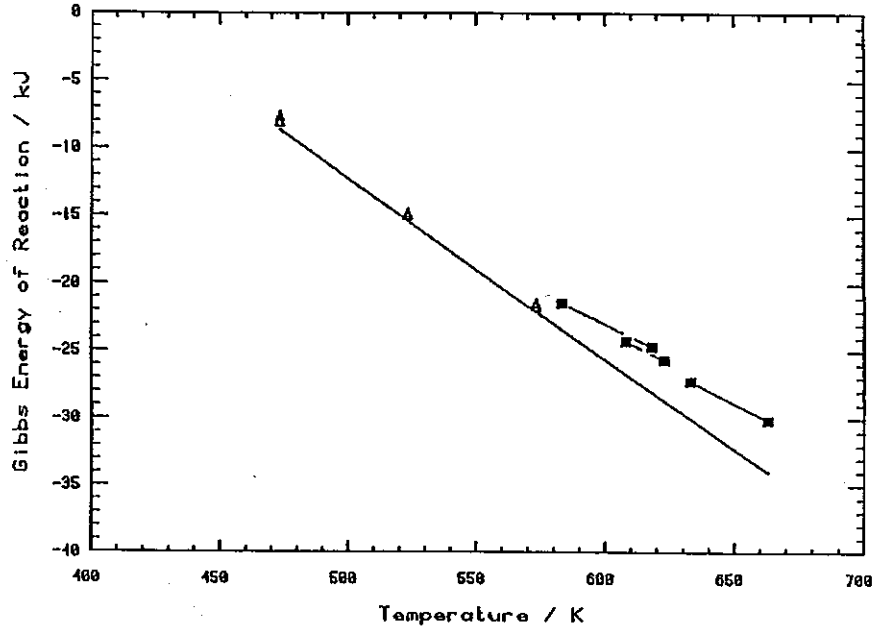


Figure 4.3.4.2_1. Standard Gibbs free energies of reaction as a function of temperature for the reaction: kaolinite + 2 SiO_2(aq) ⇌ pyrophyllite + H_2O (from Robinson *et al.*, 1983). Open symbols represent calculations based on measurements of dissolved silica concentrations reported by Hemley *et al.* (1980). Solid symbols connected by lines denote values computed from the phase-equilibrium experiments of Thompson (1970).

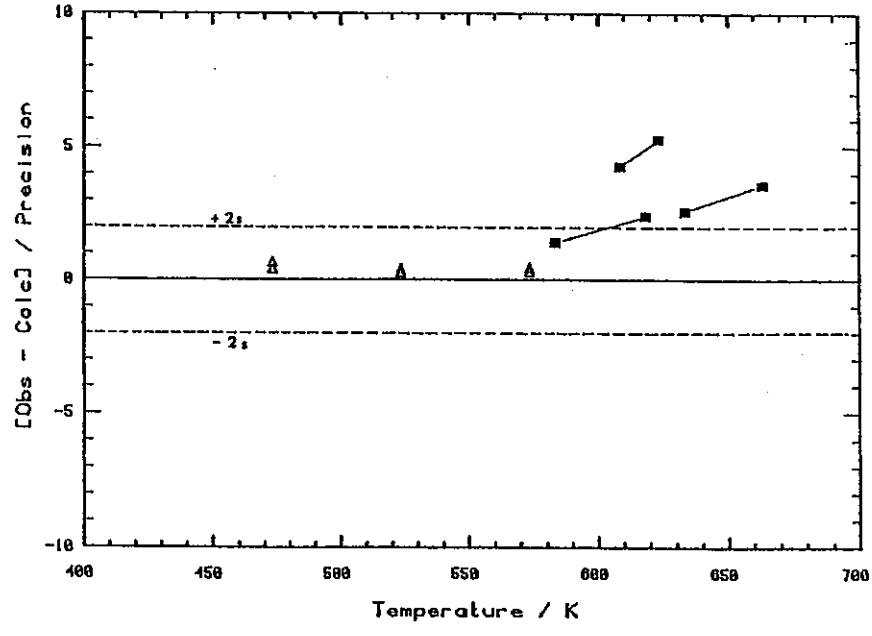


Figure 4.3.4.2_2. Error plot as a function of temperature for the reaction: kaolinite + 2 SiO_2(aq) ⇌ pyrophyllite + H_2O (from Robinson *et al.*, 1983). Open symbols represent the experimental results of Hemley *et al.* (1980). Closed symbols connected by lines represent *P-T* half brackets determined by Thompson (1970). The dashed lines denote two times the experimental precision reported by Hemley *et al.* (1980), or two times the width of the Gibbs free energy of reaction "bracket" corresponding to the *P-T* half brackets.

experiments (Robinson *et al.*, 1983). The Thompson (1970) data were finally rejected by Robinson *et al.* (1983) for these reasons, not simply because the data are discordant based on the statistical evaluation of the full data set.

This example again illustrates that discordant data can be readily identified using statistical methods, but that the cause of the disagreement may not always be as straight-forward as its detection. Thus, thermodynamic relations and statistical/mathematical evaluations are useful for detecting consistent and discordant data, but technical competence and experience in laboratory investigations is indispensable for final data selection/rejection decisions.

4.3.4.3 Simultaneous evaluation of multiple reactions. Matrix analytical methods are used in simultaneous evaluations of multiple reactions to set up a *general optimization* problem similar to that described in Section 4.3.4.2. These methods also ensure internal consistency, and have been used to construct all the internally consistent databases discussed in Sections 3.2 and 3.3.

Matrix methods are based on a constraint matrix, which consists of an ordered array of constraints written in matrix format. Constraint matrices developed for MAP analyses include two sub-matrices, which are defined separately using equality and inequality constraints. A single matrix consisting of equality constraints is set up for regression-based methods.

An instructive example of the approach is given by Powell and Holland (1985), who adopt a regression method based on calculation of enthalpies of reaction from phase-equilibrium data (Section 4.3.1.1) to construct the following matrix:

$$\mathbf{b} = \mathbf{Rh}, \qquad (4.3.4.3\_1)$$

where **R** denotes the matrix of stoichiometric coefficients among a set of reactions, **h** stands for the vector of enthalpies of formation for each of the minerals considered (i.e., these are the primary values being calculated in this example), and **b** refers to the vector of reaction enthalpies, which are calculated using an appropriate statement of Eqn. (4.2.3_1). For this particular application, **b** represents a vector of "centers" of reaction enthalpies corresponding to pairs of *P-T* half brackets determined in a set of phase-equilibrium experiments.

The objective of the calculations in this regression approach is to minimize values of the following quantity:

$$\|\mathbf{b} - \mathbf{Rh}\|^2 \qquad (4.3.4.3\_2)$$

which, for the example considered by Powell and Holland (1985) involving high albite (*ab*), paragonite (*pa*), andalusite (*and*), kyanite, (*ky*), jadeite (*jd*), corun-

dum (*cor*), quartz (*q*) and water (H_2O) is given by:

$\mathbf{h}^T$ = enthalpies of formation of

$$\mathbf{R} = \begin{array}{c} [ab \quad pa \quad and \quad ky \quad jd \quad cor \quad q \quad H_2O] \\ \left|\begin{array}{cccccccc} 1 & 0 & 0 & 0 & -1 & 0 & -1 & 0 \\ 0 & -1 & 0 & 1 & 1 & 0 & 0 & 1 \\ 1 & -1 & 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & -1 & 1 & 0 & 0 & 0 & -1 & 1 \\ 1 & -1 & 0 & 1 & 0 & 0 & -1 & 1 \end{array}\right| \end{array}$$

$$\mathbf{b} = \left|\begin{array}{l} \Delta H^\circ_{r,P,T}\ (jd+q = ab) \\ \Delta H^\circ_{r,P,T}\ (pa = jd+ky+H_2O) \\ \Delta H^\circ_{r,P,T}\ (pa = ab+cor+H_2O) \\ \Delta H^\circ_{r,P,T}\ (pa+q=ab+and+H_2O) \\ \Delta H^\circ_{r,P,T}\ (pa+q = ab+ky+H_2O) \end{array}\right|$$

Although the matrix can be solved in principle using conventional methods, i.e.,

$$\mathbf{h} = (\mathbf{R}^T\mathbf{R})^{-1}\mathbf{R}^T\mathbf{b},$$

the problem considered in this example is not amenable to solution because there are five equations (fixing the enthalpies of reaction) and eight unknowns (enthalpies of formation of *ab*, *pa*, *and*, *ky*, *jd*, *cor*, *q*, and H_2O). To overcome this problem, Powell and Holland (1985) expand **R** by six rows of the form:

[0,0,...0,1,0,..,0,0]

where the value, 1, is centered on the position of an "anchor" mineral, for which a corresponding row in **b** is added containing a calorimetrically determined reference value for the enthalpy of formation of the anchor phase.

The anchor minerals in this example are assumed to be *and*, *ky*, *jd*, *cor*, *q* and H_2O, for which calorimetric values for the enthalpy of formation at 1 bar and 25°C from Robie *et al.* (1978) are used to calculate enthalpies of formation for *ab* and *pa* (Powell and Holland, 1985). These authors also demonstrate how weighting factors can be incorporated into the matrix formulation of the residual function in regression evaluations.

Matrix analytical methods are useful because they ensure that derived databases are internally consistent (Section 3.1.1). There are two important limitations in this approach, however. First, errors in any one anchor datum will be propagated throughout the database. The database derived by Helgeson *et al.* (1978), for example, appears to suffer from this problem (Nordstrom and Munoz, 1985). Standard molal Gibbs free energies and enthalpies of formation for aluminous minerals in this database contain a systematic error of 1.55 kcal mol^{-1}, which was traced by Hemingway *et al.* (1982) to the use of an incorrect value adopted for

the reaction kaolinite + H_2O = 2 gibbsite + 2 $SiO_2(aq)$. The incorrect value was subsequently used by Helgeson *et al.* (1978) to calculate the enthalpy of formation of kaolinite. Kaolinite was adopted as a reference mineral, and the error was therefore propagated throughout all aluminous phases in this database. Re-evaluation of the Al_2O_3-H_2O-NaCl system (Pokrovskii and Helgeson, 1995) may have partially corrected this problem (Section 3.5), but associated effects on the internal consistency of the database are uncertain as a result (Section 6.4.1).

The second weakness in the use of matrix analytical methods for simultaneous evaluation of thermodynamic data is simply the fact that the matrices are difficult to evaluate for complex, multi-component systems. Thus it is not a simple matter to undertake periodic updates and revisions of internally consistent thermodynamic databases.

4.4 Estimation of Thermodynamic Properties and Equation-of-State-Parameters

The standard molal volume, entropy, heat capacity and equation-of-state parameters of several minerals in SPRONS.JNC are estimated by Helgeson *et al.* (1978) using techniques that are briefly described in Section 4.4.1. Similarly, the standard partial molal volume, entropy, heat capacity and equation-of-state parameters of many aqueous ions are estimated by Shock and Helgeson (1988), Shock *et al.* (1997a), Sverjensky *et al.* (1997) and others, based on correlations that are deduced empirically from relations observed among experimentally determined standard partial molal properties of other ionic solutes. The correlations that have been used to estimate thermodynamic properties in SPRONS.JNC are described in Section 4.4.2.

4.4.1 Minerals

Helgeson *et al.* (1978) use the concept of structurally identical, or similar, classes of minerals as the basis for estimation of standard molal entropies, volumes and heat capacities. The structural classes considered include ortho and ring silicates, chain and band silicates, framework silicates, sheet silicates and carbonates. Estimation techniques for standard molal volumes and entropies are described below. This is followed by a brief description of the technique used to estimate standard molal heat capacities.

Reasonably accurate estimates of the standard molal entropy or volume of minerals can be obtained by first writing a reversible reaction between the mineral for which the standard entropy or volume is to be estimated, and other minerals in the same or similar structural class whose entropies or volumes are known, using oxide formula units to balance the reaction if necessary. If, for example the standard entropy, or volume, of the mineral akermanite is unknown, then an appropriate reaction for estimation of these quantities is:

$$Ca_2MgSi_2O_7 + \alpha\text{-}Al_2O_3 \rightleftharpoons Ca_2Al_2SiO_7 + MgO + SiO_2$$

(akermanite) (corundum) (gehlenite) (periclase) (α-quartz)

for which,

$$\Delta S^\circ_r = S^\circ_{\text{gehlenite}} + S^\circ_{\text{periclase}} + S^\circ_{\alpha\text{-quartz}} - S^\circ_{\text{corundum}} - S^\circ_{\text{akermanite}}, \qquad (4.4.1\_1)$$

and,

$$\Delta V^\circ_r = V^\circ_{\text{gehlenite}} + V^\circ_{\text{periclase}} + V^\circ_{\alpha\text{-quartz}} - V^\circ_{\text{corundum}} - V^\circ_{\text{akermanite}}. \qquad (4.4.1\_2)$$

Helgeson *et al.* (1978) rearrange equations such as Eqn. (4.4.1_1) and (4.4.1_2) such that unknown parameters, including the unknown entropy and volume of reaction, are grouped together on the left-hand sides of these equations, i.e.,:

$$S^\circ_{\text{akermanite}} + \Delta S^\circ_r = S^\circ_{\text{gehlenite}} + S^\circ_{\text{periclase}} + S^\circ_{\alpha\text{-quartz}} - S^\circ_{\text{corundum}}, \qquad (4.4.1\_3)$$

and

$$V^\circ_{\text{akermanite}} + \Delta V^\circ_r = V^\circ_{\text{gehlenite}} + V^\circ_{\text{periclase}} + V^\circ_{\alpha\text{-quartz}} - V^\circ_{\text{corundum}}. \qquad (4.4.1\_4)$$

Then, designating the left-hand sides of such equations generally as S°_s and V°_s, respectively, the standard molal entropy of the i-th mineral (e.g., akermanite) can be estimated using:

$$S^\circ_{i,Pr,Tr} = \frac{S^\circ_{s,Pr,Tr}\left(V^\circ_{s,Pr,Tr} + V^\circ_{i,Pr,Tr}\right)}{2V^\circ_{s,Pr,Tr}}, \qquad (4.4.1\_5)$$

assuming the standard molal volume of the mineral is known. Conversely, this equation can be re-arranged to estimate the standard molal volume of the mineral if the standard molal entropy is known.

Equation (4.4.1_5) is used to estimate the standard molal entropy of several non-ferrous silicate minerals in SPRONS.JNC (see Table 3 of Helgeson *et al.*, 1978). It is also appropriate for non-ferrous carbonates, chlorides, sulfates and oxides, but inappropriate for ferrous silicates, due to crystal field stabilization effects imposed on silicate structures by the ferrous ion. As a first approximation, Helgeson *et al.* (1978) use a modified version of Eqn. (4.4.1_5) for such minerals given by:

$$S^\circ_{i,Pr,Tr} = \frac{S^\circ_{s,Pr,Tr}\left(V^\circ_{s,Pr,Tr} + V^\circ_{i,Pr,Tr}\right)}{2V^\circ_{s,Pr,Tr}} - 2\nu_{Fe,i}, \qquad (4.4.1\_6)$$

where $\nu_{Fe,i}$ stands for the number of moles of ferrous iron per mole of the mineral. Equation (4.4.1_6) is used to estimate the standard molal entropy of

several ferrous silicate minerals in SPRONS.JNC (see Table 3 of Helgeson *et al.*, 1978).

Similarly, the contribution of structural H_2O to the standard molal entropies of hydrous silicates is estimated by assigning a value of 9.6 cal mol^{-1} K^{-1} at 25°C and 1 bar to the oxide formula unit ($S^{\circ}_{H2O(s)}$) representing H_2O that is tightly bound in crystallographic lattices (Helgeson *et al.*, 1978). Loosely bound H_2O in the structural channels of zeolites is assigned a value of 8 cal mol-1 K^{-1}.

Helgeson *et al.* (1978) have shown that the estimated entropy values of ferrous and non-ferrous silicates at 25°C and 1 bar generally agree to within ±1% of values determined calorimetrically. The effects of errors of this magnitude on calculated entropies of reactions at high temperatures are negligible. The effects of such errors on calculated Gibbs free energies of formation at high temperatures may exceed several hundred cal mol^{-1} K^{-1}, but the errors tend to cancel if all the estimated data are consistent with one another, and if more than one estimated value is involved in the calculation.

Heat capacities of minerals are estimated by Helgeson *et al.* (1978) on the basis of additivity constraints and the assumption that the heat capacity of reaction among oxide and silicate minerals of the same structural class is equal to zero at all temperatures. This approach is formulated as a *structural algorithm* given by:

$$C^{\circ}_{P\,x} = \sum_{i}^{x} \nu_{i,r} C^{\circ}_{P\,i} / \nu_{x,r} \qquad (4.4.1\_7)$$

where the properties to be estimated are represented by the subscript x, those that are known are distinguished by the subscript i, and $\nu_{x,r}$ and $\nu_{i,r}$ denote stoichiometric coefficients (positive for products and negative for reactants) of the unknown and known minerals, respectively, in a given reference reaction among structurally similar phases. Comparison of heat capacities estimated using this algorithm with corresponding data determined calorimetrically indicates that discrepancies are generally less than 2% of the calorimetric values.

Restating Eqn. (4.4.1_7) in terms of equation-of-state parameters for minerals (a_i, b_i, c_i) consistent with the Maier-Kelly equation [Eqn. (4.2.1_5)] allows estimates of these parameters to be made in accordance with the following equations (Helgeson *et al.*, 1978):

$$a_x = \sum_{i}^{x-1} \nu_{i,r} a_i / \nu_{x,r}, \qquad (4.4.1\_8)$$

$$b_x = \sum_{i}^{x-1} \nu_{i,r} b_i / \nu_{x,r}, \qquad (4.4.1\_9)$$

and

$$c_x = \sum_{i}^{x-1} v_{i,r} c_i / v_{x,r} \,. \qquad (4.4.1\_10)$$

Maier-Kelly coefficients for 66 minerals in SPRONS. JNC are estimated using Eqns. (4.4.1_8) - (4.4.1_10) (Helgeson *et al.*, 1978 - Table 7). Comparison of similar estimates with experimental counterparts indicates that the estimated coefficients may differ considerably with experimental values (Helgeson *et al.*, 1978), but that corresponding heat capacities are nevertheless closely approximated at both low and high temperatures. This is because discrepancies among the coefficients tend to cancel when they are used in Eqn. (4.2.1_5).

4.4.2 Aqueous solutes

As noted in Section 4.3.3, values of the standard partial molal entropy, heat capacity, volume and conventional Born coefficient of an aqueous solute are needed at the reference temperature and pressure in order to calculate the standard partial molal Gibbs free energy and enthalpy of formation of the solute at other temperatures and pressures. Although the appropriate data have been determined experimentally for many aqueous solutes, there are numerous ions and other aqueous species for which experimental data are presently lacking.

To address this situation, Shock and Helgeson (1988) proposed several empirical correlations among $\bar{S}^\circ$, $\bar{C}_p^\circ$, and $\bar{V}^\circ$. The correlations plot as straight lines on diagrams of $\bar{S}^\circ$ *vs.* $\bar{V}^\circ$, $\bar{S}^\circ$ *vs.* $\bar{C}_p^\circ$, or $\bar{V}^\circ$ *vs.* $\bar{C}_p^\circ$, where the slopes and intercepts of the lines are determined by groups of ions or ionic species of similar type and charge. Shock *et al.* (1997a) recently proposed revisions to the original correlations of Shock and Helgeson (1988), and have also proposed new correlations for additional types of ionic species. Additional correlations for metal-ligand complexes have also been recently generated by Sverjensky *et al.* (1997). Because the correlations developed by Shock and Helgeson (1988), Shock *et al.* (1997a) and Sverjensky *et al.* (1997) are the basis for estimates of partial molal properties and equation-of-state parameters for numerous aqueous solutes in SPRONS.JNC, the correlation equations and parameters, and supporting figures illustrating correlation behavior are summarized in Table 4.4.2_1 and Figs. 4.4.2_1 to 4.4.2_23. Figures 4.4.2_1 to 4.4.2_15 are from Shock *et al.*(1997). The remaining figures are from Sverjensky *et al.* (1997).

Uncertainties in standard partial molal properties estimated using the correlations in Table 4.4.2_1 are evaluated by Sverjensky *et al.* (1997). Uncertainties in $\bar{S}^\circ$ and $\bar{C}_p^\circ$ are estimated to be within ±5 cal mol^{-1} K^{-1}. Uncertainties in $\bar{V}^\circ$ are estimated to be approximately ±5 cm^3 mol^{-1}. The uncertainties in the standard partial molal entropy and heat capacity are more significant than uncertainties in the standard partial molal volume, and would, for example, generate uncertainties in calculated values of the partial molal Gibbs free energy of formation at 500°C of ±2400 cal mol^{-1} and ±1100 cal mol^{-1},

Table 4.4.2_1. Correlations among standard partial molal volumes *(V)*, heat capacities *(C_p)* and entropies *(S)* of cationic and anionic aqueous species at 25°C and 1 bar[1].

Species	Correlation Eqn.	Parameters		Figure
Ions, Oxygen-Bearing Ionic Species and Non-Conventional Hydroxide Complexes[a]				
	$V = \mathbf{y}\,S + \mathbf{z}$	y	z	
monovalent, monatomic cations, except Li^+		1.29	-20.5	4.4.2_1
divalent transition cations		0.92	0.0	
alkaline earth cations, and Pb^{2+}		0.19	-14.8	
trivalent cations excluding rare earths		0.50	-4.0	
monovalent, monatomic halide anions		1.29	1.8	see ref. *c*
other monovalent anions		1.06	0.07	4.4.2_4
non-metal oxygen bearing species (#O = 2)		1.05	-3.3	4.4.2_5
non-metal oxygen bearing species (#O = 3)		0.87	3.0	
non-metal oxygen bearing species (#O = 4)		0.78	11.6	
metal oxygen bearing species (#O = 2)		0.25	11.7	4.4.2_6a
1st row transition elements (#O=4)		0.75	9.5	4.4.2_6c
1st row transition elements (#O=4)		0.48	-8.2	4.4.2_6d
higher-order transition elements (#O=4)		0.44	27.3	4.4.2_6b
tetravalent cations		0.1	-43.3	est.
monovalent, MO^-		0.45	-12	est.
divalent MOH^+ (transition metals)		0.45	-12	est.
divalent MOH^+ (alkaline earths)		0.16	4.9	est.
divalent $MO(aq)$ (transition metals)		0.45	-12	est.
divalent $MO(aq)$ (alkaline earths)		0.16	4.9	est.
divalent HMO_2^- (transition metals)		0.54	-4.8	est.
divalent HMO_2^- (alkaline earths)		0.25	11.7	est.
divalent MO_2^{2-} (transition metals)		0.54	-4.8	est.
divalent MO_2^{2-} (alkaline earths)		0.25	11.7	est.
trivalent MOH^{2+} (1st row transition metals)		0.45	-12	est.
trivalent MOH^{2+} (all others)		0.16	4.9	est.
trivalent MO^+ (1st row transition metals)		0.45	-12	est.
trivalent MO^+ (all others)		0.16	4.9	est.
trivalent HMO_2 (1st row transition metals)		0.54	-4.8	est.
trivalent HMO_2 (all others)		0.25	11.7	est.
tetravalent MOH^{3+}		0.16	4.9	est.
tetravalent MO^{2+}		0.16	4.9	est.
tetravalent HMO_2^+		0.25	11.7	est.
tetravalent $MO_2(aq)$		0.25	11.7	est.
tetravalent HMO_3^-		0.35	19.3	est.
	$C_p = \mathbf{u}\,S + \mathbf{v}$	u	v	
monovalent, monatomic cations, except Li^+		-0.88	22.2	4.4.2_2

Species	Correlation Eqn.	Parameters		Figure
other monovalent cations		0.064	14.2	4.4.2_2
divalent transition cations		0.53	5.5	
alkaline earth cations and Pb^{2+}		-0.19	-11.9	
trivalent cations excluding rare earths		0.91	41.7	
monovalent, monatomic halide anions		0.0	-28.2	see ref. *c*
other monovalent anions		0.62	-31.6	4.4.2_4
non-metal oxygen-bearing anions (Z_j = -1)		0.60	-33.8	4.4.2_7
non-metal oxygen-bearing anions (Z_j = -2)		0.60	-63.3	
non-metal oxygen-bearing anions (Z_j = -3)		0.60	-92.8	est.
oxyacids and acid oxyanions		1.65	-46.8	4.4.2_8
metal oxygen bearing species (unprotonated)		-2.06	-34.5	4.4.2_9
metal oxygen-bearing species (protonated)		-2.06	95.5	
tetravalent cations		0.31	31.1	est.
monovalent $MOH(aq)$		-1.14	9	est.
monovalent MO^-		-1.14	15.5	est.
divalent MOH^+		-1.14	9.0	4.4.2_10
divalent $MO(aq)$		-1.14	-15.5	
divalent HMO_2^-		-2.28	-24.	4.4.2_11
divalent MO_2^{2-}		-2.28	-106.2	est.
trivalent MOH^{2+}		-1.14	-37.2	est.
trivalent MO^+		-1.14	-60.8	est.
trivalent $HMO_2(aq)$		-2.28	-24	est.
trivalent MO_2^-		-2.06	-34.5	est.
tetravalent MOH^{3+}		-1.14	-37.2	est.
tetravalent MO^{2+}		-1.14	-60.8	est.
tetravalent HMO_2^+		-2.28	-24	est.
tetravalent $MO_2(aq)$		-2.06	-34.5	est.
tetravalent HMO_3^-		-2.28	-24	est.
	$C_P = \mathrm{w}\,V + \mathrm{x}$	w	x	
monovalent, monatomic cations, except Li^+		-0.68	8.3	4.4.2_3
divalent transition cations		0.58	5.5	
alkaline earth cations, and Pb^{2+}		-1.0	-26.7	
trivalent cations excluding rare earths		1.82	49.0	
monovalent, monatomic halide anions		0.0	-28.2	est.
non-metal oxygen-bearing anions (Z_j = -1)		0.55	-32.	4.4.2_12
non-metal oxygen-bearing anions (Z_j = -2)		0.55	-70.	
non-metal oxygen-bearing anions (Z_j = -3)		0.55	-108.	est.
oxyacids and acid oxyanions		1.94	-65.8	4.4.2_13
metal oxygen bearing species (#O = 2)		-0.12	7.3	4.4.2_14
metal oxygen bearing species (#O = 4)		0.40	45.8	

Species	Correlation Eqn.	Parameters		Figure
tetravalent cations		3.1	165.3	est.
	S correlations[2]	e	f	
monovalent MOH*(aq)*		1.32	-6	est.
monovalent MO^-		1.42	-11	est.
divalent MOH^+		1.32	24.5	4.4.2_15
divalent MO*(aq)*		1.42	20.5	
divalent HMO_2^-		1.52	15.5	
divalent MO_2^{2-}		1.62	11.	est.
trivalent MOH^{2+}		1.32	37	est.
trivalent MO^+		1.42	83	est.
trivalent HMO_2*(aq)*		1.52	123	est.
trivalent MO_2-		1.62	118	est.
tetravalent MOH^{3+}		1.32	74	est.
tetravalent MO_2^+		1.42	108	est.
tetravalent HMO_2^+		1.52	140	est.
tetravalent MO_2*(aq)*		1.62	135	est.
tetravalent HMO_3^-		1.72	130	est.
Metal-Ligand Complexes[b]				
	S correlations[3]			
neutral Cl complexes, y = 1 or 2		footnote *#3*		4.4.2_16
monovalent cations and ligands, y = 1 or 2		footnote *#7*		4.4.2_20
divalent cations, monovalent ligands, y = 1		footnote *#8*		4.4.2_21
sulfate complexes		footnote *#9*		4.4.2_22
carbonate complexes		footnote *#10*		4.4.2_23
	C_P correlations[4]	d		
monovalent cations, $y = Cl^-$		18.0		4.4.2_17
divalent cations, $y = Cl^-$		63.3		
divalent cations, $y = CH_3COO^-$		93.8		
	V correlations[5,6]			
complexes containing monovalent ligands		footnote #5		4.4.2_18
metal sulfate complexes		footnote #6		4.4.2_19

[a] - Shock *et al.*, 1997a; [b] - Sverjensky *et al.*, 1997; [c] - Shock and Helgeson, 1988.

1. #O refers to the number of oxygen atoms in the complex; "est. " stands for estimated correlation parameters; M denotes a cation; Z_j represents the charge of the j-th hydrogen-free anion.
2. The following correlation equation is used to relate the standard partial molal entropy of non conventional hydroxide complexes (Section 5.2.5) to the standard partial molal entropy of the corresponding cation:

$$\bar{S}^\circ_{complex} = e\,\bar{S}^\circ_{M^{Z+}} + f,$$

where $\bar{S}^\circ_{complex}$ and $\bar{S}^\circ_{M^{Z+}}$ denote the entropy of the complex and cation,respectively.

3. Following the notation of Sverjensky *et al.* (1997) for stepwise association reactions involving monovalent ligands,

$$ML_{y-1}^{Z+1} + L^- = ML_y^Z,$$

where M refers to a metal cation, y stands for the number of ligands (L) and Z denotes the charge on the y-th complex, the entropy correlation equation is given by:

$$\Delta\bar{S}^\circ_{r,y} = \alpha_{Z,L}\,\bar{S}^\circ_{ML_{y-1}^{Z+1}} + \beta_{Z,L},$$

where,

$$\Delta\bar{S}^\circ_{r,y} = \bar{S}^\circ_{ML_y^Z} - \bar{S}^\circ_{ML_{y-1}^{Z+1}} - \bar{S}^\circ_{L^-},$$

and, for neutral complexes with L = Cl^-,

$$\alpha_{Z=0,Cl^-} = 0.357, \text{ and } \beta_{Z=0,Cl^-} = -4.085.$$

4. For the stepwise association reaction (footnote #3), the heat-capacity correlation equation for mono- and divalent cation complexes with Cl^- and CH_3COO^- (acetate) ligands is given by:

$$\Delta\bar{C}^\circ_{P\,y=1\text{or}2} = 1.25\bar{C}^\circ_{P\,M^{Z+1}} + \mathbf{d},$$

where $\Delta\bar{C}^\circ_{P\,y=1\text{or}2}$ refers to the standard partial molal heat capacity of the association reaction, $\bar{C}^\circ_{P\,M^{Z+1}}$ stands for the standard partial molal heat capacity of the metal cation, and Z refers to the charge on the complex.

5. For the stepwise association reaction (footnote #3), the volume correlation equation for complexes containing monovalent ligands is given by:

$$\Delta\bar{V}^\circ_{r,y} = 0.11419\bar{V}^\circ_{M^{Z+1}} + 8.9432,$$

where $\Delta\bar{V}^\circ_{r,y}$ represents the standard partial molal volume of the association reaction, $\bar{V}^\circ_{M^{Z+1}}$ refers to the standard partial molal volume of the metal cation, and Z refers to the charge on the complex.

6. For the stepwise association reaction (footnote #3), the volume correlation equation for complexes containing divalent ligands is given by:

$$\Delta\bar{V}^\circ_{r,y=1} = \gamma_Z\bar{V}^\circ_{M^{2+}} + \delta_Z,$$

where $\Delta\bar{V}^\circ_{r,y}$ represents the standard partial molal volume of the association reaction, $\bar{V}^\circ_{M^{Z+1}}$ refers to the standard partial molal volume of the metal cation, and Z refers to the charge on the complex. For metal-sulfate complexes:

$$\gamma_Z = -0.25Z - 0.3 \text{ and } \delta_Z = -2.88Z + 3.32$$

where Z denotes the charge on the complex.

7. For the stepwise association reaction (footnote # 3), the parameters in analogous correlation equations for the standard partial molal entropies of association of complexes formed from

monovalent metal cations and monovalent ligands are:

$$\alpha_{Z=0,L^-} = -0.000479\bar{S}^\circ_{L^-} + 0.3185, \text{ and } \beta_{Z=0,L^-} = -0.05757\bar{S}^\circ_{L^-} - 3.4494,$$

where $\bar{S}^\circ_{L^-}$ denotes the standard partial molal entropy of ligands, which are taken by Sverjensky *et al.* (1997) from Shock and Helgeson (1988).

8. Parameters in correlation equations for the standard partial molal entropies of association of complexes formed from divalent cations and monovalent ligands (footnote #3) are:

$$\alpha_{Z=1,L^-} = 0.015762\bar{S}^\circ_{L^-} + 0.03874, \text{ and } \beta_{Z=1,L^-} = 0.10344\bar{S}^\circ_{L^-} + 7.5807$$

where $\bar{S}^\circ_{L^-}$ denotes the standard partial molal entropy of ligands, which are taken by Sverjensky *et al.* (1997) from Shock and Helgeson (1988).

9. Parameters for standard partial molal entropies of association that are consistent with the reaction:

$$M^{Z+2} + SO_4^{2-} \rightleftharpoons MSO_4^Z,$$

where M^{Z+2} refers to mono-, di- and trivalent cations, and the corresponding correlation equation;

$$\Delta\bar{S}^\circ_{r,y=1} = \alpha_{Z,SO_4^{2-}}\bar{S}^\circ_{M^{Z+2}} + \beta_{Z,SO_4^{2-}},$$

where $\bar{S}^\circ_{M^{Z+2}}$ refers to the standard partial molal of the cation (taken from Shock and Helgeson, 1988), are given by:

$$\alpha_{Z,SO_4^{2-}} = -0.055Z + 0.055, \text{ and } \beta_{Z,SO_4^{2-}} = 13.84Z + 18.16,$$

where Z refers to the charge on the complex.

10. Parameters in correlation equations analogous to that in footnote #9 for the standard partial molal entropy of association of complexes formed from mono- and divalent cations and carbonate ligands, consistent with the reaction:

$$M^{Z+2} + CO_3^{2-} \rightleftharpoons MCO_3^Z$$

are given by:

$$\alpha_{Z,CO_3^{2-}} = -1.617Z + 0.213, \text{ and } \beta_{Z,CO_3^{2-}} = 66.82Z + 28.67,$$

where Z refers to the charge on the complex.

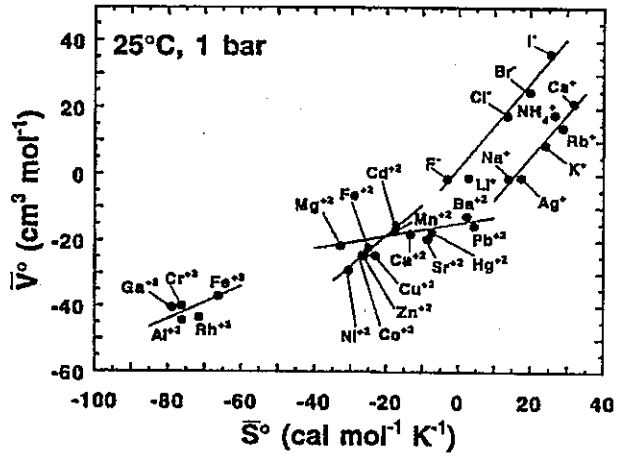


Figure 4.4.2_1. Correlation of standard partial molal volumes with entropies for monatomic ions (and NH_4^+) at 25°C and 1 bar. Symbols represent values retrieved by Shock *et al.* (1997a) and Shock and Helgeson (1988) from experimental data using the approach described in Section 4.3.3.

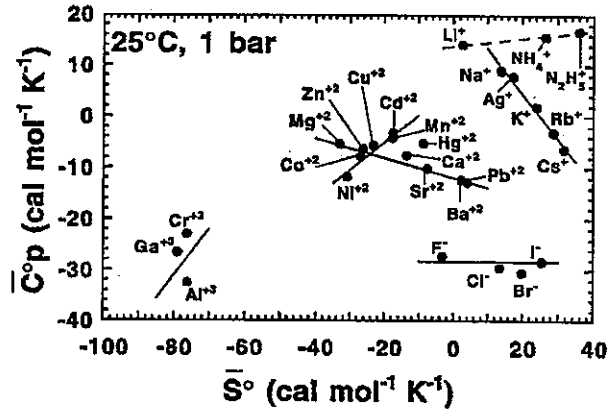


Figure 4.4.2_2. Correlation of standard partial molal heat capacities with entropies for monatomic ions (and NH_4^+ and $N_2H_5^+$) at 25°C and 1 bar. Symbols represent values retrieved by Shock *et al.* (1997a) and Shock and Helgeson (1988) from experimental results following the approach described in Section 4.3.3.

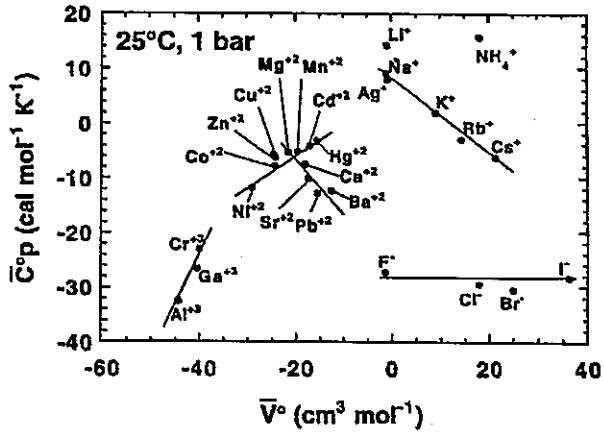
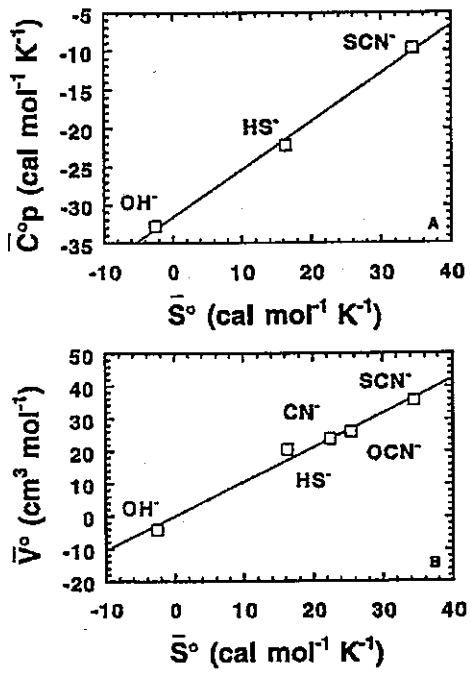
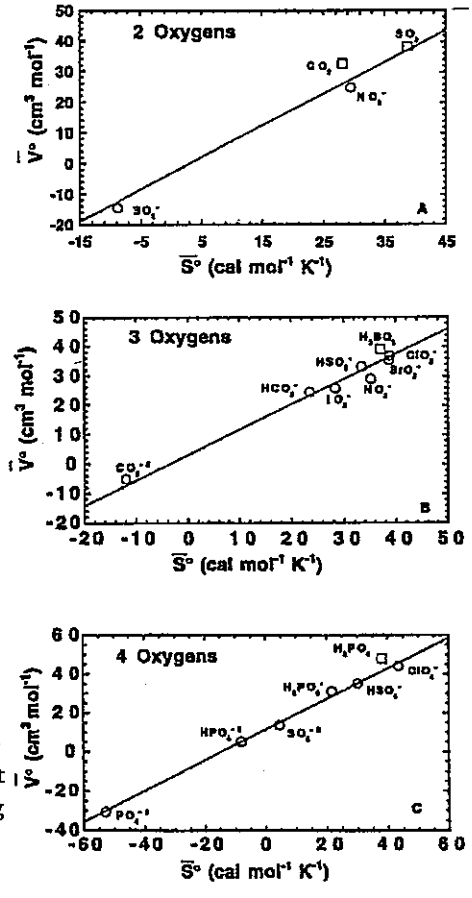
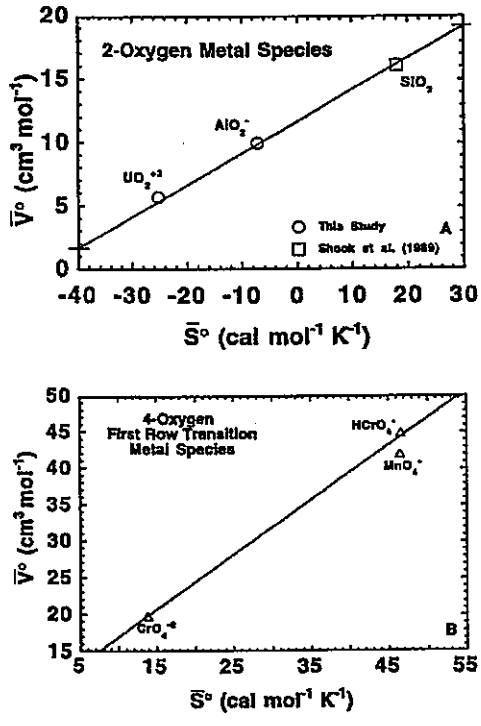


Figure 4.4.2_3. Correlation of standard partial molal heat capacities with volumes for monatomic ions (and NH_4^+) at 25°C and 1 bar. Symbols represent values retrieved by Shock *et al.* (1997a) and Shock and Helgeson (1988) from experimental data using the approach described in Section 4.3.3.





Figures 4.4.2_4 (above) and 4.4.2_5 (three figures to the right). Correlations of standard partial molal volumes with entropies at 25°C, 1 bar for monovalent anions (Fig.4.4.2_4) and non-metal oxygen-bearing species (Fig.4.4.2_5).



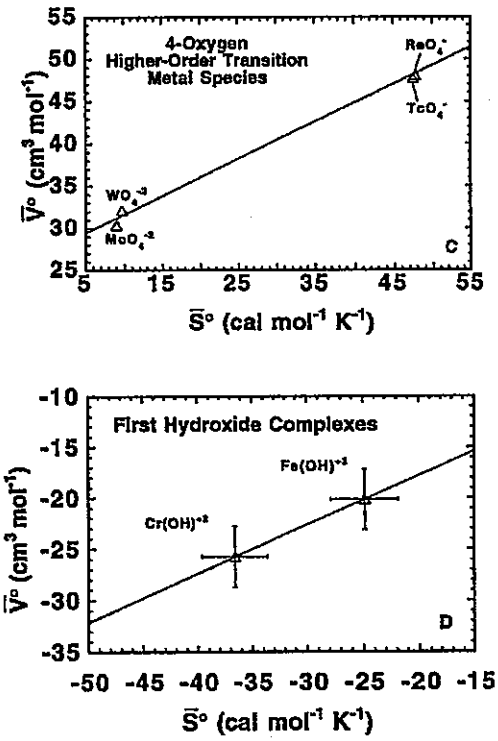
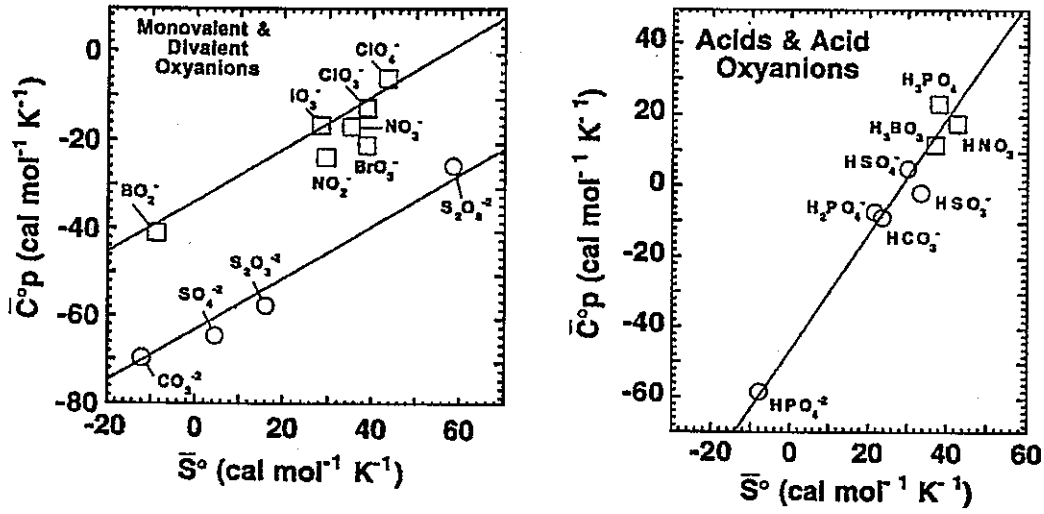
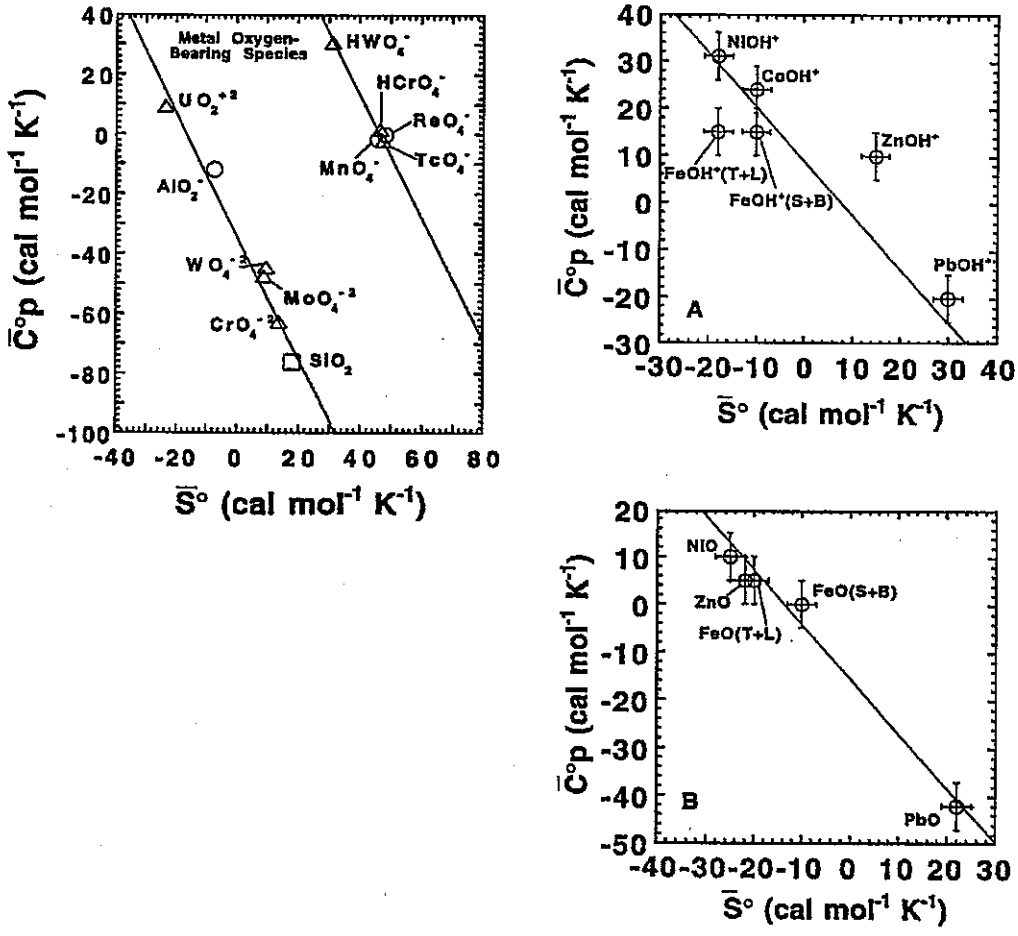


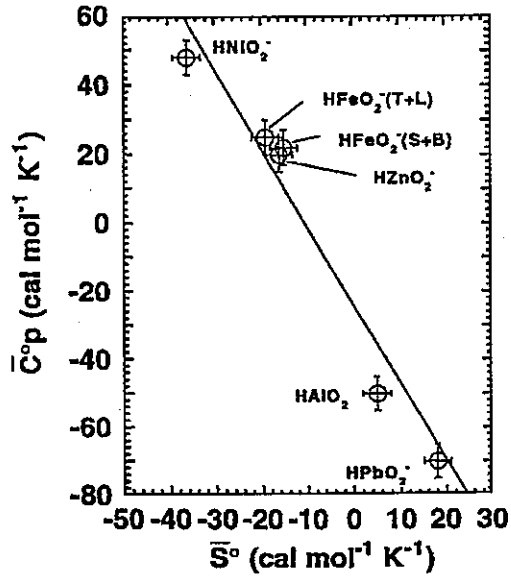
Figure 4.4.2_6 (a-d). Correlations of standard partial molal volumes with entropies at 25°C and 1 bar for metal oxygen-bearing species.

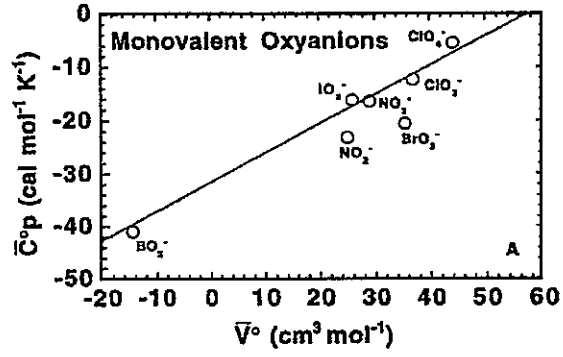


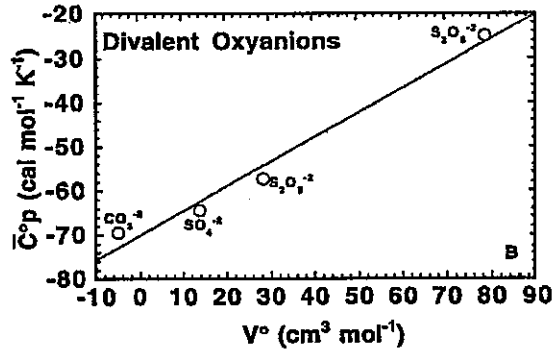
Figures 4.4.2_7 (left) and 4.4.2_8 (right). Correlations of standard partial molal heat capacities with entropies at 25°C and 1 bar for nonmetal oxygen bearing species [Fig. 4.4.2_7; monovalent anions (squares), divalent anions (circles)], and non-metal acid and acid oxyanion species [Fig. 4.2.2_8; circles from Shock *et al.* (1997a), squares from Shock and Helgeson (1988)]



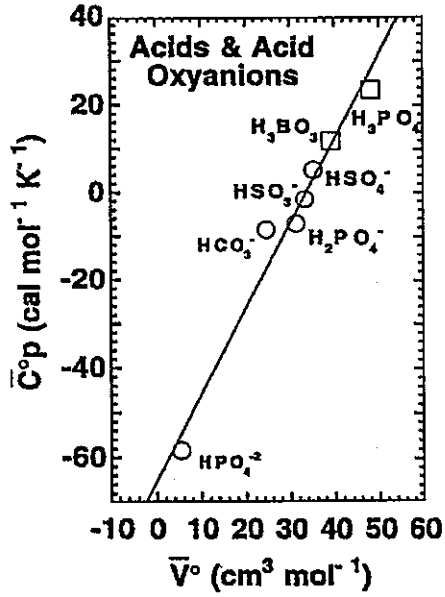
Figures 4.4.2_9 (above) and 4.4.2_10 (two figures to the right). Correlations of standard partial molal heat capacities with entropies for metal oxygen-bearing species (Fig. 4.4.2_9) and non-conventional hydroxide complexes of divalent cations (Fig. 4.4.2_10 - see Section 5.2.5).

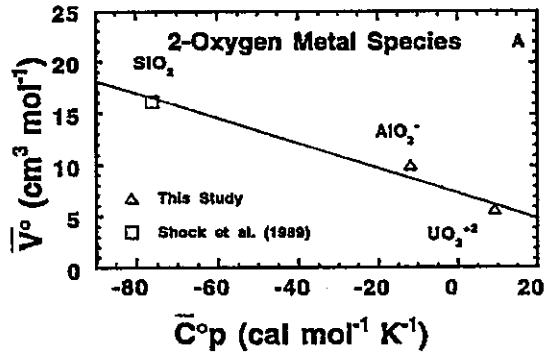


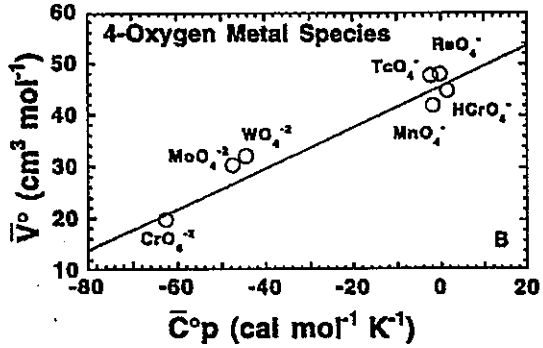




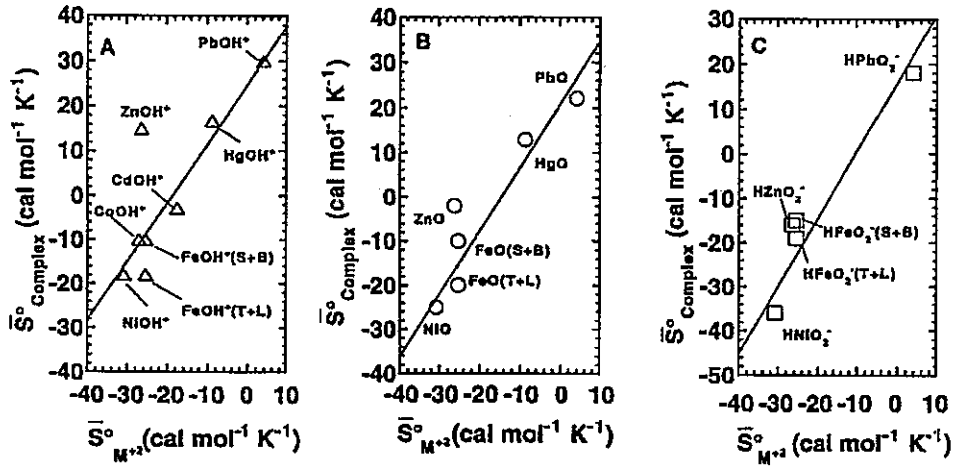
Figures 4.4.2_11 (above) and 4.4.2_12 (two figures to the right). Correlations among $\bar{C}_P^\circ$ and $\bar{V}^\circ$ for non-conventional third hydroxide complexes of divalent metals (Fig. 4.4.2_11, see Section 5.2.5) and monovalent and divalent non-metal oxygen-bearing species (Fig. 4.4.2_12).







Figures 4.4.2_13 (above) and 4.4.2_14 (two figures to the right). Correlations among $\bar{C}_P^\circ$ and $\bar{V}^\circ$ for non-metal oxygen-bearing species that contain hydrogen (Fig. 4.4.2_13) and metal oxygen-bearing species (Fig. 4.4.2_14).



Figures 4.4.2_15. Correlations of standard partial molal entropies of non-conventional hydroxide complexes (Section 5.2.5) with the entropies of corresponding divalent metal cations at 25°C and 1 bar. Symbols refer to values regressed from experimental results by Shock *et al.* (1997a), and lines are consistent with correlation equations and associated parameters in Table 4.4.2_1.

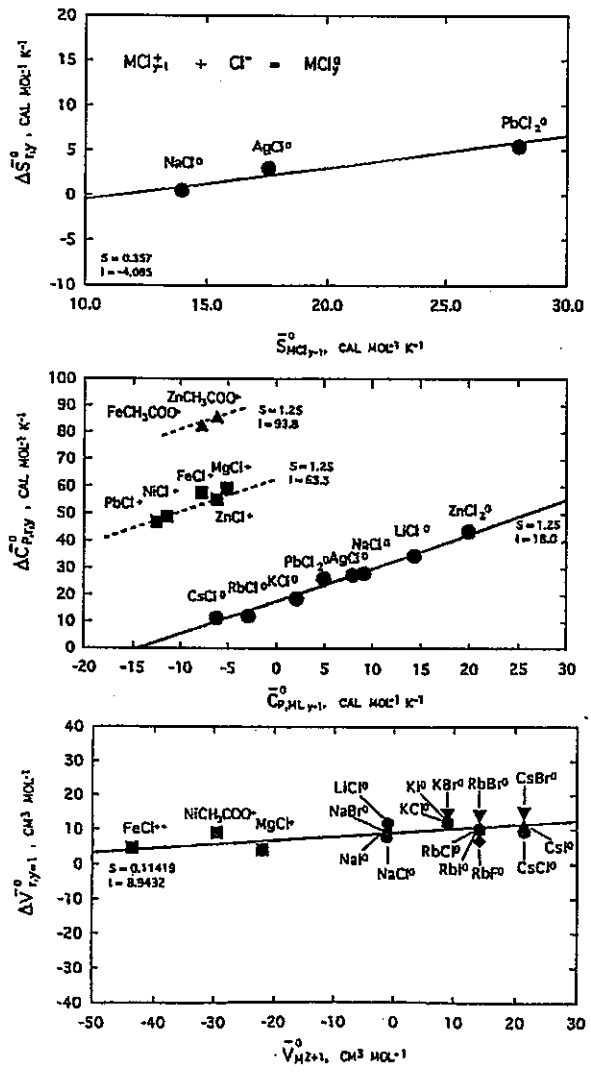


Figure 4.4.2_16. Correlation of the stepwise standard partial molal entropy of association of chloride complexes with the standard partial molal entropy of the cation at 25°C and 1 bar (see Table 4.4.2_1, footnote #3). Symbols refer to calculated values from Sverjensky *et al.* (1997) based on thermodynamic data that are incorporated in SPRONS.JNC.

Figure 4.4.2_17. Correlation of the stepwise standard partial molal heat capacity of association with the standard partial molal heat capacity of the cation at 25°C and 1 bar (see Table 4.4.2_1, footnote #4). Symbols refer to calculated values from Sverjensky *et al.* (1997) based on thermodynamic data that are incorporated in SPRONS.JNC.

Figure 4.4.2_18. Correlation of the stepwise standard partial molal volume of association with the standard partial molal volume of the cation at 25°C and 1 bar. (see Table 4.4.2_1, footnote #5). Symbols refer to calculated values from Sverjensky *et al.* (1997) based on thermodynamic data that are incorporated in SPRONS. JNC.

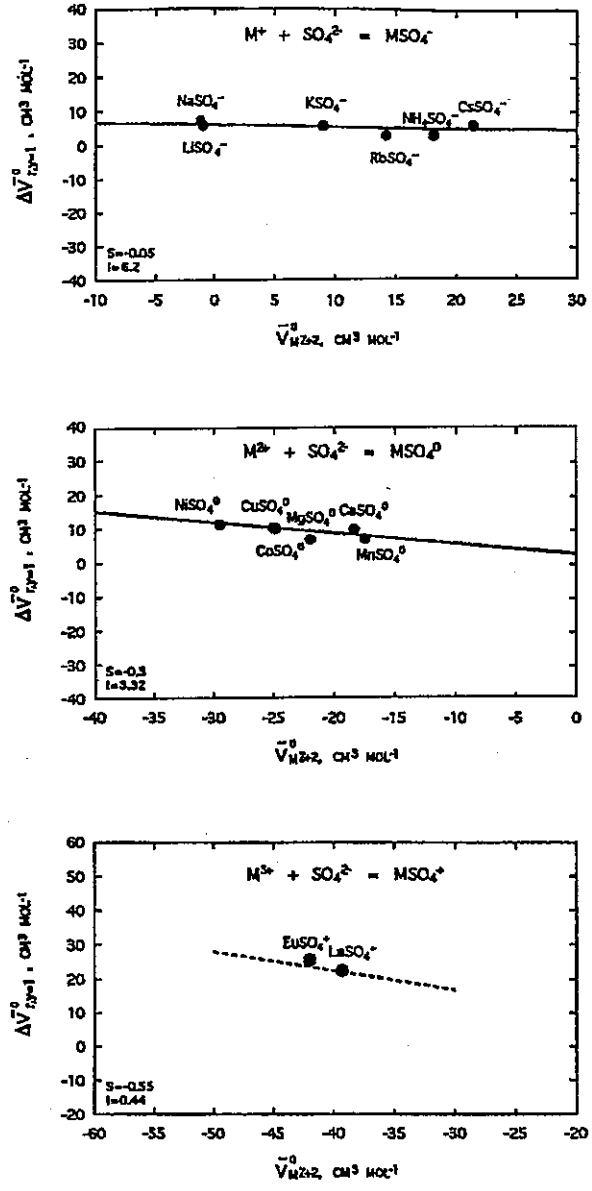


Figure 4.4.2_19. Correlation of the standard partial molal volumes of association of sulfate ion pairs involving mono-, di- and trivalent cations with the standard partial molal volumes of the cations at 25°C and 1 bar (see Table 4.2.2_1, footnote #6). Symbols refer to calculated values from Sverjensky *et al.* (1997) based on thermodynamic data that are incorporated in SPRONS.JNC.

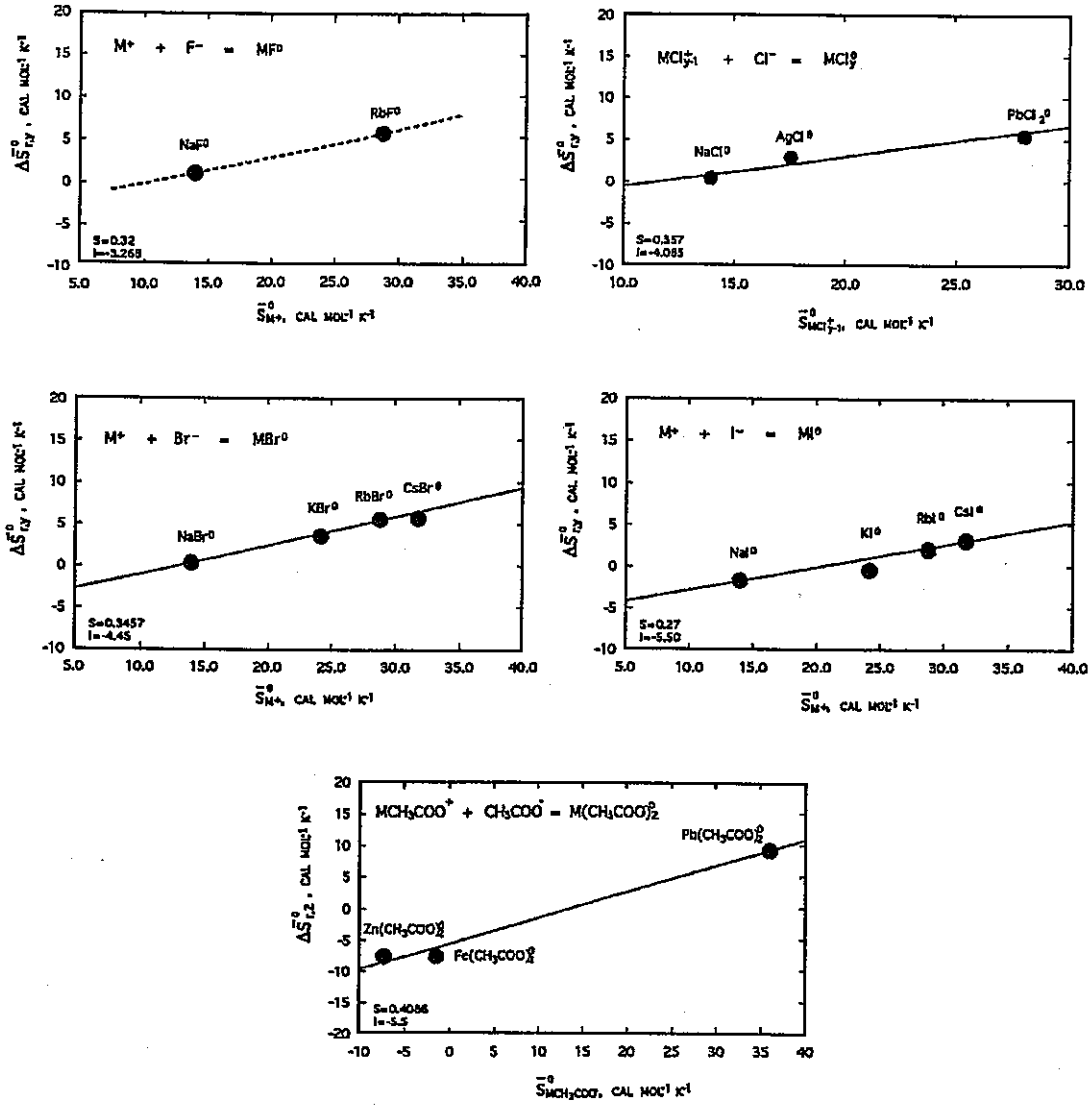
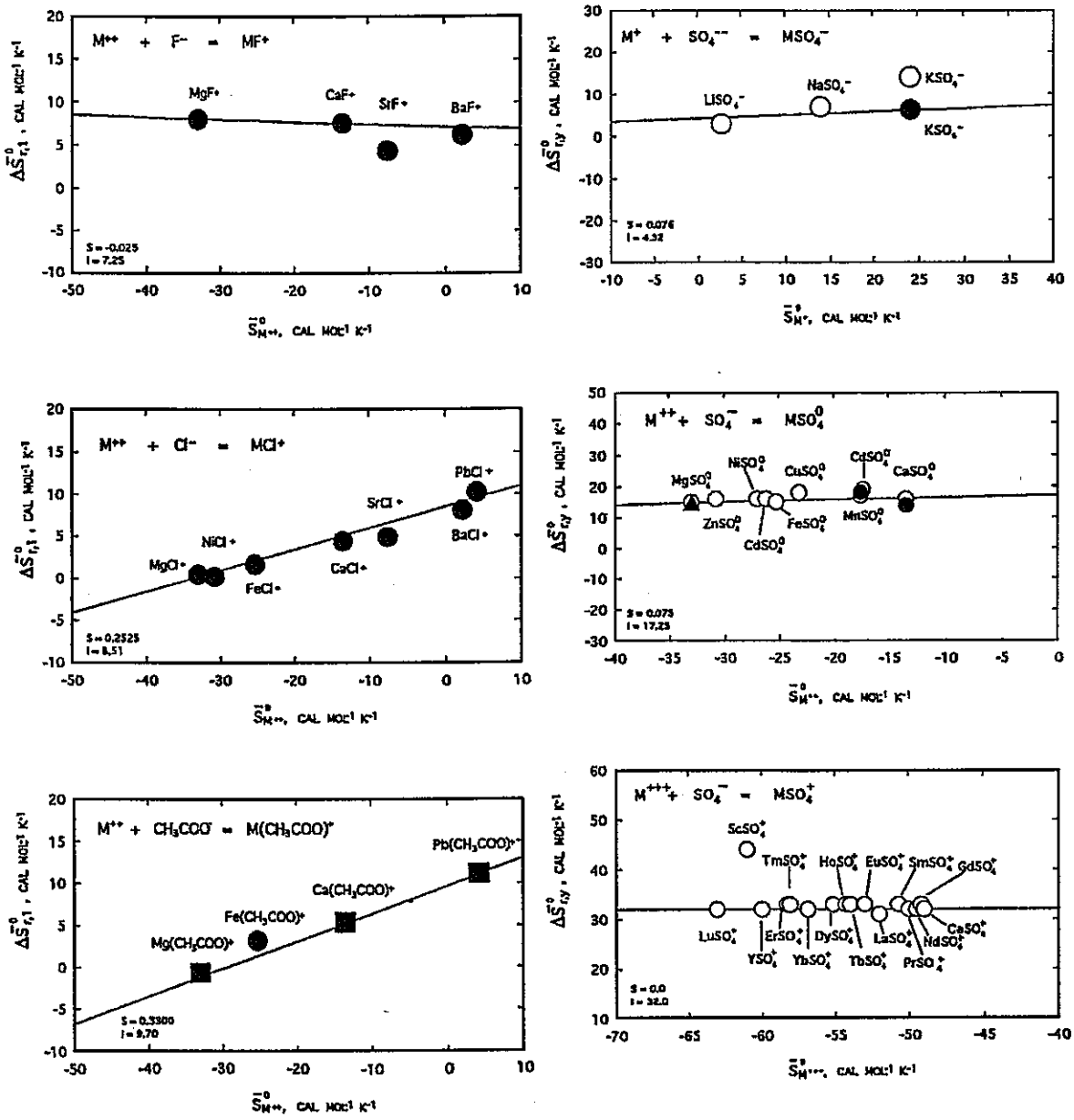


Figure 4.4.2_20. Correlation of the standard partial molal entropy of association for addition of a monovalent ligand to a cationic species with the standard partial molal entropy of the cationic species at 25°C and 1 bar (see Table 4.2.2_1, footnote #7). Symbols refer to calculated values from Sverjensky *et al.* (1997) based on thermodynamic data that are incorporated in SPRONS.JNC.



Figures 4.4.2_21 (three figures on the left) and 4.4.2_22 (three figures on the right). Correlation of the standard partial molal entropy of association for addition of a monovalent ligand to a divalent cation (Fig. 4.4.2_21), and for sulfate complexes of mono-, di- and trivalent cations (Fig. 4.4.2_22), with the standard partial molal entropies of the cations at 25°C and 1 bar. [see Table 4.2.2_1, footnotes #8 (Fig. 4.4.2_21) and #9 (Fig. 4.4.2_22)]. Symbols refer to calculated values from Sverjensky *et al.* (1997) based on thermodynamic data that are incorporated in SPRONS.JNC.

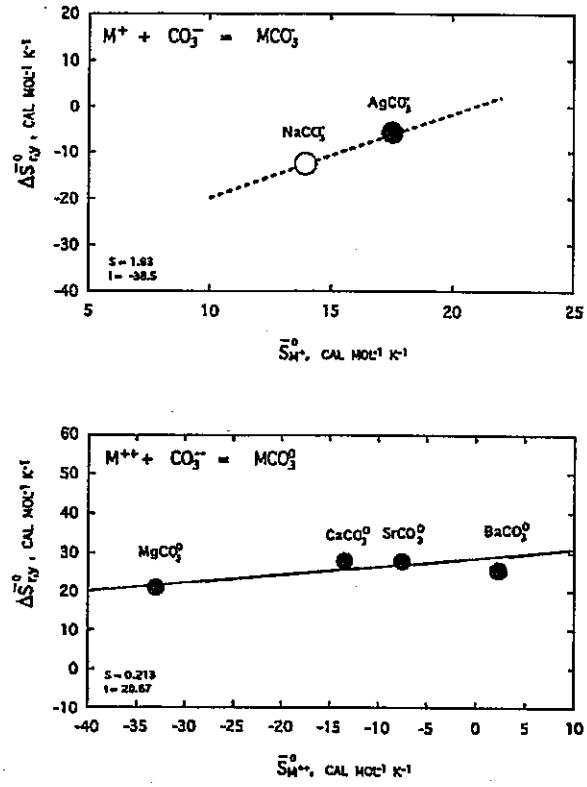


Figure 4.4.2_23. Correlation of the standard partial molal entropies of association of carbonate complexes involving mono- and divalent cations with the standard partial molal entropy of the cations at 25°C and 1 bar (see Table 4.4.2_1, footnote #10). Symbols refer to calculated values from Sverjensky *et al.* (1997) based on thermodynamic data that are incorporated in SPRONS.JNC.

respectively. Combined uncertainties in estimated equation-of-state parameters may lead to uncertainties in ΔG° as high as ± 700 cal mol-1 at 500°C and 1 kb, or ±1500 cal mol-1 at 1000 °C and 5 kb (Shock and Helgeson, 1988).

5 Description of Thermodynamic Databases

The thermodynamic databases SPRONS.JNC and PHREEQE.JNC are described in this section. Section 5.1 provides an overview of the approach used to generate these databases. SPRONS.JNC is described in Section 5.2. PHREEQE.JNC is described in Section 5.3. The databases are listed in Appendices A (SPRONS.JNC) and B (PHREEQE.JNC).

5.1 Overview

The procedure to develop SPRONS.JNC and PHREEQE.JNC is illustrated schematically in Fig. 5.1_1. SPRONS92.DAT (Johnson *et al.*, 1991) is the basic source of thermodynamic data in SPRONS.JNC, which also includes new and revised data published in the peer-reviewed scientific literature since 1991. PHREEQE.JNC is derived from SPRONS.JNC using SUPCRT to calculate thermodynamic properties of relevant reactions. Remarks concerning these calculations, and associated software, are summarized in the following paragraphs. SUPCRT is described by Johnson *et al.* (1991), and is available from the Laboratory of Theoretical Geochemistry, University of California, Berkeley.

MPRONS is a pre-processor used to modify the SPRONS database. It is an interactive program that asks the user for additions, deletions or modifications to the database, executes the requested changes, and generates a new database that incorporates the new or revised data. In practice, any suitable text editor can also be used for this purpose, in which case it is essential that formatting and

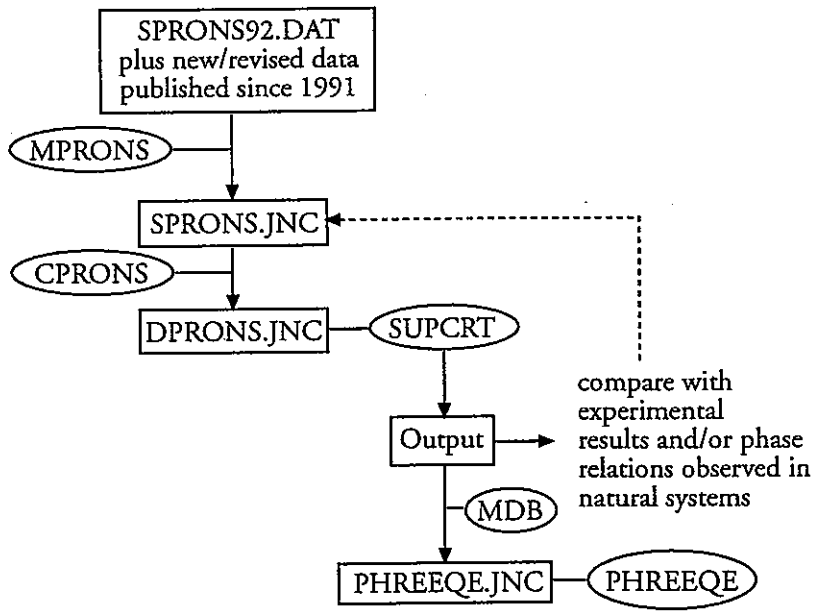


Figure 5.1_1. Schematic diagram of the procedure used to develop SPRONS.JNC and PHREEQE.JNC. Boxes refer to data or databases, ovals refer to software (see text).

unit conventions are strictly adhered to (Tables 5.1_1 to 5.1_3), and that the total numbers of minerals, gases, aqueous species and comment lines in the database are accurately updated (these totals are appended to the end of the database, as can be seen in Appendix A, for example).

CPRONS is an interactive pre-processor that converts the sequential access file SPRONS.JNC into its direct access equivalent, DPRONS.JNC. DPRONS .JNC increases the run-time efficiency of calculations carried out by SUPCRT.

SUPCRT consists of the following subprogram modules:

- *SUP* - an executive program that reads user-generated input files and the database file DPRONS.JNC, passes these data to the *REAC* module and interfaces calculated reaction properties with the reporting module *REP*,
- *REAC* - calculates the apparent standard molal Gibbs free energy and enthalpy, and the associated standard molal entropy, heat capacity and volume, of reactions among minerals, gases and aqueous species as a function of temperature and pressure,
- *H_2O* - calculates the electrostatic and standard molal thermodynamic properties of H_2O as a function of independent state conditions specified by the user, and
- *REP* - writes an output file, which lists all relevant data used in the calculations extracted from DPRONS.JNC, together with calculated standard molal thermodynamic properties of reactions (a "PLT" file, which contains calculated values in a format suitable for two-dimensional plotting, may also be written at the user's discretion).

Two input files are required for calculations using SUPCRT. One, the CON (conditions) file, specifies the range of independent state conditions to be considered in the calculations, including either:

- the liquid-phase side of the H_2O vaporization boundary, which requires user specification of the temperature, or pressure, range, or
- single-phase regions of H_2O stability, which requires user specification of temperatures and pressures, temperatures and H_2O densities, or specification of T and log K, or P and log K.

The temperature, pressure and solvent-density regions of validity of the SUPCRT model are summarized in the introductory paragraph of Section 4.

The other user-specified input file required by SUPCRT is the RXN (reactions) file. This file specifies reactions among minerals, gases and aqueous species whose standard molal thermodynamic properties are to be calculated by SUPCRT over

Line	Var	Var	Var	Var	Format
1	name	scform			1x, a20, a30
2	abbrev	ecform			1x, a15, 5x, a40
3	ref	date			1x, a5, 15x, a9
4	ΔG°_f	ΔH°_f	$S^\circ_{Pr,\,Tr}$	$V^\circ_{Pr,\,Tr}$	4x, 2(2x, f12.1), 2(2x,f 8.3)
5	a (10^0)	b (10^3)	c (10^{-5})		4x, 3(2x, f 12.6)
6	T_{max} (for a, b, c)				8x, f 7.2

Table 5.1_1. Generic species data block in SPRONS.JNC for gases, and minerals that do not undergo phase transitions. Abbreviations: Var. (variable), Format (FORTRAN77 format), abbrev. (abbreviation), scform (structural chemical formula), ecform (elemental chemical formula), ref (literature reference - see Appendix A) and date (date of last revision). Units: ΔG°_f and ΔH°_f (cal mol^{-1}), $S^\circ_{Pr,\,Tr}$ (cal mol^{-1} K^{-1}), $V^\circ_{Pr,\,Tr}$ (cm^3 mol^{-1}), a (cal mol^{-1} K^{-1}), b (cal mol^{-1} K^{-2}), c (cal K mol^{-1}), and T_{max} (K)[see Section 4.2.1].

Line	Var	Var	Var	Var	Format
1	name	scform			2x, a20, a30
2	abbrev	ecform			2x, a15, 5x, a40
3	ref	date			2x, a5, 15x, a9
4	ΔG°_f	ΔH°_f	$S^\circ_{Pr,\,Tr}$	$V^\circ_{Pr,\,Tr}$	4x, 2(2x, f12.1), 2(2x,f 8.3)
5	a_i (10^0)	b_i (10^3)	c_i (10^{-5})	$T_{Ti,\,Pr}$	4x, 3(2x, f 12.6), 2x, f 7.2
	ΔH°_{Ti}	ΔV°_{Ti}	$(dP/dT)_{Ti}$		2x, f 8.1, 2(2x, f 10.3)
6	a_n (10^0)	b_n (10^3)	c_n (10^{-5})		4x, 3(2x, f 12.6)
7	$T_{max,\,n}$ (for a_n, b_n, c_n)				8x, f 7.2

Table 5.1_2. Generic species data block in SPRONS.JNC for minerals that undergo phase transitions. Abbreviations: as in Table 5.1_1. Units: as in Table 5.1_1, and $T_{Ti,\,Pr}$ (K), ΔH°_{Ti} (cal mol^{-1}), ΔV°_{Ti} (cm^3 mol^{-1}), (dP/dT) (bar K^{-1}), $a_{i,n}$ (cal mol^{-1} K^{-1}), $b_{i,\,n}$ (cal mol^{-1} K^{-2}), $c_{i,\,n}$ (cal K mol^{-1}), and $T_{max,\,n}$ (K)[see Section 4.2.1].

Line	Var	Var	Var	Var	Format
1	name	scform			2x, a20, a30
2	abbrev	ecform			6x, a15, 5x, a40
3	ref	date			6x, a5, 15x, a9
4	ΔG°_f	ΔH°_f	$S^\circ_{Pr,\,Tr}$		4x, 2(2x, f 10.0), 4x, f 8.3
5	a_1 (10^1)	a_2 (10^{-2})	a_3 (10^0)	a_4 (10^{-4})	4x, 4(2x, f 8.4, 2x)
6	c_1 (10^0)	c_2 (10^{-4})	$\omega_{Pr,\,Tr}$ (10^{-5})	charge	4x, 3(2x, f 8.4, 2x), 9x, f3.0

Table 5.1_3. Generic species data block in SPRONS.JNC for aqueous species. Abbreviations: as in Table 5.1_1. Units: as in Table 5.1_1, and a_1 (cal mol^{-1} bar^{-1}), a_2 (cal mol^{-1}), a_3 (cal K mol^{-1} bar^{-1}), a_4 (cal K mol^{-1}), c_1 (cal mol^{-1}K^{-1}), c_2 (cal K mol^{-1}), $\omega_{Pr,\,Tr}$ (cal mol^{-1}) and charge (dimensionless) [see Section 4.2.2].

the range of conditions specified in the CON file. The reactions are specified by the user in terms of the appropriate reaction stoichiometry and corresponding names of mineral, gas and aqueous reactants and products.

The output from SUPCRT is processed by MDB (Modify DataBase; Arthur *et al.*, 1997) to generate revised versions of PHREEQE.JNC. The SUPCRT output file tabulates the standard molal thermodynamic properties of reactions at the reference temperature and pressure, and also over a range of *T-P* conditions specified in the CON file. The temperature dependence of the equilibrium constant for corresponding reactions in PHREEQE is calculated using either the van't Hoff equation or a polynomial expression constrained by empirical temperature-independent coefficients. In the former case, MDB extracts values of log *K* and the reaction enthalpy at 25°C from the SUPCRT output file, and incorporates these values into datablocks for the corresponding reaction in PHREEQE.JNC. In the latter case, MDB calculates values of the empirical coefficients by regression of log *K vs. T* values calculated by SUPCRT, and then writes these coefficients, together with log *K* at 25°C , into appropriate datablocks in PHREEQE.JNC. For each such modification, MDB appends a record to PHREEQE.JNC specifying data that were added or revised, as well as the date and identity of the person making the revisions.

The accuracy of the data in SPRONS.JNC is assessed by comparing calculated equilibrium constants for selected reactions with their experimental counterparts. A number of such assessments are documented in Section 6, where it can be seen that in some cases discrepancies exist between calculated and experimental results. Unfortunately, determining the reason for such discrepancies is not straightforward, because they may be generated by errors in the thermodynamic properties of one or more reactants or products, and/or by inappropriate experimental technique or mis-interpretation of experimental results. We expect that future revisions to SPRONS.JNC, as noted in Section 2, will partially or completely eliminate all such discrepancies (as suggested by the dashed line in Fig. 5.1_1), but this may require additional experimental work by JNC and others. Similarly, we note that despite efforts to avoid completely any errors of transcription from original data sources, some errors of this type may exist in SPRONS.JNC. Thus, if discrepancies are encountered between calculated and experimental results, it is recommended that the relevant data should first be checked to confirm that they have been correctly entered into the database.

5.2 SPRONS.JNC

5.2.1 Description

SPRONS.JNC includes standard molal Gibbs free energies and enthalpies of formation, and standard molal entropies and volumes at the reference pressure (1 bar) and temperature (25°C) for 143 minerals that do not undergo phase

transitions, 33 minerals that undergo one phase transition, 17 minerals that undergo two phase transitions, 2 minerals that undergo three phase transitions, and 16 gases. Also included are Maier-Kelly heat capacity coefficients (Eqn. 4.2.1_5) that permit calculation of corresponding apparent standard molal Gibbs free energies and enthalpies of formation, and standard molal entropies at pressures from 1 to 10000 bars and temperatures from 0°C to a maximum value consistent with the Maier-Kelly coefficients. SPRONS.JNC also includes standard molal Gibbs free energies and enthalpies of formation and standard molal entropies at the reference pressure and temperature, and HKF equation-of-state coefficients ($a_1 ... a_4$, c_1, c_2, and ω; Section 4.2.2) for 1147 aqueous species. Together with equations of state for fluid phases of H_2O and equations characterizing the dielectric properties of the solvent as functions of pressure and temperature (encoded in SUPCRT's subprogram module H_2O), apparent standard partial molal Gibbs free energies and enthalpies of formation, and standard partial molal entropies of these aqueous species can be calculated over a broad range of temperatures and pressures. The apparent standard molal thermodynamic properties of minerals, gases and aqueous species in SPRONS .JNC can be used with SUPCRT to calculate corresponding properties of reactions.

The data in SPRONS.JNC that are taken from SPRONS92.DAT are described in Section 5.2.2. Sources of new data, and of revisions to data in SPRONS92 .DAT, are discussed in Sections 5.2.3 and 5.2.4.

5.2.2 Sources of unrevised data

Unless otherwise noted (Section 5.2.3 and 5.2.4), thermodynamic data in SPRONS.JNC are from references 1 - 19, Appendix A. The data for minerals are mostly from Helgeson *et al.* (1978), but additional data for Sn-bearing minerals (Jackson and Helgeson, 1985), and a small amount of calorimetric data (references 6, 7, 8, 15 and 16, Appendix A), are also included. Standard molal Gibbs free energies and enthalpies of formation are not available for several minerals, including:

- bromellite, chabazite, chloritoid, cummingtonite, dickite, ferropargasite, ferrotremolite, fluorphlogopite, fluortremolite, glaucophane, grunerite, leonhardite, richterite, staurolite, zincite, almandine, 14Å-amesite, edenite, epistilbite, ferroedenite, fluoredenite, heulandite, natrolite, Ca-, K- and Na-phillipsite, pyrope, spessartine, stilbite, aegerine, larnite, riebeckite, 7Å-cronstedtite, ferrogedrite, hastingsite, magnesiohastingsite, magnesio-riebeckite, and PD (proton-deficient)-oxyannite

(an entry in SPRONS.JNC of "999999" is the default null value assigned to the Gibbs free energy and enthalpy of formation when these data are unavailable). Calculated results involving these minerals therefore refer only to the parenthetical terms in Eqns. (4.1_1) and (4.1_2).

The standard Gibbs free energies of formation of calcite and aragonite retrieved by Helgeson *et al.* (1978) are corrected by Johnson *et al.* (1991) in order to be consistent with the experimental solubilities of these minerals determined by Plummer and Busenberg (1982). The Gibbs free energies and enthalpies of several other Ca-bearing minerals evaluated by Helgeson *et al.* (1978), including anorthite, clinozoisite, diopside, dolomite, epidote, laumontite, wairakite, wollastonite, lawsonite, and margarite, are adjusted to be consistent with the revised data for calcite and aragonite (see reference 19, Appendix A).

Thermodynamic data and equation-of-state coefficients for aqueous ions and ionic species are from Shock and Helgeson (1988). Similar data for inorganic neutral species are from Shock *et al.* (1989). Data for inorganic metal complexes attributed to unpublished work in SPRONS92.DAT (reference 5, Appendix A) have since been published, and in some cases revised (reference 22, Appendix A). These newer data supersede those from reference 5, and are incorporated in SPRONS.JNC (Section 5.2.3). Data for many of the 86 organic species that are included in SPRONS92.DAT (reference 4, Appendix A) are omitted in SPRONS.JNC because these species are not relevant to the Japanese repository concept, nor are they helpful in retrieving thermodynamic properties of other, more relevant, aqueous species from experimental data and field observations. Recent data for organic acids and metal-organic complexes are, however, included in SPRONS.JNC (see Section 5.2.3), because these species are known to be generated by diagenetic alteration of organic matter in sedimentary environments (e.g., Kharaka *et al.*, 1983; Barth and Bjorlykke, 1993). These species may therefore be relevant to the Japanese repository concept, and may also affect groundwater chemistry at field sites that are being investigated by JNC [e.g., the Mobara site; Kamei (1997); Sasamoto *et al.* (1999c)]. Data for gases are from Wagman *et al.* (1982) and Kelley (1960).

It should perhaps be emphasized that data from the sources described above are themselves constrained by supplementary data from numerous other sources, as is generally true of all thermodynamic databases. The supplementary data for minerals and gases are documented in footnotes appended to Tables 2, 3, 7, 8 and 9 of Helgeson *et al.* (1978). These data include standard molal entropies of several elements from Wagman *et al.* (1968; 1969), and standard molal Gibbs free energies and enthalpies of formation, and standard molal entropies, derived from calorimetric studies.

Sources of supplementary data for aqueous ions and ionic species are referenced in footnotes to Tables 11 and 12 of Shock and Helgeson (1988). Standard partial molal volumes and heat capacities at the reference temperature and pressure are retrieved from experimental data on apparent molal properties of electrolytes (Section 4.3.3.1). Additional data are from Tanger and Helgeson (1988), who similarly retrieved these data from experimental measurements of apparent molal properties. Supplemental standard partial molal entropies, and

enthalpies and Gibbs free energies of formation at the reference temperature and pressure, are taken primarily from CODATA (1978) and Wagman *et al.* (1982), and also from Berg and Vanderzee (1978), Jackson and Helgeson (1985) and (for lanthanide cations) from Morss (1976).

Sources of supplementary data for inorganic neutral species are referenced in footnotes to Tables 4 and 7 of Shock *et al.* (1989). Supplemental standard partial molal volumes and heat capacities at the reference temperature and pressure are from Olofsson *et al.* (1985), Tiepel and Gubbins (1972), Allred and Woolley (1981), Barbero *et al.* (1983) and Pierotti (1965). Supplemental standard partial molal entropies, and enthalpies and Gibbs free energies of formation, are from Wagman *et al.* (1982) and Olofsson *et al.* (1985).

5.2.3 Sources of new and revised data

References 20 - 40 (Appendix A) document new and revised thermodynamic data included SPRONS.JNC. These references are briefly summarized below.

Ref. 20: Pokrovskii and Helgeson (1995) evaluate experimental solubilities reported in the literature for gibbsite, boehmite, diaspore and corundum to derive an internally consistent set of thermodynamic data for Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_3(aq)$ and $Al(OH)_4^-$, and to retrieve standard molal Gibbs free energies of formation of boehmite and diaspore at the reference pressure and temperature. This is an important study because all available calorimetric, phase-equilibrium, solubility and potentiometric data pertinent to the Al_2O_3-H_2O-NaCl system are considered over a wide range of pressures and temperatures, and because the retrieved data for this chemical subsystem are internally consistent. Standard molal thermodynamic properties and Maier-Kelley heat capacity coefficients for corundum, gibbsite, boehmite and diaspore from Table 2 of this reference are included in SPRONS.JNC. Standard partial molal thermodynamic properties and HKF equation-of-state coefficients for the aqueous aluminum species noted above, and for $NaAlO_2(aq)$ and $NaOH(aq)$, from Table 3 of this reference are also included in SPRONS.JNC. These internally consistent data are also consistent with data for Na^+, Cl^- and OH^- from Shock and Helgeson (1988) and data for $NaCl(aq)$ from Shock *et al.* (1989), and thus are consistent with the data for these species in SPRONS.JNC.

The data for Al^{3+} and $Al(OH)_4^-$ (i.e., AlO_2^-, see Section 5.2.5) from Pokrovskii and Helgeson (1995) are accepted here rather than alternative data for these species recommended by Shock *et al.* (1997a). This is because the Pokrovskii and Helgeson (1995) data are consistent with the available solubility data for gibbsite and boehmite, and because they are internally consistent with corresponding data for the other aqueous aluminum species noted above. Shock *et al.* (1997a), on the other hand, assert that there is considerable disagreement among experimental solubilities reported for gibbsite and boehmite at low pH. To avoid this confusion, they use experimental data from Couturier *et al.* (1984)

for the hydrolysis reaction:

$$Al^{3+} + 2H_2O \rightleftharpoons AlO_2^- + 4H^+,$$

to retrieve the standard partial molal entropy of Al^{3+}. While we agree there is some scatter in the solubility data (Figs. C.11 and C.15, Appendix C), we do not believe this is sufficient reason to adopt this approach. The available solubility data provide important experimental constraints on the thermodynamic properties of Al^{3+} and $Al(OH)_4^-$, and we feel it is better to account for these constraints, despite the scatter in the data, than to ignore them.

It is of interest to note that the thermodynamic properties determined by Pokrovskii and Helgeson (1995) and Shock *et al.* (1997a) for $Al(OH)_4^-$ are virtually identical, but that the standard partial molal Gibbs free energy of formation of Al^{3+} reported by Shock *et al.* (1997a) is nearly 1 kcal mol^{-1} more positive than that retrieved by Pokrovskii and Helgeson (1995). Similarly, the partial molal enthalpy of formation is nearly 2 kcal mol^{-1} more positive, and the partial molal entropy is approximately 3 cal mol^{-1} K^{-1} more positive, than corresponding values retrieved by Pokrovskii and Helgeson (1995).

Ref. 21: Shock *et al.* (1997a) use correlations among experimentally determined standard partial molal volumes, heat capacities and entropies to estimate standard partial molal properties and HKF equation-of-state parameters for more than 300 inorganic cations and anions, polyatomic anions, oxyanions, acid oxyanions, neutral oxy-acid species, dissolved gases and hydroxide complexes of metal cations. In addition to these new data, revised data for 80 species from Shock and Helgeson (1988) are also provided. These revisions are motivated by improvements to previous correlations (Sassani and Shock, 1992; 1994). The revised correlations account for the coordination of aqueous ions, and associated effects on estimates of effective ionic radii and partial molal entropies (see also Puigdomenech *et al.*, 1997). The data summarized in Tables 4, 5 and 10 of this reference, and all the revisions to data from Shock and Helgeson (1988), are included in SPRONS. JNC.

Ref. 22: Sverjensky *et al.* (1997) regressed experimental ion-association data reported in the literature to retrieve standard partial molal properties and HKF equation-of-state coefficients for 57 aqueous metal complexes with halogen (Cl^-, F^-, Br^-, I^-), carbonate, sulfate, nitrate, acetate, and $H_3SiO_4^-$ ligands. Correlations developed on the basis of experimental standard partial molal heat capacities, volumes and entropies of association, combined with similar data from Shock and Helgeson (1988) for aqueous cations and anionic ligands, are used to calculate provisional estimates of standard partial molal properties and equation-of-state coefficients for an additional 52 complexes, for which little or no experimental data are available. The data summarized in Tables 2, 3 and 12 of this reference are included in SPRONS.JNC.

Ref. 23: Pokrovskii and Helgeson (1997a) regressed experimental dissociation constants reported in the literature to retrieve standard partial molal properties and HKF equation-of-state parameters for KCl*(aq)*. The retrieval procedure used data from Shock and Helgeson (1988) for the corresponding properties of K^+ and Cl^-. The data for KCl*(aq)* are therefore consistent with these data, and with corresponding data in SPRONS.JNC.

Ref. 24: Pokrovskii and Helgeson (1997b) regressed experimental data on the solubilities of gibbsite and corundum in aqueous KOH solutions to retrieve standard partial molal properties and HKF equation-of-state coefficients for $KAlO_2$ *(aq)* and KOH*(aq)*. These data are consistent with the thermodynamic properties of K^+ and OH^- in SPRONS.JNC retrieved by Shock and Helgeson (1988), and with the revised properties of AlO_2^- in SPRONS.JNC (Ref. 20) determined by Pokrovskii and Helgeson (1995).

Ref. 25: Haas *et al.* (1995) used experimental data from the literature and correlation algorithms to retrieve or estimate standard partial molal thermodynamic properties and HKF equation-of-state parameters for 246 inorganic aqueous lanthanide complexes with halogen (Cl^-, F^-), hydroxide, carbonate, sulfate, bicarbonate, nitrate and orthophosphate ligands. The retrieval and estimation procedures are constrained by data from Shock and Helgeson (1988), and reported values are therefore consistent with the data in SPRONS.JNC. The data are listed in the appendix of this reference, and were obtained from the authors (E. L. Shock, at http://zonvark.wustl.edu/geopig/).

Ref. 27: Shock and Koretsky (1995) regressed experimental equilibrium constants for association of metal-organic complexes involving monovalent organic acid ligands to retrieve, or estimate, standard partial molal thermodynamic properties and HKF equation-of-state coefficients for 270 metal-organic species. The organic ligands and associated acids that are represented in SPRONS.JNC include formate, acetate, propanoate, butanoate, pentanoate, glycolate, lactate, oxalate and succinate [the partial molal thermodynamic properties of these ligands and their corresponding acids are from **Ref. 26** (Shock, 1995)]. Analogous data for 114 metal acetate complexes from **Ref. 33** (Shock and Koretsky, 1993) are also included in SPRONS.JNC. All the data from Refs. 26, 27 and 33 are consistent with data for inorganic aqueous ions and ionic species in SPRONS.JNC from Shock and Helgeson (1988) and Shock *et al.* (1997a). The organic-species data are reported in various tables and appendices in Refs. 26, 27 and 33, and were obtained in the present study from the senior author (E. L. Shock, at http://zonvark.wustl.edu/geopig/).

The data for the organic acids and ligands noted above are included in SPRONS.JNC because these species are found commonly in the formation waters of sedimentary basins (e.g., Carothers and Kharaka, 1978; Kharaka *et al.*, 1993). These species may also affect mineral diagenesis, and the aqueous

speciation behavior of inorganic elements such as Ca, Al and Fe (Kharaka *et al.*, 1986; Lundegard and Kharaka, 1990; Harrison and Thyne, 1992).

Ref. 29: Saccocia and Seyfried (1993) reinterpreted published experimental phase-equilibrium data involving chamosite (synonymous according these authors with 14Å-daphnite) and retrieved values of the standard molal Gibbs free energy and enthalpy of formation for 14Å-daphnite that are consistent with the standard entropy, volume and Maier-Kelley heat capacity coefficients for this mineral evaluated by Helgeson *et al.* (1978). The recommended data are included in SPRONS.JNC.

Ref. 31: Sverjensky *et al.* (1991) reconciled inconsistencies in the thermodynamic properties of minerals in the systems K_2O- and Na_2O-Al_2O_3-SiO_2-H_2O-HCl using an analysis procedure that integrates the results of phase-equilibrium and calorimetric experiments with the results of solubility experiments at high temperatures. Recommended revisions to values reported by Helgeson *et al.* (1978) for the Gibbs free energy of formation of muscovite, phlogopite, K-feldspar, sanidine and microcline are incorporated in SPRONS.JNC.

Standard partial molal thermodynamic properties and HKF equation-of-state coefficients for HCl*(aq)* are also retrieved by Sverjensky *et al.* (1991). These data are not used in SPRONS.JNC, however, because newer data for this species (Tagirov *et al.*, 1997; see Ref. 40) are more consistent with all experimentally determined dissociation constants for HCl*(aq)* over a wider range of temperatures, pressures and H_2O densities than were considered by Sverjensky *et al.*(1991). Calculated thermodynamic properties of this species nevertheless agree closely with values calculated using the data of Sverjensky *et al.* (1991).

Ref. 35: Oelkers *et al.* (1995) determined standard partial molal thermodynamic properties and HKF equation-of-state coefficients for two aluminum acetate complexes [$Al(CH_3COO)^{2+}$ and $Al(CH_3COO)_2^{+}$] using the data for Al^{3+} from Ref. 20 and the procedure described in Ref. 33. These data are accepted rather than data for these species from Ref. 33 because they are consistent with the data for Al^{3+} from Ref. 20.

Ref. 36: Shock *et al.* (1999) use experimental data from the literature and correlations to estimate partial molal thermodynamic properties and HKF equation-of-state coefficients for divalent, trivalent, quadravalent, pentavalent and hexavalent actinide ions. These data are included in SPRONS.JNC, and were obtained from the senior author (E. L. Shock, *pers. comm.*).

Ref. 37: Shock *et al.* (1997b) use the available experimental data from the literature to estimate HKF equation-of-state parameters for aqueous uranium cations and non-conventional hydroxide complexes (Section 5.2.5), and to retrieve standard molal thermodynamic properties and Maier-Kelley heat

capacity coefficients for uraninite that are consistent with thermodynamic properties reported by Grenthe *et al.* (1992) and experimental solubilities at high temperatures determined by Parks and Pohl (1988). The data summarized in Tables 1 and 2 of Shock *et al.* (1997b) are included in SPRONS.JNC.

Ref. 38: Standard partial molal thermodynamic properties and HKF equation-of-state coefficients for Pd^{2+}, $PdCl^{+}$, $PdCl_2$*(aq)*, $PdCl_3^{-}$, $PdCl_4^{2-}$, $Pd(OH)^{+}$ and PdO*(aq)* are estimated by Sassani and Shock (1990) using the limited available experimental data on dissociation constants from Droll *et al.* (1957), Biryukov and Shlenskaya (1964) and Izatt *et al.* (1967). Standard molal thermodynamic properties and Maier-Kelley heat capacity coefficients for Pd*(c)* and PdO*(c)* are also reported. The data incorporated into SPRONS.JNC are from Tables 1 and 2 of this reference. These data are provisional estimates, which may be revised in whole or in part by Sassani and Shock (1999).

Ref. 39: Standard partial molal thermodynamic properties and HKF equation-of-state parameters for the ion-pairs $NaB(OH)_4$*(aq)* and $NaSO_4^{-}$ are retrieved by Pokrovski *et al.* (1995) from potentiometric measurements of the respective association constants between 50 and 200°C. The data from Table 5 of this reference are included in SPRONS.JNC, and are consistent with thermodynamic properties and HKF equation-of-state parameters in this database for Na^{+}, OH^{-} and SO_4^{2-} from Shock and Helgeson (1988) and Shock *et al.* (1997a).

Ref. 40: Tagirov *et al.* (1997) retrieved standard partial molal thermodynamic properties and HKF equation-of-state coefficients for HCl*(aq)* based on association constants consistent with measured solubilities of AgCl*(c)* and Ag*(c)*. The experimental data determined in this study are evaluated simultaneously with association constants retrieved from other solubility and electrical conductance measurements reported in the literature between 25 and 700°C, and between 1 bar and 5 kb. The retrieved data for HCl*(aq)* from Table 6 of Tagirov *et al.* (1997) are incorporated in SPRONS.JNC. Standard partial molal properties and HKF parameters for $AgCl_2^{-}$ were also determined by Tagirov *et al.* (1997), and are included in SPRONS.JNC for completeness. The data for both HCl*(aq)* and $AgCl_2^{-}$ are consistent with data in SPRONS.JNC because they were retrieved using thermodynamic properties and HKF equation-of-state coefficients for Cl^{-} from Shock and Helgeson (1988), which are unrevised by Shock *et al.* (1997a), and thermodynamic properties and Maier-Kelley coefficients for AlCl*(c)* (chlorargyrite) and Ag*(c)* from Helgeson *et al.* (1978).

5.2.4 Data for minerals not considered by Helgeson et al (1978)

Thermodynamic data in SPRONS.JNC and PHREEQE.JNC support different models of hydrolysis reactions involving non-stoichiometric solid solutions. Helgeson *et al.* (1978) prefer a modeling approach that considers mixing of atoms among energetically equivalent sites in the crystalline lattice, as well as exchange of atoms between energetically distinct sites. A model consistent with

this approach is described by these authors and involves calculation of the activities of thermodynamic components of the solid solution from site-mixing approximations. Component activities are then correlated with the compositions of the minerals and used as descriptive variables in activity diagrams. SPRONS.JNC includes data for minerals that are stoichiometrically equivalent to the thermodynamic components of many solid solutions, including several that are important in relatively low-temperature groundwater systems. Aagaard and Helgeson (1983) and Giggenbach (1985) use similar data and the model described above to calculate equilibrium mineral-stability relations appropriate for such systems. Arthur *et al.* (1993) and Arthur (1994) use this approach to model equilibrium porewater compositions in engineered bentonite barriers.

The PHREEQE series of codes do not include solid-solution models in the general sense considered by Helgeson *et al.* (1978), although ion-exchange reactions can be simulated. Rather, solid-solution behavior is grossly approximated using a *surrogate* stoichiometric phase to represent the solid solution. The stoichiometry of the surrogate phase is defined such that it is within the range of compositions exhibited by the solid solution it represents, but the stoichiometry is not variable, as would otherwise be consistent with solid-solution behavior. The advantage of this approach is that the thermodynamic properties of the surrogate phase can be estimated using a variety of techniques, such as described by Tardy and Garrels (1974), Mattigod and Sposito (1978) and Chermak and Rimstidt (1989)[11].

For this reason, it is necessary to include thermodynamic data for such surrogate phases in SPRONS.JNC in order to calculate equilibrium constants and enthalpies using SUPCRT, which can then be incorporated into PHREEQE .JNC. Estimated thermodynamic properties for a limited number of such phases representing smectite (Na-, K-, Ca- and Mg- nontronites, beidellites and montmorillonites), saponite (greenalite and celadonite), chlorite (chamosite and 7Å-daphnite) and illite solid solutions are included in SPRONS.JNC.

These data are from **Refs. 30, 32** and **34** (Appendix A). Most of the data are estimated by Wolery (1976), who used a re-calibrated and slightly modified version of the technique described by Tardy and Garrels (1974) to estimate Gibbs free energies of formation, and methods described by Helgeson *et al.* (1978) to estimate corresponding standard molal entropies and Maier-Kelly heat capacity coefficients. Gibbs free energies and enthalpies of formation of celadonite, greenalite, 7Å-chamosite and 7Å-daphnite are combined with

[11] In passing, it is of interest to note that a third modeling approach appropriate for solid-solution minerals is described by Bourcier (1985), and is incorporated in the EQ3/6 software package (Wolery *et al.*, 1990). This approach is similar to that described by Helgeson et al. (1978), but considers ideal mixing of end-member thermodynamic components of the solid-solution, rather than ideal mixing of atoms on energetically equivalent sites.

standard entropies, volumes and heat capacities retrieved by Helgeson *et al.* (1978). All the thermodynamic properties of illite and Na-, K-, Ca- and Mg-nontronites, beidellites and montmorillonites are estimated (Wolery, 1976). It is reasonable to include these data in SPRONS.JNC because they are consistent with thermodynamic data for the other minerals retrieved by Helgeson *et al.* (1978)[T. Wolery, *pers. comm.*]. It is not possible to assess the accuracy of these data because experimental solubilities corresponding to the exact stoichiometry of the surrogate phases are not available. It is possible, however, to assess whether the data are reasonably consistent with mineral stability relations observed in natural systems. A few such assessments are described in Section 6.11 for stoichiometric surrogates of smectite and illite solid solutions.

Halloysite is metastable with respect to its isostructural and isochemical analog kaolinite, and may persist for significant periods of time in relatively low temperature geologic systems. The standard molal entropy and volume of halloysite, and associated Maier-Kelley heat capacity coefficients, are reported by Helgeson *et al.* (1978), and are included in SPRONS.JNC, but its Gibbs free energy and enthalpy of formation are not determined by these authors. Because halloysite may be important in partially controlling groundwater compositions at some of JNC's field sites (Kamaishi, Tono and Mobara), we calculated provisional estimates of its Gibbs free energy and enthalpy of formation (Ref. 28). This was accomplished by calculating the difference between calorimetric Gibbs free energies of formation of kaolinite and halloysite retrieved by Robie *et al.* (1978), and adding this difference to the Gibbs free energy of formation of kaolinite determined by Helgeson *et al.* (1978). A similar procedure was used to estimate hallosyite's enthalpy of formation. These are considered to be provisional estimates, but it is cautioned that the validity of this estimation procedure may not be supported by recent experiments on the relative stabilities of kaolinite and another of its isochemical analogs, dickite (Zotov *et al.*, 1998).

5.2.5 Conventional and non-conventional aqueous species

The non-conventional form of hydroxide complexes and other aqueous species are adopted in SPRONS.JNC, but conventional forms are represented in PHREEQE.JNC. The thermodynamic properties of conventional species are obtained by adding H_2O to the stoichiometry of their non-conventional counterparts, assuming the thermodynamic properties of the corresponding reactions, including the logarithm of the equilibrium constant, are equal to zero at any temperature and pressure (Wagman *et al.*, 1982). Such reactions are summarized in Table 5.2.5_1 for species that could be important in geologic systems. It is essential that reactions in PHREEQE.JNC that include conventional hydroxide complexes and other conventional aqueous species are written in terms of their non-conventional counterparts before thermodynamic properties of the reaction are calculated using SUPCRT and SPRONS.JNC.

Table 5.2.5_1. Selected conventional and non-conventional aqueous species in PHREEQE.JNC and SPRONS.JNC, respectively, and reactions for converting non-conventional species into their conventional counterparts (log K for all such reactions equals zero at any temperature and pressure).

Conventional Species (PHREEQE.JNC)	Non-conventional Species (SPRONS.JNC)	Conversion Reaction
$Al(OH)_2^+$	AlO^+	$AlO^+ + H_2O = Al(OH)_2^+$
$Al(OH)_3(aq)$	$HAlO_2(aq)$	$HAlO_2(aq) + H_2O = Al(OH)_3(aq)$
$Al(OH)_4^-$	AlO_2^-	$AlO_2^- + 2H_2O = Al(OH)_4^-$
$KAl(OH)_4(aq)$	$KAlO_2(aq)$	$KAlO_2(aq) + 2H_2O = KAl(OH)_4(aq)$
$NaAl(OH)_4(aq)$	$NaAlO_2(aq)$	$NaAlO_2(aq) + 2H_2O = NaAl(OH)_4(aq)$
$Bi(OH)_2^+$	BiO^+	$BiO^+ + H_2O = Bi(OH)_2^+$
$Bi(OH)_3(aq)$	$HBiO_2(aq)$	$HBiO_2(aq) + H_2O = Bi(OH)_3(aq)$
$Bi(OH)_4^-$	BiO_2^-	$BiO_2^- + 2H_2O = Bi(OH)_4^-$
$Cd(OH)_2(aq)$	$CdO(aq)$	$CdO(aq) + H_2O = Cd(OH)_2(aq)$
$Cd(OH)_3^-$	$HCdO_2^-$	$HCdO_2^- + H_2O = Cd(OH)_3^-$
$Cd(OH)_4^{2-}$	CdO_2^{2-}	$CdO_2^{2-} + 2H_2O = Cd(OH)_4^{2-}$
$H_2CO_3(aq)$	$CO_2(aq)$	$CO_2(aq) + H_2O = H_2CO_3(aq)$
$Ca(H_3SiO_4)^+$	$Ca(HSiO_3)^+$	$Ca(HSiO_3)^+ + H_2O = Ca(H_3SiO_4)^+$
$Fe(OH)_2(aq)$	$FeO(aq)$	$FeO(aq) + H_2O = Fe(OH)_2(aq)$
$Fe(OH)_3^-$	$HFeO_2^-$	$HFeO_2^- + H_2O = Fe(OH)_3^-$
$Fe(OH)_2^+$	FeO^+	$FeO^+ + H_2O = Fe(OH)_2^+$
$Fe(OH)_3(aq)$	$HFeO_2(aq)$	$HFeO_2(aq) + H_2O = Fe(OH)_3(aq)$
$Fe(OH)_4^-$	FeO_2^-	$FeO_2^- + 2H_2O = Fe(OH)_4^-$
$Mg(H_3SiO_4)^+$	$Mg(HSiO_3)^+$	$Mg(HSiO_3)^+ + H_2O = Mg(H_3SiO_4)^+$
$Mn(OH)_2(aq)$	$MnO(aq)$	$MnO(aq) + H_2O = Mn(OH)_2(aq)$
$Mn(OH)_3^-$	$HMnO_2^-$	$HMnO_2^- + H_2O = Mn(OH)_3^-$
$Mn(OH)_4^{2-}$	MnO_2^{2-}	$MnO_2^{2-} + 2H_2O = Mn(OH)_4^{2-}$
$Na(H_3SiO_4)(aq)$	$Na(HSiO_3)(aq)$	$Na(HSiO_3)(aq) + H_2O = Na(H_3SiO_4)(aq)$
$Ni(OH)_2(aq)$	$NiO(aq)$	$NiO(aq) + H_2O = Ni(OH)_2(aq)$
$Ni(OH)_3^-$	$HNiO_2^-$	$HNiO_2^- + H_2O = Ni(OH)_3^-$
$Ni(OH)_4^{2-}$	NiO_2^{2-}	$NiO_2^{2-} + 2H_2O = Ni(OH)_4^{2-}$
$H_4SiO_4(aq)$	$SiO_2(aq)$	$SiO_2(aq) + 2H_2O = H_4SiO_4(aq)$
$H_3SiO_4^-$	$HSiO_3^-$	$HSiO_3^- + H_2O = H_3SiO_4^-$
$Pb(OH)_2(aq)$	$PbO(aq)$	$PbO(aq) + H_2O = Pb(OH)_2(aq)$
$Pb(OH)_3^-$	$HPbO_2^-$	$HPbO_2^- + H_2O = Pb(OH)_3^-$
$Sn(OH)_2(aq)$	$SnO(aq)$	$SnO(aq) + H_2O = Sn(OH)_2(aq)$
$Sn(OH)_3^-$	$HSnO_2^-$	$HSnO_2^- + H_2O = Sn(OH)_3^-$
$U(OH)_2^{2+}$	UO^{2+}	$UO^{2+} + H_2O = U(OH)_2^{2+}$
$U(OH)_3^+$	HUO_2^+	$HUO_2^+ + H_2O = U(OH)_3^+$
$U(OH)_4(aq)$	$UO_2(aq)$	$UO_2(aq) + 2H_2O = U(OH)_4(aq)$
$U(OH)_5^-$	HUO_3^-	$HUO_3^- + 2H_2O = U(OH)_5^-$
$UO_2(OH)_2(aq)$	$UO_3(aq)$	$UO_3(aq) + H_2O = UO_2(OH)_2(aq)$

Conventional Species (PHREEQE.JNC)	Non-conventional Species (SPRONS.JNC)	Conversion Reaction
$UO_2(OH)_3^-$	HUO_4^-	$HUO_4^- + H_2O = UO_2(OH)_3^-$
$UO_2(OH)_4^{2-}$	UO_4^{2-}	$UO_4^{2-} + 2H_2O = UO_2(OH)_4^{2-}$
$Zn(OH)_2(aq)$	$ZnO(aq)$	$ZnO(aq) + H_2O = Zn(OH)_2(aq)$
$Zn(OH)_3^-$	$HZnO_2^-$	$HZnO_2^- + H_2O = Zn(OH)_3^-$
$Zn(OH)_4^{2-}$	ZnO_2^{2-}	$ZnO_2^{2-} + 2H_2O = Zn(OH)_4^{2-}$

5.2.6 Consistency between JNC's core thermodynamic database and SPRONS.JNC

As noted in Section 1, JNC is developing in parallel to the present study an additional thermodynamic database appropriate for minerals, gases and aqueous species of radioactive elements. Although this database and SPRONS.JNC are developed independently, there are a number of minerals, gases and aqueous species that are common to both databases. These primary, or "core", thermodynamic data in JNC's database for radioelements are from the OECD/NEA Thermodynamic Database Project (Silva *et al.*, 1995), which contains primarily CODATA key values, and additional data recommended by Grenthe *et al.* (1992). In this section we compare these data with their counterparts in SPRONS.JNC to determine if the data that are common to both databases are self-consistent, i.e., if they are identical within stated uncertainty limits.

Although uncertainties are assigned to the core data [at the statistically defined 95% confidence interval (Silva *et al.*, 1995)], absolute uncertainties in the SPRONS.JNC data cannot be assessed unequivocally. This is because there are multiple sources of uncertainty and ambiguity in interpretive methods used to retrieve these data from experimental results, and additional limitations associated with simultaneous evaluation of thermodynamic properties for multiple reactions (Section 4.3.4.3; Helgeson *et al.*, 1978). For these reasons it is considered preferable not to assign absolute uncertainties to the SPRONS.JNC data, rather than to estimate uncertainties that may be both inaccurate and misleading. We therefore consider the data in these two databases to be conservatively self consistent if reported values in SPRONS.JNC lie within the range of uncertainties assigned to data in the core database, but we do not explicitly account for uncertainties in the SPRONS.JNC data.

Minerals that are common to both SPRONS.JNC and the JNC core database include $Cu(c)$, $C(c)$(graphite), corundum, lime, periclase, and α-quartz. The standard molal entropy of lime in SPRONS.JNC (9.5 cal mol^{-1} K^{-1}) differs from the corresponding nominal value and associated uncertainty limits in the core database (9.106 ± 0.096 cal mol^{-1} K^{-1}). The data for minerals that are common to these databases are otherwise self-consistent

Discrepancies between SPRONS.JNC and the core database in ΔG_f°, ΔH_f° and S° for aqueous species and gases are shown in Figs. 5.2.6_1 - 5.2.6_3, respectively. The ordinate in these figures refers to the respective value in SPRONS.JNC minus the corresponding nominal value in the core database. When this difference exceeds uncertainty limits assigned to the nominal value in the core database (indicated by the error bars in Figs. 5.2.6_1 - 5.2.6_3), we take this to mean that the respective data in SPRONS.JNC and the core database are discrepant, in the conservative sense noted above. As can be seen in Fig. 5.2.6_1, the discrepancies defined in this manner in Gibbs free energies of formation are less than 1 kcal mol^{-1}, except for $H_3PO_4(aq)$, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and HF_2^-. Discrepancies in enthalpies of formation, as shown in Fig. 5.2.6_2, are also less than 1 kcal mol^{-1}, except for the phosphate species, HF_2^- and $SiO_2(aq)$. Discrepancies in entropies (Fig. 5.2.6_3) are less than 1 cal mol^{-1} K^{-1}, except for $HF(aq)$ and HSO_4^-.

The significance of these apparent discrepancies is difficult to assess, however. It is possible that even crude estimates of absolute uncertainties in SPRONS.JNC, although ill-advised for reasons noted above, would eliminate most of the discrepancies, but probably not all [e.g., ΔG_f° and ΔH_f° for the phosphate species and ΔH_f° for $SiO_2(aq)$]. It is also possible to incorporate the core data into SPRONS.JNC, but this would entail revisions to the thermodynamic properties of other minerals, gases and aqueous species that are directly or indirectly

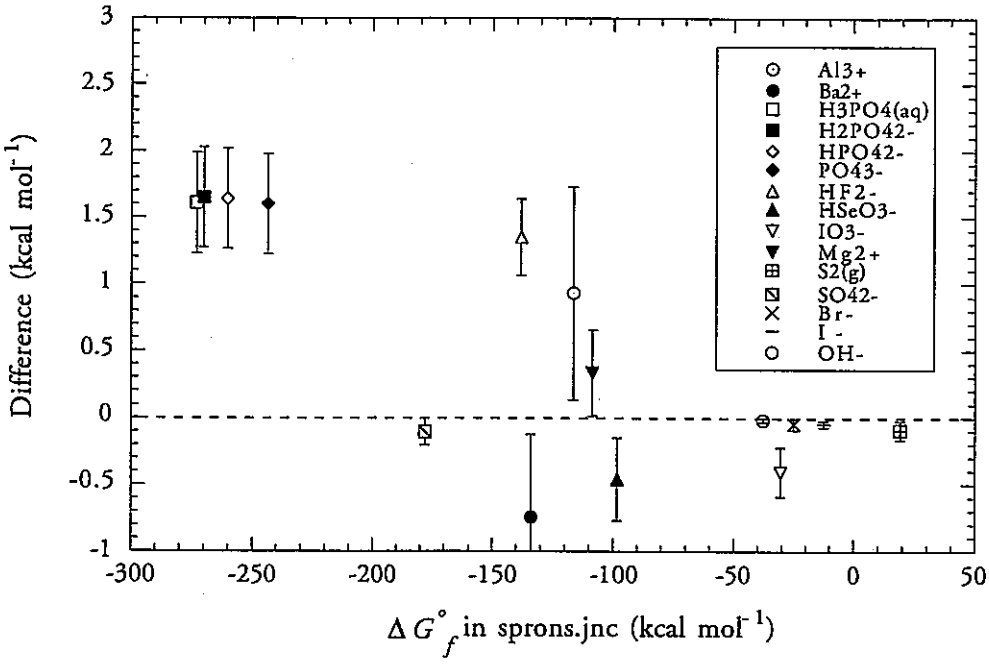


Figure 5.2.6_1. Differences between the standard Gibbs free energies of formation of aqueous species and $S_2(g)$ in SPRONS.JNC and JNC's core thermodynamic database at 25°C and 1 bar versus ΔG°_f for each species or gas in SPRONS.JNC. Discrepancies in the data for these species are possible because calculated differences exceed uncertainty limits in the core database (indicated by error bars).

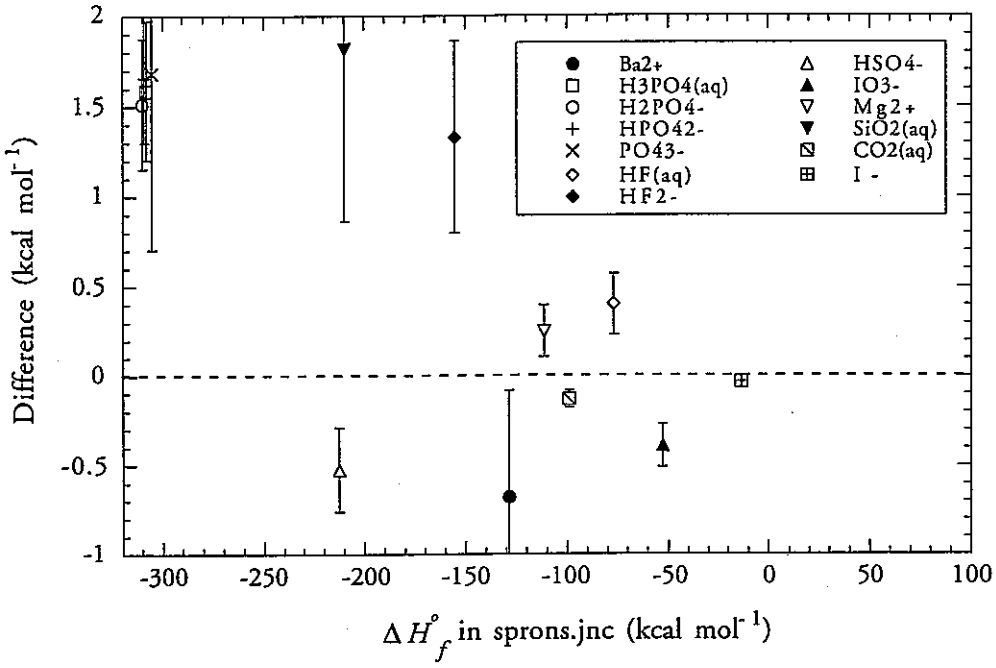


Figure 5.2.6_2. Differences between the standard partial molal enthalpies of formation of aqueous species in SPRONS.JNC and JNC's core thermodynamic database at 25°C and 1 bar versus ΔH°_{f} for each species in SPRONS.JNC. Discrepancies in the data for these solutes are possible because calculated differences exceed uncertainty limits in the core database (indicated by error bars).

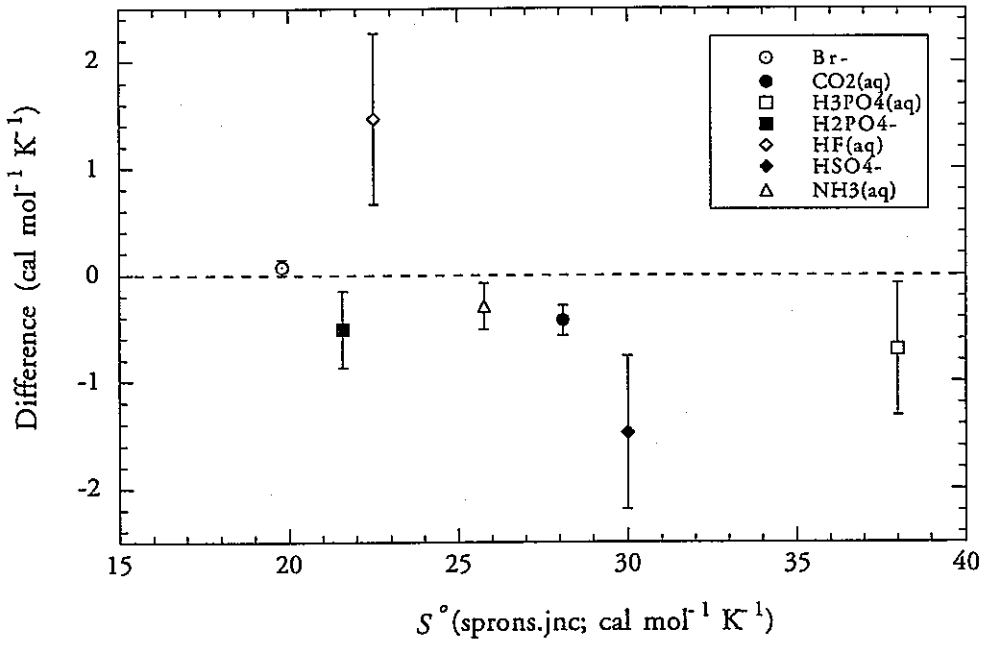


Figure 5.2.6_3. Differences between the standard partial molal entropies of aqueous species in SPRONS.JNC and JNC's core thermodynamic database at 25°C and 1 bar versus S° for each species in SPRONS.JNC. Discrepancies in the data for these aqueous ions and neutral species are possible because calculated differences exceed uncertainty limits in the core database (indicated by error bars).

constrained by the substituted data. This is certain to require a considerable amount of time that cannot be accommodated in the present study. Thus, although it is important to resolve the possible discrepancies noted above, such work must be deferred until future revisions to SPRONS.JNC are undertaken.

5.3 PHREEQE.JNC

5.3.1 Description

PHREEQE.JNC supports geochemical models of groundwater chemistry and evolution, laboratory investigations of water-rock interaction, and safety assessments of the Japanese repository concept consistent with JNC's reference scenario (Section 2). Relevant temperatures for these investigations are between 0 and 100°C. Corresponding pressures are in the range of 1 to 100 bars. Because such low pressures have negligible effects on most heterogeneous and homogeneous equilibria, however, a total pressure of 1 bar is considered adequate for these studies.

The PHREEQE.JNC database is listed in Appendix B. Format and unit conventions are specified in Tables 5.3.1_1 to 5.3.1_3. Thermodynamic data include equilibrium constants for mineral-dissolution and aqueous-association reactions at the reference pressure (1 bar) and reference temperature (25°C). As noted in Section 5.1, the temperature dependence of the equilibrium constant is calculated in the PHREEQE series of codes using either the van't Hoff equation, or empirical coefficients in an analytical expression representing log $K(T)$. In the former case, MDB (Section 5.1) extracts values of log K and the reaction enthalpy at 25°C from the corresponding SUPCRT output file, and incorporates these values into datablocks for the reaction in PHREEQE.JNC. In the latter case, MDB calculates values of the empirical coefficients by regression of log K *vs.* T values calculated by SUPCRT, and then writes these coefficients, together with log K at 25°C, into appropriate datablocks in PHREEQE.JNC. Both approaches require the reaction enthalpy at the reference pressure and temperature, and these data are therefore included in PHREEQE.JNC.

All equilibrium constants and reaction enthalpies in PHREEQE.JNC are calculated using SUPCRT and SPRONS.JNC following the procedure described in Section 5.1 and illustrated in Fig. 5.1_1. This ensures that thermodynamic data in PHREEQE.JNC are in all cases consistent with the data in SPRONS.JNC. The sources of these data are documented in Sections 5.2.2 and 5.2.3.

PHREEQE.JNC includes data for minerals, gases and aqueous species that are relevant to geologic systems, and thus which contain the *geoelements* O, H, Na, Ca, Mg, K, P, F, Cl, Fe, S, C, N, Si, Al, B, Mn and I. Revisions to this database are planned, and may include data for minerals, gases and aqueous species of radioelements, and similar data for other elements (e.g., lanthanides and organic

Line	Var	Var	Var	Format
1	tname	nelt	tgfw	a8, 2x, i2, 3x, 3 f10.0

Table 5.3.1_1. Generic data block for elements in PHREEQE.JNC. Abbreviations: Var. (variable), tname (alphanumeric name of the element), nelt (index number of the element: number must be between 4 and 99), tgfw (gram formula weight).

Line	Var	Var	Var	Var	Var	Var	Var	Var	Var	Var	Format
1	I										i4
2	sname	nsp	kflag	gflag	zsp	thsp	dha	adhsp1	adhsp2	alksp	a8, 2x, i3 , 2i1, 6f10.3
3	lktosp	dhsp	asp1	asp2	asp3	asp4	asp5				2f10.3, 5e12.5
4	lsp(I)	csp(I)									6(i3, f 7.3)

Table 5.3.1_2. Generic data block for aqueous association reactions in PHREEQE.JNC. Abbreviations: Var. (variable), I (index number assigned to the aqueous species formed in the reaction; number must be between 4 and 99 for master species, or between 100 and 1500 for other species), sname (alphanumeric species name), nsp (number of master species in the reaction), kflag [= 0 - van't Hoff equation is used to calculate log *K(T)*; =1 analytical expression is used to calculate log *K(T)*, see below], gflag (activity coefficient flag, see Parkhurst *et al.* (1980), zsp (species charge), thsp [sum of operational valences of redox species involved in the reaction , see Parkhurst *et al.* (1980], dha (the extended Debye-Hückel a°_i term), adhsp1 [the a_i term used in the WATEQ Debye-Hückel equation, see Parkhurst *et al.* (1980)], adhsp2 [the b_i term used in the WATEQ Debye-Hückel equation, see Parkhurst *et al.* (1980)], alksp (species alkalinity), lktosp (logarithm of the association constant), dhsp [enthalpy of association (kcal mol^{-1})], asp1-5 [temperature independent coefficients used in the analytical expression log $K(T)$ = asp1 + asp2 T + asp3/T + asp4 log$T$ + asp5/T^2, for T(°K)], lsp(I) (index number of master species in the reaction), csp(I)(stoichiometric coefficient of master species I in the reaction (positive for reactants, negative for products of the association reaction).

Line	Var	Var	Var	Var	Var	Var	Var	Format
1	mname	nmin0	thmin	lktom	dhmin	mflag	simin	a8, 2x, i2, 3x, 3 f10.2, 5x, i1, 9x, f10.3
2	lmin(I)	cmin(I)						5(i4, f11.3)
3	amin1	amin2	amin3	amin4	amin5			5e12.5

Table 5.3.1_3. Generic data block for mineral dissociation reactions in PHREEQE.JNC. Abbreviations: Var. (variable), mname (alphanumeric name of the mineral), nmin0 (number of aqueous species in the reaction), thmin [sum of the operational valences of redox species in the reaction , see Parkhurst *et al.* (1980)], lktom (logarithm of the equilibrium constant at 25°C), dhmin (reaction enthalpy, kcal mol^{-1}), mflag [= 0 - van't Hoff equation is used to calculate log *K(T)*; =1 analytical expression is used to calculate log *K(T)*, see below], simin [saturation index desired in the final solution (simin = 0 corresponds to equilibrium)], lmin(I) [index number of an aqueous species (I) in the reaction], cmin(I) [stoichiometric coefficient of an aqueous species (I) in the reaction], amin1-5 [temperature independent coefficients used in the analytical expression log $K(T)$ = amin1 + amin2T + amin3/T + amin4 log$T$ + amin5/T^2, for T(°K)].

aqueous species). To accommodate these future revisions, PHREEQE.JNC is dimensioned to include data for 1500 aqueous species. The first 99 index numbers are reserved for basis species. The first non-basis species (OH^-) is assigned the index number 100.

Mineral names in PHREEQE.JNC are in some cases shortened using the corresponding abbreviations in SPRONS.JNC (Appendix A). This is necessary because PHREEQE requires mineral names to be less than 9 characters in length. The abbreviations for some minerals are cryptic, including: CaAlpyrx (Ca-Al-pyroxene); Chm-7A (7Å chamosite); Cnc-7A (7Å clinochlore); Cnc-14A (14Å clinochlore); Czo (clinozoisite) a-Crs (α-cristobalite); b-Crs (β-cristobalite); K-fs (K-feldspar); Grn (greenalite); Hd (hedenbergite); Lmt (laumontite); Mng (manganosite); Max-mc (maximum microcline); Mnn (minnesotaite); Mtc (monticellite); Nesque (nesquehonite) and Hi-sa (high sanidine).

5.3.2 Redox reactions

Because the thermodynamic properties of the aqueous electron and H^+ are taken by convention to be equal to zero at any temperature and pressure (Section 4.1), equilibrium constants and reaction enthalpies for heterogeneous and homogeneous redox reactions in PHREEQE.JNC can be directly calculated using SUPCRT and SPRONS.JNC. For example, the conventional standard molal Gibbs free energy of the reaction:

$$SO_4^{2-} + 9H^+ + 8e^- \rightleftharpoons HS^- + 4H_2O(l), \qquad (5.3.2\_1)$$

given by,

$$\Delta G_r^\circ = \left(\Delta \bar{G}^\circ_{f,HS^-} + 4\Delta \bar{G}^\circ_{f,H_2O}\right) - \left(\Delta \bar{G}^\circ_{f,SO_4^{2-}} + 9\Delta \bar{G}^\circ_{f,H^+} + 8\Delta \bar{G}^\circ_{f,e^-}\right),$$

is equivalent to

$$\Delta G_r^\circ = \left(\Delta \bar{G}^\circ_{f,HS^-} + 4\Delta \bar{G}^\circ_{f,H_2O}\right) - \Delta \bar{G}^\circ_{f,SO_4^{2-}}, \qquad (5.3.2\_2)$$

because the conventional Gibbs free energies of formation of H^+ and e^- are equal to zero. The quantities on the right-hand side of Eqn. (5.3.2_2) are evaluated using SUPCRT by specifying the following *fictive* reaction in the RXN file (see Section 5.1).

$$SO_4^{2-} \rightleftharpoons HS^- + 4H_2O(l).$$

This "reaction" is chemically unrealistic because mass and charge are not conserved, but SUPCRT nevertheless calculates the standard Gibbs free energy change according to Eqn. (5.3.2_2). The result is therefore consistent with the

conventional thermodynamic properties of H^+ and e^-, and hence with the conventional thermodynamic properties of reaction (5.3.2_1). Equilibrium constants and enthalpies for all redox reactions in PHREEQE.JNC are calculated in this manner.

5.3.3 Comparison of thermodynamic data in PHREEQE.JNC and the H3 TDB

JNC's Heisei 3 (H3) thermodynamic database (TDB) is compared in this section with PHREEQE.JNC. The purpose of the comparison is to establish some continuity with regard to previous work carried out by JNC that includes thermodynamic calculations using the H3 database. That is, we assess the level of agreement among data that are common to both databases, and also identify minerals, gases and aqueous species that are included in one database, but not the other. The H3 database is described by Yui *et al.* (1992b). It includes data from several sources in a format that is compatible with PHREEQE software.

Equilibrium constants and enthalpies of aqueous association reactions in the H3 TDB and PHREEQE.JNC are shown in Table 5.3.3_1. The table includes all aqueous ions and complexes that are relevant to geologic systems, and also a limited number of radioelement ions and complexes that are common to both databases. As can be seen, many of the geologically relevant species in the H3 database are also present in PHREEQE.JNC. Equilibrium constants (25°C) are generally in close agreement. Reaction enthalpies (25°C) also compare favorably, although discrepancies exceeding a few kcal mol^{-1} are not uncommon. Many aqueous species in the H3 database are not present in PHREEQE.JNC, however, and *vice versa*. Phosphate, carbonate, sulfate and nitrate complexes are generally better represented in the H3 TDB, whereas hydroxide and halogen complexes are more prevalent in PHREEQE.JNC.

Distinctly different approaches are associated with the H3 TDB and PHREEQE .JNC to account for the temperature dependence of the equilibrium constant of aqueous association reactions. As can be seen in Table 5.3.3_1, the H3 database requires equilibrium constants at temperatures other than 25°C to be estimated using the van't Hoff equation [i.e., flag (=kflag) = 0 (Table 5.3.1_2)]. Moreover, the association enthalpies of many complexes in this database are equal to zero, and equilibrium constants for the corresponding reactions at any temperature must therefore be equal to the value of the equilibrium constant at 25°C. In contrast, equilibrium constants between 0 and 100°C in PHREEQE.JNC are derived from calculations using SUPCRT and SPRONS.JNC (i.e., flag = 1; see Section 5.1). A comparison of log K values calculated in this manner at 25 and 60°C (Table 5.3.3_1) suggests that even relatively small increases in temperature can cause the equilibrium constant to increase, or decrease, by several orders of magnitude. This suggests that the van't Hoff equation may not be appropriate for estimating equilibrium constants at temperatures that are relevant to the Japanese repository concept, particularly if it is assumed that the reaction enthalpy equals zero. Moreover, the good agreement noted above among

Table 5.3.3_1. Equilibrium constants and reaction enthalpies for aqueous association reactions in the H3 TDB and PHREEQE.JNC.

Aqueous Species	H3 TDB			PHREEQE.JNC			
	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	Log K (60°C)
OH^-	0	13.345	-14.000	1	13.340	-13.995	
$O_2(aq)$	0	134.79	-86.08	1	133.734	-86.003	
$H_2(aq)$	0	-1.759	-3.15	1	-1.000	-3.105	
HCO_3^-	1	-3.561	10.33	1	-3.513	10.329	
$H_2CO_3(aq)$	1	-5.738	16.68	1	-5.832	16.673	
HSO_4^-	1	4.91	2.000	1	4.90	1.979	
$H_2S(aq)$	0	-65.179	40.681	1	-64.868	40.677	
HS^-	0	-40.14	33.652	1	-59.717	33.690	
$H_2S_2O_3(aq)$				1	-57.184	40.739	
$HS_2O_3^-$	0	0.	39.605	1	-60.684	40.153	38.615
HSO_3^-	0	0.	3.823	1	-0.587	3.583	4.35
$H_2BO_3^-$	0	3.224	-9.240	1	3.907	-9.249	
HPO_4^{2-}	0	-3.53	12.350	1	-3.515	12.322	
$H_2PO_4^-$	0	-4.52	19.55	1	-4.52	19.527	
$HF(aq)$	0	3.46	3.17	1	3.315	3.168	
HF_2^-	0	4.55	3.749	1	4.960	2.551	
$H_3SiO_4^-$	0	0.	-9.810	1	4.220	-9.585	-9.241
$H_2SiO_4^{2-}$	0	0.	-23.141				
$HCl(aq)$				1	9.648	-0.710	
$HNO_3(aq)$				1	4.019	-1.303	
$H_3PO_4(aq)$				1	-2.620	21.697	
$HIO_3(aq)$	0	168.0	-111.0	1	168.05	-110.518	
$H_2Se(aq)$	0	0.	85.1				
HSe^-	0	0.	81.2	1	-126.267	81.181	74.463
$HSeO_3^-$	0	0.	36.3	1	-48.097	36.304	33.416
$H_2SeO_3(aq)$	0	0.	38.9	1	-46.407	38.877	36.152
$HSeO_4^-$	0	0.	1.9	1	4.200	1.906	2.309
$AlOH^{2+}$	0	11.9	-4.99	1	11.902	-4.957	
$Al(OH)_2^+$	0	0.	-10.1	1	23.490	-10.594	-8.745
$Al(OH)_3(aq)$	0	0	-16.0	1	34.585	-16.433	-13.725
$Al(OH)_4^-$	0	44.06	-23.0	1	43.236	-22.883	
AlF^{2+}	0	0.	7.01				
AlF_2^+	0	20.0	12.75				
$AlF_3(aq)$	0	2.5	17.02				
AlF_4^-	0	0.	19.72				
$AlSO_4^+$	0	2.15	3.02				
$Al(SO_4)_2^-$	0	2.84	4.92				

Aqueous Species	H3 TDB			PHREEQE.JNC			
	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	Log K (60°C)
$BaOH^+$	0	15.095	-13.358	1	20.917	-13.500	
$BaCl^+$				1	3.110	-0.498	
BaF^+				1	2.140	-0.183	
$BaCO_3(aq)$				1	4.035	2.645	
$BaHCO_3^+$				1	1.999	11.311	
$BiOH^{2+}$				1	4.157	-1.105	
$Bi(OH)_2^+$				1	18.657	-3.304	
$Bi(OH)_3(aq)$				1	30.974	-8.206	
$Bi(OH)_4^-$				1	45.674	-21.107	
$BF(OH)_3^-$	0	1.85	-0.40				
$BF_2(OH)_2^-$	0	1.635	7.628				
BF_3OH^-	0	-1.58	13.666				
BF_4^-	0	-1.795	20.274				
$CaOH^+$	0	14.535	-12.598	1	18.517	-12.833	
$CaCl^+$				1	1.126	-0.292	
$CaCl_2(aq)$				1	-1.394	-0.644	
CaF^+	0	3.798	0.940	1	1.350	0.682	
$Ca(HCO_3)^+$	1	-0.869	11.435	1	-3.165	11.376	
$CaCO_3(aq)$	1	3.547	3.225	1	3.795	3.327	
$CaSO_4(aq)$	1	1.470	2.309	1	1.300	2.111	
$CaPO_4^-$	0	3.100	6.459				
$CaHPO_4(aq)$	0	-0.230	15.085				
$CaH_2PO_4^+$	0	-1.120	20.961				
$CaH_3SiO_4^+$				1	4.783	-8.575	
$CH_4(aq)$	0	-61.039	41.071	1	-64.575	38.194	
$FeOH^+$	0	13.2	-9.5	1	12.287	-9.315	
$Fe(OH)_2(aq)$	0	28.565	-20.57	1	27.417	-20.405	
$Fe(OH)_3^-$	0	30.3	-31.0	1	32.984	-29.207	
$FeCl^+$				1	0.723	-0.161	
$Fe(Cl)_2(aq)$				1	23.426	-8.172	
FeF^+				1	0.748	1.427	
$FeSO_4(aq)$	0	3.23	2.25				
$Fe(HS)_2(aq)$	0	-120.280	76.250				
$Fe(HS)_3^-$	0	-180.420	111.937				
$FeHPO_4(aq)$	0	-3.530	15.946				
$FeH_2PO_4^+$	0	-4.520	22.253				
Fe^{3+}	0	10.0	-13.032	1	10.200	-13.011	
$FeOH^{2+}$	0	20.4	-15.22	1	20.367	-15.216	

Aqueous Species	H3 TDB			PHREEQE.JNC			
	flag*	ΔH°_r (kcal/mol)	Log K (25°C)	flag*	ΔH°_r (kcal/mol)	Log K (25°C)	Log K (60°C)
$Fe(OH)_2^+$	0	10.0	-18.70	1	29.367	-18.661	
$Fe(OH)_3(aq)$	0	10.0	-26.63	1	38.384	-25.029	
$Fe(OH)_4^-$	0	10.0	-34.63	1	47.984	-34.631	
$Fe_2(OH)_2^{4+}$	0	33.5	-29.01				
$Fe_3(OH)_4^{5+}$	0	44.3	-45.4				
$FeCl^{2+}$	0	15.6	-11.55	1	11.163	-11.531	
$FeCl_2^+$	0	10.0	-10.90				
$FeCl_3(aq)$	0	10.0	-11.90				
FeF^{2+}	0	12.7	-6.80	1	15.059	-7.011	
FeF_2^+	0	14.7	-2.2				
$FeF_3(aq)$	0	15.4	0.97				
$FeSO_4^+$	0	13.91	-9.11				
$Fe(SO_4)^{2-}$	0	14.60	-7.61				
$FeHPO_4^+$	0	12.23	4.74				
FeH_2P^{2+}	0	5.48	11.95				
IO_3^-	0	0.	-111.0	1	165.65	-111.324	-100.769
IO_4^-	0	251.0	-165.0	1	250.667	-165.044	
$KOH(aq)$				1	16.483	-14.895	
$KCl(aq)$				1	2.803	-1.751	
$KBr(aq)$				1	2.990	-1.737	
$KI(aq)$				1	2.041	-1.598	
$KHSO_4(aq)$				1	277.67	-179.909	
KSO_4^-	0	2.25	0.85	1	0.690	0.880	
$KHPO_4^-$	0	-3.530	12.636				
$KAl(OH)_4(aq)$				1	50.603	-24.224	
$LiOH(aq)$				1	13.369	-13.649	
$LiCl(aq)$				1	0.805	-1.511	
$LiSO_4^-$	0	0.	0.64				
$MgOH^+$	0	15.419	-11.794	1	26.729	-11.682	
$MgCl^+$				1	0.367	-0.135	
MgF^+	0	4.674	1.82	1	0.567	1.352	
$Mg(HCO_3)^+$	1	-2.775	11.397	1	-2.998	11.365	
$MgCO_3(aq)$	1	2.535	2.981	1	2.182	2.979	
$MgSO_4(aq)$	0	1.4	2.25				
$MgPO_4^-$	0	3.100	6.589				
$MgHPO_4(aq)$	0	-0.2	15.216				
$MgH_2PO_4^+$	0	-1.120	21.066				
$MgH_3SiO_4^+$				1	3.759	-8.325	

Aqueous Species	H3 TDB			PHREEQE.JNC			
	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	Log K (60°C)
$MnOH^+$	0	14.40	-10.59	1	14.417	-10.59	
$Mn(OH)_2(aq)$				1	22.117	-22.201	
$Mn(OH)_3^-$	0	0.	-34.8	1	39.634	-34.800	-31.794
$Mn(OH)_4^{2-}$				1	56.234	-48.287	
$MnCl^+$	0	0.	0.607	1	4.553	-0.139	0.282
$MnCl_2(aq)$	0	0.	0.041				
$MnCl_3^-$	0	0.	-0.305				
MnF^+	0	0.	0.85	1	0.596	0.88	0.997
$MnHCO_3^+$	0	-3.604	11.60				
$MnSO_4(aq)$	0	2.17	2.26	1	3.55	1.913	
$Mn(NO_3)_2(aq)$	0	-0.3	0.6				
Mn^{3+}	0	25.76	-25.507	1	22.2	-25.509	
MnO_4^{2-}	0	150.02	-118.44	1	169.567	-118.345	
$NaOH(aq)$				1	12.823	-14.795	
$NaCl(aq)$				1	1.206	-0.777	
$NaF(aq)$				1	1.723	-0.998	
$NaBr(aq)$				1	1.643	-1.357	
$NaI(aq)$				1	1.932	-1.540	
$NaHCO_3(aq)$	0	-3.604	10.080				
$NaCO_3^-$	0	8.911	1.268				
$NaSO_4^-$	0	1.12	0.70	1	-0.647	0.923	
$NaHPO_4^-$	0	-3.53	12.636				
$NaAl(OH)_4(aq)$				1	45.489	-23.627	
$NaH_2BO_3(aq)$				1	-64.557	32.581	
$NaH_3SiO_4(aq)$				1	1.631	-7.754	
$NdOH^{2+}$	0	0.	-8.0	1	19.317	-8.127	-6.608
$Nd(OH)_2^+$	0	0.	-16.9	1	27.817	-17.070	-14.293
$Nd(OH)_3(aq)$	0	0.	-26.5	1	55.134	-26.37	-22.284
$Nd(OH)_4^-$	0	0.	-37.1	1	71.434	-37.072	-32.068
$NiOH^+$	0	0.	-9.9	1	13.567	-10.803	-9.731
$Ni(OH)_2(aq)$	0	0.	-19.0	1	24.987	-20.706	-17.630
$Ni(OH)_3^-$	0	0.	-30.0	1	30.774	-31.003	-28.610
$Ni(OH)_4^{2-}$				1	47.734	-44.036	
$Ni_2(OH)_3^+$	0	0.	-10.7				
$Ni_4(OH)_4^{4+}$	0	0.	-27.7				
$NiSO_4(aq)$	0	0.	2.3				
$NiCl^+$				1	1.433	-0.996	
NiF^+				1	0.735	1.120	

Aqueous Species	H3 TDB			PHREEQE.JNC			
	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	Log K (60°C)
Np^{3+}	0	0.	3.03	1	7.000	3.445	4.304
NpO_2^+	0	35.73	-11.37	1	35.834	-9.145	
NpO_2^{2+}	0	0.	-32.29	1	63.934	-30.035	-25.859
$NH_3(aq)$	0	-174.58	109.83	1	-174.961	109.906	
NH_4^+	1	-187.055	119.070	1	-187.371	119.147	
$NH_4SO_4^-$	1	-187.055	120.19				
$N_2(aq)$	0	-312.13	207.08	1	-313.538	207.269	
NO_2^-	0	-43.76	28.57	1	-43.888	27.767	
$PbOH^+$	0	0.	-7.7	1	-0.803	-6.192	-6.283
$Pb(OH)_2(aq)$	0	0.	-17.1	1	23.397	-16.894	-15.152
$Pb(OH)_3^-$	0	0.	-27.3	1	32.214	-27.917	-25.548
Pb_2OH^{3+}	0	0.	-6.4				
$Pb_3(OH)_4^{2+}$	0	0.	-23.9				
$Pb_4(OH)_4^{4+}$	0	0.	-20.88				
$Pb_6(OH)_8^{4+}$	0	0.	-43.6				
$PbCl^+$	0	0.	1.61	1	1.083	1.437	1.578
$PbCl_2(aq)$	0	0.	2.44	1	1.946	2.003	2.24
$PbCl_3^-$	0	0.	2.01	1	1.879	1.688	1.941
$PbCl_4^{2-}$				1	0.303	1.43	
PbF^+				1	-0.661	2.06	
$PbF_2(aq)$				1	-2.703	3.420	
$Pb(HS)_2(aq)$				1	-134.805	82.089	
$Pb(HS)_3^-$				1	-196.525	117.078	
$PbCO_3(aq)$	0	0.	7.3				
$Pb(CO_3)_2^{2-}$	0	0.	10.78				
$PbSO_4(aq)$	0	0.	2.59				
$Pb(SO_4)_2^{2-}$	0	0.	3.5				
$PdOH^+$	0	0.	-2.12	1	-0.763	-1.091	-1.131
$Pd(OH)_2(aq)$	0	0.	-4.62	1	1.537	-2.190	-2.071
Pu^{3+}	0	0.	16.9	1	-13.300	17.006	16.399
PuO_2^+	0	46.23	-18.6	1	46.234	-17.941	-14.713
PuO_2^{2+}	0	0.	-34.9	1	68.334	-34.213	-29.603
S^{2-}	0	-28.04	20.735				
S_2^{2-}				1	-104.534	57.645	
S_3^{2-}				1	-161.401	94.457	
S_4^{2-}				1	-217.968	131.049	
S_5^{2-}				1	-274.235	167.422	
$S_2O_3^{2-}$	0	0.	38.015	1	-61.784	38.467	36.701

Aqueous Species	H3 TDB			PHREEQE.JNC			
	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	Log K (60°C)
$S_2O_4^{2-}$				1	-18.567	10.549	
$S_2O_5^{2-}$				1	-2.150	2.348	
$S_2O_6^{2-}$				1	17.766	-8.418	
$S_2O_8^{2-}$				1	113.400	-65.501	
$S_3O_6^{2-}$				1	-36.701	25.902	
$S_4O_6^{2-}$				1	-106.168	76.128	
$S_5O_6^{2-}$				1	-150.435	97.474	
SO_3^{2-}	0	0.	-3.397	1	-2.817	-3.623	-3.105
$SO_2(aq)$				1	3.572	5.443	
Se^{2-}	0	0.	66.3				
SeO_3^{2-}	0	0.	29.0	1	-46.817	29.018	26.145
$SnOH^+$	0	0.	-3.89	1	6.617	-3.414	-2.927
$Sn(OH)_2(aq)$	0	0.	-7.90	1	10.317	-7.079	-6.33
$Sn(OH)_3^-$	0	0.	-17.39	1	16.634	-16.599	-15.397
$SnCl^+$	0	0.	1.05				
$SnCl_2(aq)$	0	0.	1.71				
$SnCl_3^-$	0	0.	1.69				
SnF^+	0	0.	4.08				
$SnF_2(aq)$	0	0.	6.68				
SnF_3^-	0	0.	9.46				
Sn^{4+}	0	0.	-5.38				
$SnOH^{3+}$	0	0.	-4.77				
$Sn(OH)_4(aq)$	0	0.	-4.53				
$Sn(OH)_2^{2+}$	0	0.	-5.56				
$Sn(OH)_3^+$	0	0.	-4.85				
SnF^{3+}	0	0.	-6.57				
SnF_2^{2+}	0	0.	-4.6				
SnF_3^+	0	0.	-6.31				
$SnF_4(aq)$	0	0.	4.34				
$SnSO_4^{2+}$	0	0.	-19.6				
$Sn(SO_4)_2(aq)$	0	0.	-6.14				
$SrOH^+$	0	14.495	-13.178	1	19.987	-13.302	
$SrCl^+$	0	0.	-0.2	1	1.183	-0.248	-0.047
$SrCl_2(aq)$	0	0.	0.				
SrF^+				1	1.150	0.139	
$SrHCO_3^+$	1	2.486	11.513	1	2.489	11.509	
$SrCO_3(aq)$	1	5.217	2.805	1	4.435	2.865	
$SrSO_4(aq)$	0	1.6	2.55				

Aqueous Species	H3 TDB			PHREEQE.JNC			
	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	Log K (60°C)
$SrNO_3^+$	0	0.	0.8				
$SrPO_4^-$	0	0.	4.2				
SiF_6^{2-}	0	-16.26	30.18	1	-16.959	26.275	
U^{3+}	0	24.414	-8.615	1	24.400	-9.602	
UOH^{3+}	0	11.217	-0.540	1	11.217	-0.541	
$U(OH)_4(aq)$	0	0.	-4.479	1	18.234	-4.563	-3.185
UO_2^+	0	32.932	-7.507	1	32.934	-7.576	
$UO_2OH(aq)$				1	50.35	-25.738	
$UO_2(OH)_2^-$				1	72.650	-44.063	
UO_2^{2+}	0	34.4	-8.993	1	34.384	-9.049	
UO_2OH^+	0	44.723	-14.193	1	44.750	-14.267	
$UO_2(OH)_2(aq)$	0	0.	-20.994	1	46.650	-19.361	-16.557
$UO_2(OH)_3^-$	0	0.	-28.994	1	51.667	-28.295	-25.099
$UO_2(OH)_4^{2-}$	0	0.	-41.994	1	68.367	-42.075	-37.671
$ZrOH^{3+}$	0	0.	0.3	1	6.147	0.324	0.828
$Zr(OH)_2^{2+}$				1	14.347	-1.728	
$Zr(OH)_3^+$				1	21.664	-5.091	
$Zr(OH)_4(aq)$	0	0.	-9.7	1	23.164	-9.709	-7.904
$Zr(OH)_5^-$	0	0.	-16.0	1	21.980	-16.004	-13.699
$Zr_3(OH)_4^{8+}$	0	0.	-0.6				
$Zr_4(OH)_8^{8+}$	0	0.	6.0				
$ZrSO_4^{2+}$	0	0.	2.5				

* - kflag, see Table 5.3.1_2.

equilibrium constants at 25°C is probably not valid at other temperatures.

Thermodynamic data for a limited number of mineral dissolution reactions that have been considered by JNC in previous modeling studies of groundwater evolution are shown in Table 5.3.3_2. As can be seen, equilibrium constants at 25°C are generally in close agreement, but significant discrepancies (e.g., greater than about one order of magnitude) are evident for dolomite, kaolinite, K-feldspar, clinochlore, tremolite and pyrite dissolution. Reaction enthalpies (25°C) are also similar, but discrepancies exceeding a few kcal mol^{-1} are apparent for dolomite, siderite, kaolinite and K-feldspar. Comments noted above on the use of the van't Hoff equation for estimating equilibrium constants at high temperatures also pertain to mineral dissolution reactions, as can be seen by comparing log K values at 25 and 60°C in the PHREEQE.JNC data base.

Mineral	H3 TDB			PHREEQE.JNC			
	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	flag*	$\Delta H°_r$ (kcal/mol)	Log K (25°C)	Log K (60°C)
Calcite	1	-2.30	-8.48	1	-2.633	-8.480	
Aragonite	1	-2.59	-8.34	1	-2.654	-8.336	
Dolomite	0	-9.44	-17.09	1	-7.306	-18.144	
Siderite	0	-6.14	-10.57	1	-4.262	-10.521	
Strontianite	1	-0.40	-9.27	1	1.545	-10.643	
Gypsum	1	-0.03	-4.60				
Anhydrite	0	-4.30	-4.38	1	-4.44	-4.306	
Celestite	0	0.23	-6.58	1	-1.770	-5.677	
Barite	0	6.14	-9.98	1	6.20	-9.971	
Fluorite	0	4.71	-10.96	1	2.90	-10.037	
Amorph. $Fe(OH)_3$	0	0.	4.89				
Quartz			-3.78	1	7.875	-3.999	
Gibbsite	0	-22.80	8.77	1	-24.566	7.756	
Chalcedony			-3.49	1	7.507	-3.728	
Kaolinite	0	49.15	-36.92	1	58.637	-38.957	
Phlogopite	0	0.	36.33	1	-73.975	37.267	31.355
K-feldspar	0	-12.47	1.78	1	-5.486	-0.448	
Albite**	0	0.	3.54	1	-12.393	2.764	1.568
Anorthite**	0	0.	26.37	1	-72.427	26.578	20.809
Clinochlore	0	0.	68.35	1	-146.359	67.239	55.772
Tremolite	0	0.	57.7	1	-97.131	61.237	53.171
Epidote	0	0.	45.43	1	-102.562	45.940	25.551
Muscovite	0	-59.38	14.60	1	-57.895	14.05	
Pyrite**	0	130.0	-86.0	1	130.684	-83.610	

* - mflag, see Table 5.3.1_3; ** - reaction stoichiometry in the H3 TDB

Table 5.3.3_2. Equilibrium constants and reaction enthalpies for selected mineral dissolution reactions in the H3 TDB and PHREEQE.JNC.

5.3.4 Excluded reactions

As noted in the preceding section, there are a number of aqueous species and minerals that are not represented in PHREEQE.JNC for which thermodynamic data are available in the H3 TDB (and numerous other databases). Several of these species and minerals could be important in experimental, field and modeling studies carried out by JNC. This raises the question whether such data should be included in PHREEQE.JNC.

Consistent with the objectives of this project (Section 2), we believe such data should not be included until an evaluation is made of their reliability at reference

conditions, and perhaps more importantly at other temperatures considered in the Japanese repository concept, and until it can be determined that they are internally consistent with respect to other data in PHREEQE.JNC and SPRONS.JNC. Due to time constraints in the present study, such assessments will have to be made by individual users as the need arises.

6 Evaluation of Database Reliability

The reliability of thermodynamic data in SPRONS.JNC (and, hence, PHREEQE.JNC) is evaluated in this section, where equilibrium constants for selected reactions calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts. The comparisons are summarized in the form of diagrams showing calculated and experimental values of log K as a function of temperature at pressures corresponding to the liquid-phase side of the H_2O vaporization boundary *(Psat)*, or at higher pressures representing single-phase regions of H_2O stability. Diagrams for heterogeneous reactions (gas-solubility and mineral-solution equilibria) comprise Appendix C. Similar diagrams for homogeneous reactions (aqueous-speciation reactions) are included in Appendix D.

Equilibrium constants are chosen as the basis for this evaluation because they represent the most direct link between the thermodynamic properties of a reaction and experimental measurements (e.g., Nordstrom *et al.*, 1990). Some refinement of basic experimental data is usually necessary to determine values of log K, however. For example, an appropriate chemical model of the aqueous system and total analytical solute concentrations may be needed to calculate the activities of species at reference conditions of infinite dilution, which partially or completely define the equilibrium constant. Time constraints in the present study do not permit independent retrievals of equilibrium constants from primary experimental results, however, and log K values reported in the literature must therefore be accepted at face value. For this reason, our objective is limited to identifying reactions for which calculated and experimental equilibrium constants agree favorably, as well as reactions where the agreement is less favorable, suggesting that future revisions to data in SPRONS.JNC and PHREEQE.JNC may be needed.

The thermodynamic properties of minerals in SPRONS.JNC are constrained primarily by the results of high-temperature and high-pressure phase-equilibrium experiments, and by a limited amount of calorimetric data (Section 3.2.1). The reliability of these data is evaluated by Helgeson *et al.* (1978), who compared experimental solution compositions, or phase-equilibrium reversal temperatures, for over 130 reactions with calculated mineral-stability relations, or univariant /divariant equilibrium curves. Comparisons of calculated and experimental equilibrium constants for mineral-solution equilibria and aqueous-speciation reactions are similarly documented in other sources of thermodynamic data incorporated in SPRONS.JNC (see Sections 5.2.2 and 5.2.3).

We supplement these earlier evaluations in the present study, focussing on heterogeneous and homogeneous equilibria at relatively low temperatures and pressures. Although the available experimental data referring to these conditions is still rather limited, the evaluations documented below are important because

they constitute independent checks on the reliability of data in SPRONS.JNC and PHREEQE.JNC at conditions that are most relevant to the Japanese repository concept. We also consider a few reactions involving common rock-forming minerals that are known to dissolve incongruently at low temperatures, because the dissolution and precipitation kinetics of these reactions is partially controlled by the equilibrium constant under near-to-equilibrium conditions. Comments on the reliability of thermodynamic data in SPRONS.JNC and PHREEQE.JNC are summarized in Sections 6.1 - 6.12. Laboratory and field experiments needed to improve these databases, and procedures to manage them, are summarized in Section 6.13.

6.1 Gas Solubilities and Acid Dissociation Constants

Plots of calculated and experimental equilibrium constants for gas solubility reactions are shown in the following figures (Appendix C):

- Fig. C.1; $CO_2(g)$,
- Fig. C.2; $CH_4(g)$,
- Fig. C.3; $H_2S(g)$,
- Fig. C.4; $H_2(g)$, and
- Fig. C.5; $Ne(g)$, $Kr(g)$, $N_2(g)$, $Rn(g)$, $SO_2(g)$, $Ar(g)$ and $O_2(g)$,

where sources of the experimentally determined equilibrium constants are also documented. As can be seen, calculated equilibrium constants represented by the curves in these figures are in close agreement with most of their experimental counterparts, represented by symbols (experimental uncertainties are indicated by the size of the symbols in Fig. C.5, and are estimated to be slightly larger than the size of the symbols in Figs. C.1-C.4 ($\approx \pm 0.1$ log K units)]. Thermodynamic data and equation-of-state parameters for gases from Helgeson *et al.* (1978) and corresponding data for neutral aqueous species retrieved by Shock *et al.* (1989) are incorporated in SPRONS.JNC and were used to calculate all the curves in Figs C.1 - C.5. Shock *et al.* (1989) generate figures similar to Figs C.1 and C.4, and also document comparisons between calculated and experimental equilibrium constants for solubility reactions involving $He(g)$ and $Xe(g)$. The curves in Fig. C.5 for reactions involving $Ne(g)$, $Kr(g)$, $SO_2(g)$ and $Ar(g)$ are independent of the experimental data at temperatures greater than 25°C, because equation-of-state parameters for these gases are estimated using empirical correlation algorithms, as described by Shock *et al.* (1989). The agreement shown in Fig C.5 between calculated and experimental equilibrium constants at temperatures greater than 25°C is therefore noteworthy. Shock *et al.* (1989) also cite numerous references to experimental gas solubility data not shown in Figs. C.1 - C.5, which they assert are also closely consistent with the calculated curves in these figures. This wealth of experimental gas solubility data leaves little doubt that accurate gas solubilities can be calculated using SUPCRT and SPRONS.JNC between 0 and 100°C at 1 bar, and at considerably higher

temperatures and pressures.

Several of the gases noted above form weak acids when dissolved in aqueous solution. Plots of calculated and experimentally determined dissociation constants for these acids, and related ionic species, are shown in the following figures (Appendix D):

- Fig. D.1; H_2O,
- Fig. D.2; $CO_2(aq)$ (i.e., $H_2CO_3(aq)$ - see Section 5.2.5),
- Fig. D.3; HCO_3^-,
- Fig. D.4; $H_2S(aq)$,
- Fig. D.5; HSO_4^-,
- Fig. D.6; $HF(aq)$,
- Fig. D.7; $H_3BO_3(aq)$,
- Fig. D.8; $H_3PO_4(aq)$,
- Fig. D.9; NH_4^+, and
- Fig. D.10; CH_3COOH.

As can be seen, the calculated equilibrium constants are closely consistent with most of their experimental counterparts. Diagrams similar to Figs. D.2, D.4, D.6, D.7, D.8 and D.9 are generated by Shock *et al.* (1989), who also include diagrams for $HNO_3(aq)$ and $SO_2(aq)$ dissociation. These authors note that experimental equilibrium constants retrieved by Ellis and Giggenbach (1971) for $H_2S(aq)$ dissociation at temperatures greater than 100°C (Fig. D.4), and the equilibrium constants retrieved by Read (1975) for $H_2CO_3(aq)$ dissociation between 1 and 2 kb at temperatures less than 150°C (conditions not considered in Fig. D.2), are the only experimental values available that differ by more than ±0.2 log K units from values calculated using SUPCRT and thermodynamic data that are incorporated in SPRONS.JNC.

6.2 System SiO_2-H_2O

6.2.1 Quartz

The solubility of quartz has been experimentally investigated over a broad range of pressures and temperatures (Kennedy, 1950; Morey and Hesselgesser, 1951; Khitarov, 1956; Kitahara, 1960; van Lier *et al.*, 1960; Siever, 1962; Morey *et al.*, 1962; Weill and Fyfe, 1964; Anderson and Burnham, 1965, 1967; Crerar and Anderson, 1971; Hemley *et al.*, 1980; Walther and Orville, 1983; and Rimstidt, 1997). Shock *et al.* (1989) regressed experimental values of log K reported in many of these studies using the revised HKF model (Section 4.2.2) to retrieve equation-of-state coefficients and the standard partial molal volume, entropy and heat capacity of $SiO_2(aq)$ at 25°C and 1 bar. The conventional born coefficient for $SiO_2(aq)$ determined by Walther and Helgeson (1977) and thermodynamic properties of quartz from Helgeson *et al.* (1978) were adopted

in the regression procedure. The retrieved coefficients and properties of $SiO_2(aq)$ are used to generate the curves shown in Fig. C.6, where it can be seen that the curves accurately represent the available experimental data at temperatures between 0 and 900°C and pressures from 1 bar to 9 kb. The thermodynamic properties of $SiO_2(aq)$ retrieved by Shock *et al.* (1989) and the thermodynamic properties of quartz from Helgeson *et al.* (1978) are included in SPRONS.JNC.

Quartz solubilities calculated in the present study between 0 and 300°C at *Psat* are shown in Fig C.7, which represents an expanded view of a portion of diagram A, Fig. C.6. As can be seen, the calculated equilibrium curve lies near all the experimental points, but it is apparent that the curve consistently under-predicts measured solubilities slightly over this temperature range. Error bars representing experimental uncertainties are probably smaller than the size of the plot symbols in this figure. These uncertainties are not documented in all the experimental studies, but we note that silica concentrations are routinely measured (e.g., using colorimetric methods; see Govett, 1961) with a precision of ±5%, and that temperatures are probably accurate to at least ±5°C over this temperature range. The systematic deviation of the calculated curve from the experimental data in Fig C.7 is therefore probably real, even when experimental uncertainties are taken into account.

Figure C.7 incorporates recent experimental data from Rimstidt (1997) on quartz solubilities between 0 an 100°C. These experiments were designed to approach equilibrium from conditions of undersaturation in pure water at 21, 50, 74 and 96°C over equilibration periods ranging from 54 days (74°C) to 4917 days (21°C). Rimstidt (1997) combined his results with critically selected quartz solubility data from the literature to derive an empirical log *K(T)* function, which predicts that quartz solubility at 25°C is consistent with equilibrium $SiO_2(aq)$ concentrations of 10.8 ppm, rather than the widely accepted value of 6 ppm (Walther and Helgeson, 1977; Fournier and Potter, 1982). Using this function, Rimstidt (1997) calculates revised standard partial molal properties of $SiO_2(aq)$, which are consistent with the solubility of amorphous silica, and with silica concentrations in ancient groundwaters.

Quartz solubilities determined by Rimstidt (1997) between 0 and 100°C are compared in Fig. C.8 with solubilities calculated using SUPCRT and SPRONS.JNC. Also shown in the figure are experimental data from van Lier *et al.* (1960), which Rimstidt (1997) concludes are from equilibrated experiments, and data from Mackenzie and Gees (1971), Morey *et al.* (1962) and Fournier (1960), which Rimstidt (1997) suggests are from experiments that did not reach equilibrium. As can be seen, the calculated curve under-predicts the solubility data of Rimstidt (1997) and van Lier *et al.* (1960) by a factor less than 2 over this temperature range.

The observations summarized above with regard to Figs. C.7 and C.8 suggest that the thermodynamic properties of $SiO_2(aq)$ in SPRONS.JNC may need to be revised. Although such revisions are probably minor, they are important because this would entail revising the properties of several other minerals in SPRONS.JNC, which were retrieved by Helgeson *et al.* (1978) using the standard Gibbs free energy of formation of $SiO_2(aq)$ determined by Walther and Helgeson (1977).

6.2.2 Amorphous silica

The solubility of amorphous silica has been experimentally investigated over a range of pressures and temperatures (Hitchen, 1935; Okamoto *et al.*, 1957; Elmer and Nordberg, 1958; Kitahara, 1960; Morey *et al.*, 1964; Fournier and Rowe, 1977; Chen and Marshall, 1982). The thermodynamic properties of amorphous silica in SPRONS.JNC are from Helgeson *et al.* (1978), who adopted the standard Gibbs free energy at 25°C recommended by Walther and Helgeson (1977).

The solubilities of amorphous silica between 0 and 300°C calculated using SUPCRT and SPRONS.JNC are compared with experimental solubilities in Fig. C.9. The calculated values agree closely with their experimental counterparts over this temperature range. In contrast, solubilities determined in some of the older studies noted above do not agree with the calculated values. This is apparently because the earlier studies failed to allow sufficient time for the solid and solution phases to equilibrate (Morey *et al.*, 1964).

6.2.3 Chalcedony

The solubility of chalcedony was determined by Fournier and Rowe (1966) between 125 and 255°C at *Psat*. Fournier (1973) later measured its solubility between 92 and 259°C. Fournier (1977) fit the combined data points from these two studies to an empirical log *K(T)* function. Walther and Helgeson (1977) digitized figures displaying the solubility data of Fournier and Rowe (1966) and Fournier (1973) and similarly fit these data to an empirical log *K(T)* function, which enabled the standard Gibbs free energy of formation of chalcedony to be estimated at 25°C and 1 bar, assuming chalcedony in fact consists solely of microcrystalline quartz (see Section 6.2.4, however). This value was adopted by Helgeson *et al.* (1978), and is incorporated in SPRONS.JNC.

Chalcedony solubilities between 0 and 100°C calculated using SUPCRT and SPRONS.JNC are compared in Fig. C.10 with values calculated using the temperature functions of Walther and Helgeson (1977) and Fournier (1977). The close agreement among solubilities calculated using SPRONS.JNC and the empirical function of Walther and Helgeson (1977) is expected because the same Gibbs free energy for chalcedony constrains both these calculations. Solubilities calculated using the log *K(T)* function of Fournier (1977) are greater

than those calculated using SPRONS.JNC at low temperatures, but converge at higher temperatures as the lower temperature limit of the experimentally calibrated range (92°C) is approached.

6.2.4 Moganite

Heaney and Post (1992) suggest that chalcedony is a mixture of microcrystalline quartz and moganite, a little known silica polymorph. Gislason *et al.* (1997) use the principle of detailed balancing and experimentally determined rates of moganite dissolution to recommend provisional estimates of its standard Gibbs free energy and enthalpy of formation, and standard entropy, at 25°C and 1 bar. The corresponding value of log K for moganite hydrolysis equals -3.14, which corresponds to a dissolved silica concentration of 44 mg kg^{-1}. We have not included these data in SPRONS.JNC, given the provisional nature of these results, but such data should be included in future revisions of this database when more definitive experimental data characterizing moganite's thermodynamic properties become available.

6.2.5 Aqueous speciation

As noted in Section 6.2.1, Shock *et al.* (1989) regressed experimental constants for the quartz solubility reaction using the revised HKF model to retrieve equation-of-state coefficients and the standard partial molal volume, entropy and heat capacity of $SiO_2(aq)$ at 25°C and 1 bar. The retrieved coefficients and properties of $SiO_2(aq)$ are used to generate the curves in Fig. C.6, where it can be seen that calculated and experimental quartz solubilities are in close agreement over a broad range of pressures and temperatures. The thermodynamic properties of $SiO_2(aq)$ may need to be revised, however, to be consistent with recent experimental quartz solubilities determined by Rimstidt (1997) between 0 and 100°C.

Sverjensky *et al.* (1997) regressed experimental equilibrium constants between 0 and 350°C at *Psat* reported by Harman (1928), Roller and Ervin (1940), Greenberg and Price (1957), Schwarz and Muller (1958), Ingri (1959), Lagerstrom (1959), van Lier *et al.* (1960), Volosov *et al.*(1972), Seward (1974) and Busey and Mesmer (1977) for the reaction

$$H_4SiO_4(aq) \rightleftharpoons H_3SiO_4^- + H^+$$

to retrieve thermodynamic properties and HKF equation-of-state coefficients for $H_3SiO_4^-$, using thermodynamic data for $H_4SiO_4(aq)$ from Shock *et al.* (1989). The results are shown in Fig. D.11, where the curve represents values calculated using SUPCRT and SPRONS.JNC and symbols refer to most of the experimental studies noted above. As can be seen, the calculated values agree with experimental counterparts to within about ±0.1 log K units at temperatures greater than 60°C, but the agreement is notably poorer at lower temperatures.

6.3 System Al_2O_3-H_2O

Mineral solubilities and the thermodynamic properties of minerals and aqueous species in this chemical subsystem have been studied intensively over the past 100 years. A thorough review of the experimental studies is summarized by Pokrovskii and Helgeson (1995). As noted in Section 5.2.3, thermodynamic data and equation-of-state coefficients in SPRONS.JNC for minerals and aqueous species comprising this subsystem are from this reference.

6.3.1 Gibbsite

Gibbsite solubilities in dilute acidic solutions, where Al^{3+} is the dominant Al species in solution, have been experimentally determined between 0 and 100°C by Frink and Peech (1962), Kittrick (1966a), Singh (1974), May *et al.* (1979), Bloom and Weaver (1982), Peryea and Kittrick (1988), Nagy and Lasaga (1992) and Palmer and Wesolowski (1992). The standard molal Gibbs free energy and enthalpy of formation, and standard entropy and volume, of gibbsite at the reference temperature and pressure in SPRONS.JNC are from Pokrovskii and Helgeson (1995), who adopted the calorimetric values recommended by Robie *et al.* (1978). The experimental solubilities of gibbsite at 25°C determined by Peryea and Kittrick (1988) and Palmer and Wesolowski (1992) were selected by Pokrovskii and Helgeson (1995) to calculate the standard partial molal Gibbs free energy of formation of Al^{3+}. This value and the corresponding standard partial molal enthalpy of formation from Cox *et al.* (1989) are used to calculate the standard partial molal entropy of Al^{3+} at 25°C and 1 bar. Calculated equilibrium constants using SUPCRT and SPRONS.JNC for the gibbsite solubility reaction between 0 and 100°C at 1 bar are compared with experimental values determined in the studies noted above in Fig. C.11, where it can be seen that the calculated curve is consistent with most of the experimental data. The experimentally determined equilibrium constants determined by Frink and Peech (1962) and Kittrick (1966a) were later questioned by Bloom and Weaver (1982) because the gibbsite used in these older experiments was covered with a reactive surface material suspected to be microcrystalline gibbsite.

Gibbsite solubilities in dilute alkaline solutions, where AlO_2^- [or, equivalently, $Al(OH)_4^-$; see Section 5.2.5] is the dominant Al species in solution, have been experimentally determined between 6.4 and 130°C by Fricke and Jucaitis (1930), Tsirlina (1936), Fulda and Ginsberg (1951), Russell *et al.* (1955), Ikkatai and Okada (1962) Lyapunov *et al.* (1964), Kittrick (1966a), Apps (1970), Berecz and Szita (1970), Packter (1979), Apps and Neil (1990), Wesolowski (1992) and Verdes *et al.* (1992). Pokrovskii and Helgeson (1995) regressed experimental equilibrium constants retrieved from these studies to determine the standard partial molal Gibbs free energy of formation of AlO_2^-. The regression curve generated by Pokrovskii and Helgeson (1995) is compared in Fig. C.12 with experimental equilibrium constants. As can be seen, the calculated curve agrees

closely with most of the experimental values. The same agreement is expected using SUPCRT and SPRONS.JNC because thermodynamic data from Pokrovskii and Helgeson (1995) are adopted in the present study. This is confirmed in Fig. C.13, where equilibrium constants calculated using SUPCRT and SPRONS.JNC for the gibbsite solubility reaction in alkaline solutions are compared with experimental values determined by Apps and Neil (1990), Wesolowski (1992) and Verdes *et al.* (1992).

6.3.2 Boehmite

Experimental data characterizing the solubility of gibbsite at low temperatures in slightly acidic to moderately alkaline solutions, where $AlOH^{2+}$, $Al(OH)_2^+$ and/or $Al(OH)_3(aq)$ are the dominant Al species, are difficult to evaluate because the solubilities are extremely low. At higher temperatures, gibbsite dehydrates to form boehmite (Russell *et al.*, 1955; Khodakovsky *et al.*, 1980). Pokrovskii and Helgeson (1995) therefore evaluate the thermodynamic properties and HKF equation-of-state coefficients for $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3(aq)$ from experimental data on boehmite solubilities at relatively high temperatures (≈ 50 to 300°C).

Experimental solubilities of boehmite [γAlO(OH)] in alkaline solutions (Russell *et al.*, 1955; Kuyunko *et al.*, 1983; Apps *et al.*, 1989; Verdes, 1990; Verdes *et al.*, 1992; Bourcier *et al.*, 1993; Castet *et al.*, 1993) are used by Pokrovskii and Helgeson (1995), together with the thermodynamic properties of AlO_2^- determined as noted above (and properties of $NaAlO_2(aq)$ also determined by these authors), to calculate the standard Gibbs free energy of formation of boehmite at 25°C and 1 bar. Calculations using the thermodynamic data retrieved by Pokrovskii and Helgeson (1995) of equilibrium constants for the boehmite solubility reaction in alkaline solutions are compared with their experimental counterparts in Fig. C.14. As can be seen, the calculated values are closely consistent with the available experimental data between 50 and 300°C at *Psat*, but there is a tendency for the calculations to slightly underpredict the experimentally determined values at temperatures less than about 160°C. Experimental uncertainties are not reported in all cases, but we estimate them conservatively to be about ±0.1 log K units and ±5°C, which is roughly comparable to the size of the plot symbols in this figure.

A similar comparison of calculated and experimental equilibrium constants for the boehmite solubility reaction in acidic solutions (where Al^{3+} is the dominant Al species in solution) is shown in Fig. C.15, where it can be seen that the calculated curve agrees closely with all the experimental data, except equilibrium constants retrieved by Verdes (1990) at 70°C and Verdes *et al.* (1992) at 90°C. The otherwise close correspondence between calculated and experimental values is noteworthy because the thermodynamic properties of Al^{3+} retrieved by Pokrovskii and Helgeson (1995) are independent of the experimental data on boehmite solubilities. The size of the plot symbols in Fig. C.15 is probably

comparable to, or smaller than, experimental uncertainties, which are attributable primarily to the low concentrations of Al^{3+} in the experimental solutions, and to ambiguities in evaluating the activity coefficient of Al^{3+} in solutions with high ionic strength (Pokrovskii and Helgeson, 1995).

As noted above, thermodynamic properties and HKF equation-of-state coefficients for $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3(aq)$ in SPRONS.JNC are based on experimental measurements of boehmite solubility in moderately acidic to moderately alkaline solutions (Kuyunko *et al.*, 1983; Verdes, 1990; Verdes *et al.*, 1992; Bourcier *et al.*, 1993; Castet *et al.*, 1993). Comparisons of calculated and experimental equilibrium constants for the boehmite solubility reaction in systems where $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3(aq)$ are the dominant Al species in solution are depicted in Figs. C.16, C.17 and C.18, respectively, as functions of temperature at *Psat*. As can be seen in these figures, there is considerable scatter in the experimental data. The calculated curves in Figs. C.16 and C.17 are within the combined experimental and computational uncertainty reported by Bourcier *et al.* (1993). The thermodynamic properties and equation-of-state parameters for $AlOH^{2+}$ and $Al(OH)_2^+$ in SPRONS.JNC are therefore consistent with these experimental results, but not with the results of the other experimental measurements noted in the figures. The curve in Fig. C.18 was generated by Pokrovskii and Helgeson (1995) by regression of the experimental values of log K for the indicated reaction, and using supplemental data on corundum solubilities (see below). The curve falls within the scatter of the data, but there is considerable disagreement among the experimental values, and between most of these values and the calculated curve.

The experimental confusion regarding boehmite solubilities in moderately acidic to moderately alkaline solutions, as shown in Figs. C.16 - C.18, can only be resolved by additional experimentation. The thermodynamic properties and HKF coefficients for $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3(aq)$ recommended by Pokrovskii and Helgeson (1995) are provisionally included in SPRONS.JNC pending experimental clarification of boehmite's solubility behavior.

6.3.3 Diaspore

Experimental data on the solubility of diaspore in NaOH solutions between 200 and 350°C at *Psat* (Druzhinina, 1955; Bernshtein and Matsenok, 1965; Wefers, 1967; Chang *et al.*, 1979; Verdes *et al.*, 1992) were regressed by Pokrovskii and Helgeson (1995) using their thermodynamic properties and HKF equation-of-state parameters for AlO_2^- and $NaAlO_2(aq)$ to determine the standard Gibbs free energy of formation of diaspore at 25°C and 1 bar. Diaspore solubilities in dilute NaCl - NaOH solutions between 100 at 325°C and *Psat* are calculated by Pokrovskii and Helgeson (1995) and compared with experimental values determined by Apps *et al.* (1989), which were not considered in the regression procedure. The results (Fig. 9, Pokrovskii and Helgeson, 1995) indicate that the thermodynamic properties of diaspore and AlO_2^- are consistent with the

experimentally determined solubilities.

6.3.4 Corundum

Experimental data from Becker *et al.* (1983) on the solubility of corundum between 2.5 and 6 kb at 670°C were regressed by Pokrovskii and Helgeson (1995) using their retrieved thermodynamic properties and HKF equation-of-state coefficients for AlO_2^-, and thermodynamic properties for corundum at 25°C and 1 bar from Cox *et al.* (1989), to determine the partial molal thermodynamic properties of $Al(OH)_3(aq)$. The retrieved data are used to calculate corundum solubilities between 1 and 2.5 kb at 500°C, and the predicted values are compared with experimental values reported by Morey (1957) and Ragnarsdottir and Walther (1985). The calculated values of log K are within 0.3 log units or less of their experimental counterparts (see Fig. 23. Pokrovskii and Helgeson, 1995).

6.3.5 Aqueous speciation

As noted in Section 6.3.1, partial molal thermodynamic properties and HKF equation-of-state coefficients for Al^{3+} are determined by Pokrovskii and Helgeson (1995) by regression of experimental data on gibbsite solubilities. These properties are used by Pokrovskii and Helgeson (1995), together with potentiometric data on Al^{3+} hydrolysis and boehmite solubility data reported in the literature, to calculate corresponding thermodynamic properties and equation-of-state coefficients for $Al(OH)^{2+}$. Equilibrium constants for the hydrolysis reaction calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts between 0 and 100°C at 1 bar in Fig. D.12, where it can be seen that the calculated constants agree to within 0.1 log K units (approximately equal to the size of plot symbols) with most of the experimental data. Additional experimental data for this reaction between 50 and 250°C reported by Nikolaeva and Tolpygina (1969), Verdes (1990) Castet *et al.* (1993) and Bourcier *et al.* (1993) are considered by Pokrovskii and Helgeson (1995), but are not shown in Fig. D.12. The experimental equilibrium constants determined by Verdes (1990), and the value reported by Bourcier *et al.* (1993) at 250°C, differ by more than 0.1 log K units from the values calculated using SUPCRT and SPRONS.JNC.

The reliability of thermodynamic data and equation-of-state coefficients for the species $Al(OH)_2^+$ and $Al(OH)_3(aq)$ is difficult to assess at low temperatures and pressures, and in near-neutral pH solutions where these species are important, because gibbsite solubilities under such conditions are of the same order of magnitude as the analytical detection limit for dissolved aluminum. Wesolowski and Palmer (1994), however, have developed a general model of aluminum's speciation behavior based on their experimental measurements of gibbsite solubilities at 50°C in 0.1 molal NaCl solutions containing acetate, bistris and tris pH-buffers, which is consistent with earlier studies by these

authors on gibbsite's solubility behavior in acidic and alkaline solutions (Palmer and Wesolowski, 1992; Wesolowski, 1992), and experimental measurements of boehmite solubilities at temperatures between 50 and 250°C at *Psat* (Verdes, 1990; Bourcier *et al.*, 1993; Castet *et al.*, 1993). The model permits calculation of hydrolysis constants for $Al(OH)_2^+$ and $Al(OH)_3(aq)$ at temperatures between 0 and 100°C at 1 bar that are consistent with all these experimental constraints.

These constants are compared with corresponding values calculated using SUPCRT and SPRONS.JNC in Figs. D.13 and D.14, respectively. As can be seen, the hydrolysis constants for $Al(OH)_2^+$ determined by Wesolowski and Palmer (1994) are closely consistent with values calculated using SUPCRT and SPRONS.JNC over this temperature range (Fig. D.13). Hydrolysis constants for $Al(OH)_3(aq)$ from Wesolowski and Palmer (1994), however, agree with the value calculated using SUPCRT and SPRONS.JNC only at 100°C (Fig. D.14). The experimental uncertainty assigned to this constant is less than 0.2 log K units (Wesolowski and Palmer, 1994), which suggests that the discrepancies indicated in the figure are significant. Wesolowski and Palmer (1994) demonstrate that $Al(OH)_3(aq)$ does not contribute significantly to the aqueous speciation of aluminum between 0 and 100°C, however, which suggests that the discrepancies indicated in Fig. D.14 would not generate serious errors in geochemical calculations referring to these conditions.

As noted in Section 6.3.1, the partial molal thermodynamic properties and HKF equation-of-state coefficients for AlO_2^- [i.e., $Al(OH)_4^-$; see Section 5.2.5] are determined by Pokrovskii and Helgeson (1995) by regression of experimental data on gibbsite solubilities. Equilibrium constants for the corresponding hydrolysis reaction calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts between 0 and 100°C at 1 bar in Fig. D.15, where it can be seen that the calculated constants are closely consistent with experimental values determined by Palmer and Wesolowski (1992) and Wesolowski and Palmer (1994), but that a discrepancy between 0.5 and 1 log K units is generated with respect to experimental constants determined by May *et al.* (1979). Palmer and Wesolowski (1992) suggest that the anomalously high solubilities determined by May *et al.* (1979) are due to some form of metastable material or extremely fine-grained gibbsite on the surface of the solid used in those experiments.

6.4 System SiO_2-Al_2O_3-H_2O

6.4.1 Kaolinite

The standard molal Gibbs free energy and enthalpy of formation, and standard entropy and volume, of kaolinite at the reference temperature and pressure in SPRONS.JNC are from Helgeson *et al.* (1978). These authors computed the standard Gibbs free energy of formation of gibbsite from the calorimetric value

of its standard enthalpy of formation determined by Hemingway and Robie (1977), and used these data together with the compositions of mineral assemblages and coexisting interstitial waters in Jamaican bauxite deposits and weathered Hawaiian basalts to calculate the standard Gibbs free energy of formation of kaolinite consistent with the following reaction:

$$\text{kaolinite} + H_2O = 2\ \text{gibbsite} + 2\ SiO_2(aq).$$

Helgeson *et al.* (1978) note that the ΔG°_f for kaolinite derived in this manner is consistent with solubility data from Kittrick (1966b) for coarsely crystalline kaolinite, but that the ΔH°_f of kaolinite is 2510 cal mol^{-1} less negative than the calorimetric value determined by Hemingway and Robie (1977). The approach taken by Helgeson *et al.* (1978) is critically evaluated by Hemingway *et al.* (1982), who conclude that this enthalpy is incorrect.

The thermodynamic properties of kaolinite recommended by Helgeson *et al.* (1978) are therefore questionable. We note, however, that revisions to the thermodynamic properties of minerals and aqueous species in the system Al_2O_3-H_2O recommended by Pokrovskii and Helgeson (1995) are incorporated in SPRONS.JNC, and that the results of recent experimental studies on the solubility of kaolinite are now available. It is therefore possible to evaluate the accuracy of the thermodynamic data for kaolinite adopted in the present study by comparison of equilibrium constants for the kaolinite solubility reaction computed using SUPCRT and SPRONS.JNC with their experimental counterparts.

The solubility of kaolinite in dilute acidic solutions, where Al^{3+} is the dominant Al species in solution, has been experimentally determined at 25 and 80°C by May *et al.* (1986) and Nagy *et al.* (1991). Polzer and Hem (1965), Kittrick (1966b), Reesman and Keller (1968), Huang and Keller (1973), Devidal *et al.* (1996) and Zotov *et al.* (1998) have measured its solubility in alkaline solutions between 25 and 300°C at *Psat*. Equilibrium constants calculated using SUPCRT and SPRONS.JNC for the kaolinite solubility reaction in acidic solutions are compared with the relevant experimental data in Fig. C.19 . The experimental data referring to alkaline conditions from Devidal *et al.* (1996), Kittrick (1966b) and Zotov *et al.* (1998) are recalculated in the present study for conditions in acidic solutions using equilibrium constants for the reaction,

$$Al^{3+} + 4\ H_2O = Al(OH)_4^- + 4\ H^+,$$

based on data for the aqueous aluminum species from Pokrovskii and Helgeson (1995) [see Fig. D.15]. As can be seen, the calculated solubility of kaolinite is in excellent agreement with the experimentally determined values reported by Kittrick (1966b) and May *et al.* (1986) at the reference temperature and pressure. There is considerable scatter, however, in the experimental solubility

data at higher temperatures and pressures. The calculated curve passes within this scatter, but calculated and experimental values at a given temperature differ by as much as 3 orders of magnitude. Zotov *et al.* (1998) evaluate the effects of grain size on kaolinite solubilities. As can be seen in Fig C.19, the solubility increases slightly with decreasing grain size, but the effects are too small to explain the scatter in experimental solubilities shown in this figure.

The equilibrium constant calculated using the data for kaolinite from Helgeson *et al.* (1978) and unrevised data for the Al^{3+} ion from Shock and Helgeson (1988) [inverted solid triangle in Fig. C.19] is nearly two orders of magnitude smaller at 25°C and 1 bar than the corresponding experimental data and the value of the equilibrium constant calculated in the present study (open circle). This suggests that the revised thermodynamic properties for Al^{3+} from Pokrovskii and Helgeson (1995), which are consistent with the thermodynamic properties of gibbsite determined by Robie *et al.* (1978), have resolved some of the confusion concerning kaolinite's solubility behavior.

Equilibrium constants for the kaolinite solubility reaction in alkaline solutions between 25 and 150°C at *Psat* measured by Devidal (1996), and recalculated by these authors based on experimental results from Polzer and Hem (1965), Reesman and Keller (1968) and Huang and Keller (1973), are shown in Fig. C.20. As can be seen, there is also considerable scatter among these experimental data. The curve calculated using SUPCRT and SPRONS.JNC passes within this scatter, but calculated and experimental values differ by as much as 2 orders of magnitude.

Additional experimentation is clearly needed to resolve the discrepancies in kaolinite's solubility behavior at temperatures greater than 25°C. In the meantime, the thermodynamic properties of this mineral determined by Helgeson *et al.* (1978), and included in SPRONS.JNC, are accepted provisionally. It is important to note that questions raised by Hemingway *et al.* (1982) concerning the standard enthalpy of formation of kaolinite calculated by Helgeson *et al.* (1978) are still unresolved. Moreover, because kaolinite is used as a reference phase in simultaneous evaluations of aluminous mineral equilibria by Helgeson *et al.* (1978), the enthalpies of formation of these phases may also be questionable (see Section 4.3.4.3). Unfortunately, the scatter in experimental solubilities depicted in Figs. C.19 and C.20 preclude the use of these data to help clarify the thermodynamic properties of kaolinite.

6.4.2 Kaolinite, boehmite, diaspore, andalusite and pyrophyllite

Equilibria among various minerals in the Al_2O_3-SiO_2-H_2O system are examined in a series of experiments at high temperatures and pressures by Hemley *et al.* (1980), Huang (1993) and Zotov *et al.* (1998). The following diagrams document comparisons of equilibrium constants calculated using SUPCRT and SPRONS.JNC for the investigated reactions among the indicated minerals and

an aqueous phase:

- Fig C.21; kaolinite-boehmite,
- Fig C.22; kaolinite-diaspore,
- Fig C.23; pyrophyllite-kaolinite,
- Fig C.24; pyrophyllite-diaspore,
- Fig C.25; pyrophyllite-andalusite,
- Fig C.26; andalusite-corundum, and
- Fig C.27; andalusite-diaspore.

The equilibrium activity of $SiO_2(aq)$ at the experimental pressures and temperatures determines the value of the equilibrium constant for all these reactions. Silica activity is closely approximated by the total molality of dissolved silica because the solutions are sufficiently dilute and acidic that the concentrations of other silica species would be vanishingly small under such conditions, and because $SiO_2(aq)$ is uncharged. Dissolved silica is determined with a precision of ±5% of the measured value in the experiments of Hemley *et al.* (1980), and temperature is accurate to ±5°C. Similar experimental uncertainties are assumed here for the experimental results reported by Huang (1993) and Zotov *et al.* (1998). As can be seen in these figures, the calculated equilibrium constants agree in some cases to within a few tenths of a log K unit with their experimental counterparts (Figs. C.23, C.24 and C.25), but in other cases discrepancies on the order of 0.5 to 1 log K units are apparent (Figs. C.21, C.22, C.26 and C.27).

Figures C.21-C.23 and C.25-C.27 are similar to Fig. 47(a-d) of Helgeson *et al.* (1978), who compared calculated equilibrium constants with unpublished experimental results from J. J. Hemley, which presumably are the same results later reported by Hemley *et al.* (1980). Comparison of our figures with Fig. 47 of Helgeson *et al.* (1978) indicates that our calculated curves in Figs. C.21, C.22, C.26 and C.27 are offset slightly from those generated by Helgeson *et al.* (1978), and that the latter curves agree significantly better with the experimental data. We note that the reactions considered in Figs. C.21, C.22, C.26 and C.27 involve minerals (boehmite, diaspore and corundum) whose thermodynamic properties are revised by Pokrovskii and Helgeson (1995) from values originally retrieved by Helgeson *et al.* (1978), based, in part, on the experimental results portrayed in their Fig. 47. This suggests that additional work may be needed to reconcile the discrepancies documented in Figs. C.21, C.22, C.26 and C.27 such that the resulting calculated curves are consistent with the experimental data of Hemley *et al.* (1980), as well as with the generally lower temperature and pressure experimental constraints evaluated by Pokrovskii and Helgeson (1995).

6.5 System Na_2O-K_2O-SiO_2-Al_2O_3-H_2O

Equilibria among various minerals in this system are examined in a series of experiments, generally at high temperatures and pressures, by Montoya and

Hemley (1975), Sverjensky *et al.* (1991), Burch (1993), Murphy *et al.* (1996) and Wilkin and Barnes (1998). The following diagrams document comparisons of equilibrium constants calculated using SUPCRT and SPRONS.JNC for the investigated reactions among the indicated minerals and an aqueous solution:

- Fig C.28; K-feldspar-muscovite-quartz (0.5 kb),
- Fig C.29; K-feldspar-muscovite-quartz (1.0 kb),
- Fig C.30; K-feldspar-muscovite-quartz (2.0 kb),
- Fig C.31; muscovite-andalusite-quartz,
- Fig C.32; muscovite-kaolinite,
- Fig C.33; muscovite-quartz-pyrophyllite,
- Fig C.34; albite-paragonite-quartz,
- Fig C.35; albite, and
- Fig C.36; analcime.

Equilibria among K-bearing minerals in this system at temperatures between 300 and 600°C and pressures from 0.5 to 2 kb were determined experimentally by Sverjensky *et al.* (1991). The results of this study are consistent with earlier investigations by Hemley (1959), Hemley and Jones (1964) and Montoya and Hemley (1975), which therefore are not considered further in the present study. Sverjensky *et al.* (1991) evaluated the thermodynamic properties of the following reactions (structural formulas of minerals as noted in Appendix A):

- 1.5 K-feldspar + $H^+ \rightleftharpoons$ 0.5 muscovite + 3 quartz + K^+,
- K-feldspar + $H^+ \rightleftharpoons$ 0.5 andalusite + 2.5 quartz + K^+,
- muscovite + H^+ + 1.5 $H_2O \rightleftharpoons$ 1.5 kaolinite + K^+
- muscovite + H^+ + 3 quartz $\rightleftharpoons$ 1.5 pyrophyllite + K^+, and
- muscovite + $H^+ \rightleftharpoons$ 1.5 andalusite + 1.5 quartz + 1.5 H_2O + K^+,

by measuring the total analytical concentrations of K^+ and H^+ in quenched solutions equilibrated with the mineral reactants and products. It was assumed as a first approximation that the ratio of these concentrations, $m_{t,K} / m_{t,H}$ (where m denotes molality), defines the equilibrium constant because the activity coefficients for K^+ and H^+ are approximately equal (and therefore cancel) and because the presence of other K- and H-bearing aqueous species are assumed to be present in negligible concentrations. Reactions analogous to the above were also considered by these authors to account for $HCl(aq)$ and $KCl(aq)$ complex formation, which it was assumed becomes significant at temperatures greater than about 300°C. Sverjensky *et al.* (1991) retrieved thermodynamic properties and HKF equation-of-state coefficients for $HCl(aq)$ from the results of their experiments on K-feldspar-muscovite-quartz equilibrium, but these data are not included in SPRONS.JNC for reasons discussed in Section 5.2.3.

Equilibria among Na-bearing minerals in this system were determined experimentally by Montoya and Hemley (1975), Burch (1993), Murphy *et al.* (1996) and Wilkin and Barnes (1998). Montoya and Hemley (1975) used the

same experimental approach as Hemley (1959), Hemley and Jones (1964) and Sverjensky *et al.* (1991) to evaluate the thermodynamic properties of the following reactions between 300 and 500°C at 1 kb (structural formulas of minerals as noted in Appendix A):

- 3 albite + 2 H^+ ⇌ paragonite + 6 quartz + 2 Na^+,
- 2 paragonite + 2 H^+ ⇌ 3 kaolinite + 2 Na^+,
- 2 paragonite + 6 quartz + 2 H^+ ⇌ 3 pyrophyllite + 2 Na^+, and
- 2 paragonite + 2 H^+ ⇌ 3 andalusite + 3 quartz + 2 Na^+,

by measuring the total analytical concentrations of Na^+ and H^+ in quenched solutions equilibrated with the mineral reactants and products. It was assumed that the ratio of these concentrations, $m_{t,\,Na}/m_{t,\,H}$, defines the equilibrium constant. Burch (1993; see also Burch *et al.*, 1993) determined steady-state dissolution rates of albite at 80°C and pH 8.8 using a continuously-stirred flow-through reactor. The solubility of albite under these conditions was estimated from solution compositions sampled at steady-state in the dissolution and precipitation experiments nearest to equilibrium, as well as from near-equilibrium batch experiments. Murphy *et al.* (1996) and Wilkin and Barnes (1998) investigated the solubility of analcime. The experiments carried out by Murphy *et al.* (1996) reacted analcime (from Mt. St. Hilaire, Quebec) at 25°C in 0.1 molal NaCl - 0.01 molal $NaHCO_3$ solutions that were continuously equilibrated with atmospheric $CO_2(g)$. Wilkin and Barnes (1998) reacted analcime (from Mt. St. Hilaire, Quebec and Wikieup, Arizona) in doubly distilled H_2O purged of CO_2 and O_2 in rocking autoclaves from 25 to 300°C at *Psat*.

6.5.1 K-feldspar, muscovite, quartz

Equilibrium constants for the reaction

1.5 K-feldspar + H^+ ⇌ 0.5 muscovite + 3 quartz + K^+,

between 300 and 600°C at 0.5, 1 and 2 kb calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts determined by Sverjensky *et al.* (1991) in Figs. C.28-C.30, respectively. Two calculated curves are shown in each figure representing solutions in which K^+ and H^+, or $KCl(aq)$ and $HCl(aq)$, are assumed to be the dominant species in solution (reactions "1" and "2" as labelled in the figures, respectively). Experimental uncertainties (±0.15 log K units) are estimated by Sverjensky *et al.* (1991). As can be seen, most of the experimentally determined equilibrium constants are consistent with calculated values for reaction 1 at 300°C, or reaction 2 at temperatures greater than 300°C. Discrepancies significantly exceeding experimental uncertainties are apparent, however, for the experimental datum at 500°C and 0.5 kb (Fig. C.28), and the experimental data at temperatures greater than 300°C at 2 kb (Fig. C.30).

6.5.2 Muscovite, andalusite, quartz

Equilibrium constants calculated using SUPCRT and SPRONS.JNC for the reaction

$$\text{muscovite} + HCl(aq) \rightleftharpoons 1.5\ \text{andalusite} + 1.5\ \text{quartz} + 1.5\ H_2O + KCl(aq),$$

between 0 and 600°C at 1 and 2 kb are compared with their experimental counterparts determined by Sverjensky *et al.* (1991) in Fig. C.31. Experimental uncertainties (±0.15 log K units) are omitted in this figure for clarity. As can be seen, the experimentally determined equilibrium constants are generally consistent with the calculated curves, but discrepancies slightly exceeding experimental uncertainties are apparent.

6.5.3 Muscovite, kaolinite

Equilibrium constants calculated using SUPCRT and SPRONS.JNC for the reaction

$$\text{muscovite} + H^+ + 1.5\ H_2O \rightleftharpoons 1.5\ \text{kaolinite} + K^+,$$

between 0 and 350°C at 1 kb are compared in Fig. C.32 with the experimental value at 300°C determined by Sverjensky *et al.* (1991). The calculated curve is consistent with this value and its associated uncertainty (±0.15 log K units).

6.5.4 Muscovite, quartz, pyrophyllite

Equilibrium constants for the reaction

$$\text{muscovite} + H^+ + 3\ \text{quartz} \rightleftharpoons 1.5\ \text{pyrophyllite} + K^+,$$

between 0 and 400°C at 1 kb calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts determined by Sverjensky *et al.* (1991) in Fig. C.31. The two calculated curves in this figure represent solutions in which K^+ and H^+, or $KCl(aq)$ and $HCl(aq)$, are assumed to be the dominant species in solution (reactions "1" and "2" as labelled in the figure, respectively). As can be seen, the calculated curve for reaction 1 is consistent with the experimental data and their associated uncertainties (±0.15 log K units). The calculated curve for reaction 2 is inconsistent with these data. Complex formation of $KCl(aq)$ and $HCl(aq)$ is apparently unimportant at temperatures below about 300°C, although the exact temperature and pressure at which this transition in complexing behavior occurs is uncertain (Sverjensky *et al.*, 1991).

6.5.5 Albite, paragonite, kaolinite, pyrophyllite, andalusite, quartz

Helgeson *et al.* (1978) compare calculated equilibrium constants for the

reactions:

3 albite + 2 H^+ ⇌ paragonite + 6 quartz + 2 Na^+,
2 paragonite + 2 H^+ ⇌ 3 kaolinite + 2 Na^+,
2 paragonite + 6 quartz + 2 H^+ ⇌ 3 pyrophyllite + 2 Na^+, and
2 paragonite + 2 H^+ ⇌ 3 andalusite + 3 quartz + 2 Na^+

with their respective experimental counterparts determined by Montoya and Hemley (1975) (see Figs. 68a-d of Helgeson *et al.*, 1978, respectively). Calculated equilibrium constants are closely consistent with all the experimental values, except for the last reaction above where discrepancies on the order of 0.5 log K units are evident. Thermodynamic properties and equation-of-state parameters for H^+ and Na^+ from Helgeson and Kirkham (1976), and standard molal thermodynamic properties for the minerals in these reactions determined by Helgeson *et al.* (1978), were used in the calculations. These data are incorporated in SPRONS.JNC, and similar agreement between equilibrium constants computed using this database and experimental values determined by Montoya and Hemley (1975) is therefore expected. This is confirmed in Fig. C.34, which is similar to Fig 68a of Helgeson *et al.* (1978).

6.5.6 Albite

The equilibrium constant determined by Burch (1993) for the albite solubility reaction at 80°C is compared with values calculated using SUPCRT and SPRONS.JNC in Fig. C.35. The state of order/disorder of the albite used in the experiments is unknown, and two calculated curves are therefore shown representing equilibrium with respect to high albite (completely disordered) and low albite (completely ordered). As can be seen, the experimental solubility is nearly an order of magnitude more soluble than that calculated for the disordered phase, and nearly two orders of magnitude more soluble than that calculated for the ordered phase. Burch (1993) calculated the solubility of albite from steady-state solution compositions observed in dissolution and precipitation experiments that were "nearest" equilibrium. The equilibrium constant determined in this study is thus an approximation, but it is unclear how close the approximate value is to the actual equilibrium value.

6.5.7 Analcime

Equilibrium constants for the reaction

$$(NaAl)_{1+x}Si_{2-x}O_6 \cdot nH_2O \rightleftharpoons$$

$$(1+x)Na^+ + (1+x)Al(OH)_4^- + (2-x)SiO_2(aq) + [n-2(1+x)]H_2O$$

between 0 and 300°C at *Psat* calculated using SUPCRT and SPRONS.JNC (x = 1, n = 1) are compared with their experimental counterparts determined by

Murphy *et al.* (1996) [Mt. St. Hilaire analcime: x = 1.05, n = 1] and Wilkin and Barnes (1998) [Mt. St. Hilaire analcime: x = 1, n = 1; Wikieup analcime: x = 0.85, n = 1] in Fig. C.36. As can be seen, the experimental values determined by Wilkin and Barnes (1998) for the Mt. St. Hilaire sample are remarkably consistent with calculated counterparts over the full range of temperatures considered, taking into account the experimental uncertainties determined by these authors. Significant discrepancies between calculated and observed solubilities are evident for the Wikieup analcime, however, presumably because this phase is significantly enriched in Si and deficient in Al relative to the idealized composition assumed for analcime in SPRONS.JNC. The solubility of Mt. St. Hilaire analcime determined by Murphy *et al.* (1996) at 25°C is more than an order of magnitude greater than that determined by Wilkin and Barnes (1998) and calculated using SUPCRT and SPRONS.JNC. The sample used by Murphy *et al.* (1996) is slightly richer in Si and poorer in Al than that used by Wilkin and Barnes (1998), but it is unlikely that this can explain the discrepancy between these experimental equilibrium constants.

6.6 System MgO-SiO_2-H_2O

Equilibrium relations among various minerals in this system have been characterized experimentally by Christ *et al.* (1973) and Hemley *et al.* (1977a, b). The latter study evaluated the thermodynamic properties of the following reactions (structural formulas of minerals as noted in Appendix A):

- 2 talc $\rightleftharpoons$ 3 forsterite + 5 $SiO_2(aq)$ + 2 H_2O,
- talc + H_2O $\rightleftharpoons$ chrysotile + 2 $SiO_2(aq)$
- 16 talc + 15 H_2O $\rightleftharpoons$ antigorite + 30 $SiO_2(aq)$,
- 7 talc $\rightleftharpoons$ 3 anthophyllite + 4 $SiO_2(aq)$ + 4 H_2O,
- talc $\rightleftharpoons$ 3 enstatite + $SiO_2(aq)$ + H_2O,
- 2 anthophyllite $\rightleftharpoons$ 7 forsterite + 9 $SiO_2(aq)$ + 2 H_2O,
- anthophyllite $\rightleftharpoons$ 7 enstatite + $SiO_2(aq)$ + H_2O, and
- 2 enstatite $\rightleftharpoons$ forsterite + SiO_2(aq),

at relatively high temperatures and pressures by measuring the total analytical concentrations of $SiO_2(aq)$ in quenched solutions equilibrated with the respective mineral reactants and products. The equilibrium activity of $SiO_2(aq)$ (which is approximately equal to its molality, see Section 6.4.2) determines the value of the equilibrium constant for all these reactions. Christ *et al.* (1973) similarly evaluated the thermodynamic properties of the following reaction (structural formula of sepiolite as noted in Appendix A):

- sepiolite + 8 H^+ $\rightleftharpoons$ 4 Mg^{2+} + 6 $SiO_2(aq)$ + 11 H_2O,

between 50 and 90°C at 1 bar by analyzing equilibrated solutions for pH and for total concentrations of Mg^{2+} and $SiO_2(aq)$ to estimate corresponding activities

of the aqueous reactants and products using the Debye-Hückel equation (e.g., Garrels and Christ, 1965).

Helgeson *et al.* (1978) compare calculated equilibrium constants with the experimentally determined values for all the above reactions (Figs. 27-30 and Fig. 34 of Helgeson *et al.*, 1978, respectively). Calculated equilibrium constants agree closely with all the experimental data. Thermodynamic properties and equation-of-state parameters for Mg^{2+} from Helgeson and Kirkham (1976), similar data for $SiO_2(aq)$ from Walther and Helgeson (1977), and standard molal thermodynamic properties for the minerals in these reactions from Helgeson *et al.* (1978) were used in the calculations. Most of these data are incorporated in SPRONS.JNC, but thermodynamic properties and equation-of-state coefficients for $SiO_2(aq)$ are revised by Shock *et al.* (1989) from those determined by Walther and Helgeson (1977), as noted in Section 6.2.1. The revisions are relatively minor, however, and are not expected to significantly alter the consistency among experimental and calculated equilibrium constants for the minerals in this system, as documented by Helgeson *et al.* (1978). This is confirmed in Figs. C.37 and C.38, which exhibit the same close correspondence among calculated and experimental results as Figs. 27 and 34, respectively, of Helgeson *et al.* (1978).

6.6.1 Aqueous speciation

Experimental data for the hydrolysis of Mg^{2+} between 0 and 150°C at *Psat* are compared in Fig. D.16 with equilibrium constants calculated for this reaction using SUPCRT and SPRONS.JNC. As noted by Shock *et al.* (1997a), the close agreement among most of the experimental data and the calculated curve is remarkable because the HKF equation-of-state parameters for $MgOH^+$ are estimated independently of experimental constraints, using the correlation algorithms developed by these authors.

6.7 System CaO-SiO_2-Al_2O_3-H_2O

There are few experimental data characterizing the solubilities of minerals in this system. Roselle and Baumgartner (1995) measured the solubility of the assemblage:

- anorthite + 2 $HCl(aq)$ = $CaCl_2(aq)$ + andalusite + quartz + H_2O

in supercritical chloride solutions from 400 to 600°C at 2 kb. Equilibrium constants retrieved by these authors are compared with equilibrium constants calculated using SUPCRT and SPRONS.JNC in Fig. C.39. As can be seen, the calculated curve is consistent with the experimental data at 500 and 600°C, but the discrepancy at 400°C is significantly greater than the experimental uncertainty.

6.7.1 Aqueous speciation

Experimental data for the hydrolysis of Ca^{2+} between 0 and 450°C at *Psat* and at 0.5 and 1 kb are compared in Fig. D.17 with equilibrium constants calculated for this reaction using SUPCRT and SPRONS.JNC. As can be seen, the experimental data are closely consistent with the calculated curve over this range of temperatures and pressures. This supports the validity of correlations developed by Shock *et al.* (1997a), because equation-of-state coefficients for $CaOH^+$ were estimated using these correlations independently of the experimental data shown in the figure.

6.8 System CaO-MgO-FeO-BaO-SrO-H_2O-CO_2

Plummer and Busenberg (1982), Busenberg *et al.* (1984) and Busenberg and Plummer (1986) carried out a series of experiments between 0 and 91°C at 1 bar to investigate mineral-solution and aqueous-speciation equilibria in this system. These authors determined the solubility of aragonite, calcite, vaterite, strontianite and witherite over this temperature range, and corresponding ion-pair formation constants for $CaHCO_3^+$, $CaCO_3(aq)$, $SrHCO_3^+$, $SrCO_3(aq)$, $BaHCO_3^+$ and $BaCO_3(aq)$ that are internally consistent with the solubility data. The experimental data and thermodynamic properties retrieved from them by Plummer and Busenberg (1982), Busenberg *et al.* (1984) and Busenberg and Plummer (1986) supersede numerous earlier investigations, which are critically evaluated for the CaO-CO_2-H_2O system by Langmuir (1968) and Jacobsen and Langmuir (1974), summarized by Busenberg *et al.* (1984) for the SrO-CO_2-H_2O system, and summarized by Busenberg and Plummer (1986) for the BaO-CO_2-H_2O system. The comprehensive experimental investigations of this chemical system by Plummer and Busenberg (1982), Busenberg *et al.* (1984) and Busenberg and Plummer (1986) did not include Fe, and corresponding thermodynamic properties of siderite and ferrous-carbonate complexes.

As noted in Section 5.2.2, Johnson *et al.* (1991) corrected the standard Gibbs free energy and enthalpy of formation of calcite and aragonite in their SPRONS database (SPRONS92.DAT) to be consistent with the solubility data for these phases determined by Plummer and Busenberg (1982). The data for strontianite and witherite were unrevised, however, and are therefore unconstrained by the experimental solubilities determined by Busenberg *et al.* (1984) and Busenberg and Plummer (1986), respectively. The thermodynamic properties of strontianite and witherite in SPRONS.JNC are thus the original data from Helgeson *et al.* (1978), which are constrained solely by calorimetric measurements (Table 9 of Helgeson *et al.*, 1978). The thermodynamic properties of siderite are similarly constrained only by calorimetric data. Helgeson *et al.* (1978) did not compare these calorimetric-based properties with other experimental observations, and notes that they are therefore subject to greater uncertainty.

Experimental data reported by Plummer and Busenberg (1982), Busenberg *et al.* (1984) and Busenberg and Plummer (1986) were regressed by Sverjensky *et al.* (1997) to determine partial molal thermodynamic properties and HKF equation-of-state coefficients for $CaCO_3(aq)$, $SrCO_3(aq)$ and $BaCO_3(aq)$. These data are included in SPRONS.JNC. Similar data for the $CaHCO_3^+$ ion-pair in this database are attributed by Johnson *et al.* (1991) to unpublished work from Sverjensky (ref. 5, Appendix A), but these data are not documented by Sverjensky *et al.* (1997). Data for the $SrHCO_3^+$ and $BaHCO_3^+$ ion pairs also were not evaluated by these authors, and are not included in SPRONS.JNC.

6.8.1 Aragonite and calcite

Equilibrium constants for the reactions

$$\text{aragonite} \rightleftharpoons Ca^{2+} + CO_3^{2-}, \text{ and}$$
$$\text{calcite} \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

between 0 and 100°C at 1 bar calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts determined by Plummer and Busenberg (1982) in Figs. C.40 and C.41, respectively. As can be seen, the calculated curves agree closely with all the experimental data. This is expected because these experimental data partially constrain the standard molal thermodynamic properties of aragonite and calcite in SPRONS.JNC.

6.8.2 Strontianite

Equilibrium constants for the reaction

$$\text{strontianite} \rightleftharpoons Sr^{2+} + CO_3^{2-},$$

between 0 and 100°C at 1 bar calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts determined by Busenberg *et al.* (1984) in Fig. C.42. The calculated curve underpredicts the experimentally determined solubility product of strontianite by more than an order of magnitude over this temperature range. As noted above, the thermodynamic properties of strontianite in SPRONS.JNC are constrained only by calorimetric measurements. The discrepancies in Fig. C.42 suggest these data should be revised to be consistent with both the calorimetric constraints and solubility data that are now available.

6.8.3 Witherite

Equilibrium constants for the reaction

$$\text{witherite} \rightleftharpoons Ba^{2+} + CO_3^{2-},$$

between 0 and 100°C at 1 bar calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts determined by Busenberg and Plummer (1986) in Fig. C.43. The calculated curve severely underpredicts the experimentally determined solubility product of witherite by 3 to 4 orders of magnitude over this temperature range. As noted above, the thermodynamic properties of witherite in SPRONS.JNC are constrained by calorimetric measurements alone. The discrepancies in Fig. C.43 suggest these data should be revised to be consistent with the available calorimetric and solubility data.

6.8.4 Siderite

Equilibrium constants for the reaction

$$\text{siderite} \rightleftharpoons Fe^{2+} + CO_3^{2-},$$

between 0 and 100°C at 1 bar calculated using SUPCRT and SPRONS.JNC are compared with experimentally determined solubility products at 25°C in Fig. C.44. As can be seen, the curve falls within the scatter of the data, but there is considerable disagreement among the experimental values, and between most of these values and the calculated curve. Additional experimentation is needed to resolve experimental discrepancies in the solubility product of siderite at 25°C and at higher temperatures to better constrain siderite's standard molal thermodynamic properties.

6.8.5 Aqueous speciation

Dissociation constants for the ion pairs $CaHCO_3^+$, $CaCO_3(aq)$, $SrCO_3(aq)$ and $BaCO_3(aq)$ calculated using SUPCRT and SPRONS.JNC between 0 and 100°C are compared with experimentally determined dissociation constants in Figs. D.18-D.21, respectively. As can be seen in Fig. D.18, calculated dissociation constants for $CaHCO_3^+$ are reasonably consistent with experimental values determined by Plummer and Busenberg (1982), but discrepancies slightly exceeding experimental uncertainties are apparent at temperatures less than 65°C. Calculated dissociation constants for $CaCO_3(aq)$, shown in Fig. D.19, are closely consistent with all but one of the experimentally determined values reported by Plummer and Busenberg (1982), as is expected because these experimental data were regressed by Sverjensky *et al.* (1997) to retrieve the partial molal thermodynamic properties and equation-of-state coefficients for this species. Experimental data determined by Reardon and Langmuir (1974) also lie within 0.1 to 0.2 log K units of calculated equilibrium constants for this reaction. The excellent agreement among calculated and experimental dissociation constants for $SrCO_3(aq)$ and $BaCO_3(aq)$, as can be seen in Figs. D.20 and D.21, respectively, is similarly due to the fact that experimental data for $SrCO_3(aq)$ dissociation from Busenberg *et al.* (1984) and for $BaCO_3(aq)$ dissociation from Busenberg and Plummer (1986) were used in the regression calculations by Sverjensky *et al.* (1997) to retrieve the thermodynamic properties

of these species. Experimental data on the dissociation constant of $SrCO_3(aq)$ at 25°C from Hasegawa *et al.* (1970) are clearly discrepant with respect to the calculated curve in Fig. D.20, and the experimental value determined by Busenberg *et al.* (1984). Experimental data on the dissociation constant of $BaCO_3(aq)$ at 25°C from Benes and Selecka (1973) are similarly discrepant with respect to the calculated curve in Fig. D.21, and the experimental value from Busenberg and Plummer (1986). The experimentally determined dissociation constant for $BaCO_3(aq)$ reported by Palmer and Van Eldik (1983) agrees closely with that determined by Busenberg and Plummer (1986).

Sverjensky *et al.* (1997) regressed experimental data from Reardon and Langmuir (1974) and Siebert and Hostettler (1977) on the dissociation constant of $MgCO_3(aq)$ between 10 and 90°C to retrieve partial molal thermodynamic properties and equation-of-state coefficients for this species. As can be seen in Fig. D.22, equilibrium constants for this reaction calculated using SUPCRT and SPRONS.JNC agree closely with the data from Siebert and Hostettler (1997), and lie within 0.2 log K units of the values determined by Reardon and Langmuir (1974). There is considerable scatter among the other experimental data at 25°C, however.

Correlation algorithms developed by Shock *et al.* (1997a) were used by these authors to predict the standard partial molal properties of $SrOH^+$. Association constants for this species calculated using SUPCRT and SPRONS.JNC are compared in Fig. D.23 with values determined experimentally between 5 and 50°C by Gimblett and Monk (1954). As can be seen, the calculated curve is closely consistent with all the experimental data, which supports the validity of the correlation approach used by Shock *et al.* (1997a).

6.9 System CaO-BaO-SrO-SO_3-H_2O

6.9.1 Anhydrite

The solubility of anhydrite between 0 and 350°C at *Psat* determined experimentally by Yeatts and Marshall (1969) is compared in Fig. C.45 with calculated solubilities using SUPCRT and SPRONS.JNC. The standard molal thermodynamic properties of anhydrite in SPRONS.JNC are from Helgeson *et al.* (1978). Sverjensky *et al.* (1997) regressed the solubility data of Yeatts and Marshall (1969) to retrieve the standard partial molal thermodynamic properties and HKF equation-of-state coefficients for the $CaSO_4(aq)$ ion pair, and this is reflected by the close agreement among calculated and experimental solubilities shown in Fig. C.45.

6.9.2 Barite

The solubilities of barite between 0 and 300°C at *Psat* determined experimental-

ly by Blount (1977), Strübel (1967), Melcher (1910), Templeton (1960), Malinin *et al.* (1969), Felmy *et al.* (1990) and Jiang (1996) are compared with equilibrium constants for this reaction calculated using SUPCRT and SPRONS.JNC in Fig. C.46. The standard molal thermodynamic properties of barite in SPRONS.JNC are from Helgeson *et al.* (1978), and are based solely on calorimetric measurements. The partial molal thermodynamic properties and equation-of-state coefficients of Ba^{2+} and SO_4^{2-} are from Shock and Helgeson (1988), and were retrieved independently of the solubility data for barite. The close correspondence among most of the calculated and experimental solubilities for this phase is therefore noteworthy, because it constitutes independent confirmation that the thermodynamic data for barite and the aqueous ions Ba^{2+} and SO_4^{2-} are reliable over this temperature range. Experimental equilibrium constants for this reaction reported by Strübel (1967) are clearly discrepant with respect to calculated counterparts and the other experimental data.

6.9.3 Celestite

The solubility of celestite at 25°C determined by Felmy *et al.* (1990) is compared with the equilibrium constant for this reaction calculated using SUPCRT and SPRONS.JNC in Fig. C.47. The standard molal thermodynamic properties of celestite in SPRONS.JNC are from Helgeson *et al.* (1978), and are constrained solely by calorimetric measurements. The partial molal thermodynamic properties and equation-of-state coefficients of Sr^{2+} and SO_4^{2-} are from Shock and Helgeson (1988), and were retrieved independently of the solubility data for celestite. As can be seen, this mineral is calculated to be nearly an order of magnitude more soluble at 25°C than measured by Felmy *et al.* (1990).

6.10 System FeO-S*(rh)*-H_2O-HCl

6.10.1 Pyrite

The solubility of pyrite in chloride solutions has been determined experimentally by Crerar *et al.* (1978) between 200 and 350°C at *Psat*. Calculated pyrite solubilities using SUPCRT and SPRONS.JNC in solutions equilibrated with $FeCl^+$ or $FeCl_2(aq)$ are compared with experimental values determined by Crerar *et al.* (1978) in Figs. C.48 and C.49, respectively. The thermodynamic properties of pyrite in SPRONS.JNC are constrained only by calorimetric data (Helgeson *et al.*, 1978). Sverjensky *et al.* (1997) regressed experimental dissociation constants for $FeCl^+$ from Heinrich and Seward (1990) and Palmer and Hyde (1993), and total dissociation constants for $FeCl_2(aq)$ reported by Wood and Crerar (1985), Heinrich and Seward (1990) and Fein *et al.* (1992), to retrieve the standard partial molal thermodynamic properties and HKF equation-of-state coefficients for these species. The close correspondence among the calculated and experimental solubilities for pyrite shown in Figs. C.48 and C.49 constitutes independent confirmation that the thermodynamic data for

pyrite and both ferrous chloride complexes are reliable over this temperature range.

6.10.2 Pyrrhotite

Crerar *et al.* (1978) measured the solubility of pyrrhotite in chloride solutions between 200 and 350°C at *Psat*. Berner (1967) also measured the solubility of a sample of nearly stoichiometric pyrrhotite ($Fe_{0.98}S$) at 25°C and 1 bar in dilute solutions equilibrated with $H_2S(g)$. Pyrrhotite solubilities calculated using SUPCRT and SPRONS.JNC are compared with the experimental value determined by Berner (1967) in Fig. C.50, and with solubilities measured by Crerar *et al.* (1978) in Figs. C.51 and C.52. The thermodynamic properties of pyrrhotite in SPRONS.JNC are constrained only by calorimetric data (Helgeson *et al.*, 1978). The standard partial molal thermodynamic properties and HKF equation-of-state coefficients for Fe^{2+} were revised from values recommended by Shock and Helgeson (1988) by Shock *et al.* (1997a).The standard partial molal thermodynamic properties and HKF equation-of-state coefficients for $FeCl^+$ and $FeCl_2(aq)$ were determined by Sverjensky *et al.* (1997), as noted above. As can be seen in Fig. C.50, pyrrhotite is calculated to be more than an order of magnitude more soluble at 25°C than measured by Berner (1967). A similar discrepancy is noted in Fig. C.51 for the solubility at 200°C, but better agreement is apparent in this figure, and in Fig. C.52, for the solubilities measured at higher temperatures. Additional experimentation is needed to better constrain the solubility behavior of pyrrhotite at temperatures between 0 and 300°C.

6.10.3 Magnetite

Two experimental datasets characterizing the solubility of magnetite and relative stabilities of ferrous hydroxide complexes between 25 and 300°C at *Psat* are reported by Sweeton and Baes (1970) and Tremaine and LeBlanc (1980). Both sets of data were obtained from measurements of magnetite solubility in solutions of varying pH, but equilibrium constants derived from these data for the hydroxide complexes differ by as much as two log units. Shock *et al.* (1997a) note that it is not evident that the dataset of Sweeton and Baes (1970) is intrinsically more accurate than that of Tremaine and LeBlanc (1980), but nevertheless select the data of Sweeton and Baes (1970) to retrieve by regression the partial molal thermodynamic properties and equation-of-state coefficients for ferrous hydroxide complexes that are incorporated in SPRONS.JNC. The rationale for this decision is that retrieved parameters, such as the standard partial molal entropies of these complexes, are more consistent with empirical correlations constructed by Shock *et al.* (1997a) than are similar parameters retrieved from the dataset of Tremaine and LeBlanc (1980). Calculated magnetite solubilities using SUPCRT and SPRONS.JNC between 0 and 300°C at *Psat* in solutions equilibrated with Fe^{2+}, $FeOH^+$, $Fe(OH)_2(aq)$ and $Fe(OH)_3^-$ are compared with their experimental counterparts determined by Sweeton and

Baes (1970) in Fig. C.53. As can be seen, the agreement between calculated and experimental equilibrium constants is excellent over this temperature range, as expected.

6.10.4 Aqueous speciation

Association constants for the first, second and third hydrolysis constants of Fe(II) calculated using SUPCRT and SPRONS.JNC between 0 and 350°C at *Psat* are compared with their experimental counterparts measured by Sweeton and Baes (1970) and Tremaine and LeBlanc (1980) in Figs. D.24, D.25 and D.26, respectively. As expected, there is close agreement between calculated values and the experimental constants determined by Sweeton and Baes (1970) because these experimental data constrain the partial molal thermodynamic properties and equation-of-state coefficients of the ferrous hydroxide complexes in SPRONS.JNC. Significant discrepancies are evident, however, between calculated association constants and the experimental values determined by Tremaine and LeBlanc (1980). As noted above, there is no reason to believe the experimental data of Sweeton and Baes (1970) are more accurate than those of Tremaine and LeBlanc (1980), other than the fact that thermodynamic properties of the hydroxide complexes retrieved from the former dataset are more consistent with correlations developed by Shock *et al.* (1997a) than are the latter. Additional experimentation is needed to resolve the discrepancies between these two experimental datasets.

Sverjensky *et al.* (1997) document comparisons of experimental and calculated dissociation constants for $FeCl^+$ and $FeCl_2(aq)$ over a wide range of temperatures and pressures (Figs. 4 and 17, respectively, of Sverjensky *et al.*, 1997). The excellent agreement between calculated and experimental dissociation constants documented by Sverjensky *et al.* (1997) would be expected in similar calculations using SUPCRT and SPRONS.JNC, because the partial molal thermodynamic properties and equation-of-state coefficients for $FeCl^+$ and $FeCl_2(aq)$ in this database are from Sverjensky *et al.* (1997). This is confirmed in Fig. D.46, which illustrates comparisons between calculated and experimentally determined dissociation constants for $FeCl^+$ between 0 and 600°C at *Psat* and at 0.5, 1 and 2 kb.

6.11 Stability Relations Among Smectites, and the Solubility of Illite

As noted in Section 5.2.4, thermodynamic data in SPRONS.JNC and PHREEQE.JNC support different models of hydrolysis reactions involving non-stoichiometric solid solutions. The PHREEQE series of codes do not include solid-solution models in the general sense considered by Helgeson *et al.* (1978), although ion-exchange reactions can be simulated. Rather, solid-solution behavior is approximated using a *surrogate* stoichiometric phase to represent the solid solution. The stoichiometry of the surrogate phase is defined such that it is within the range of compositions exhibited by the solid solution it represents,

but the stoichiometry is not variable, as would otherwise be consistent with solid-solution behavior. For this reason, estimated thermodynamic properties for a limited number of such phases, including those representing di-octahedral smectites (Na-, K-, Ca- and Mg- nontronites, beidellites and montmorillonites) and illite, are included in SPRONS.JNC. These data are estimated by Wolery (1976), who used a re-calibrated and slightly modified version of the technique described by Tardy and Garrels (1974) to estimate Gibbs free energies of formation, and methods described by Helgeson *et al.* (1978) to estimate standard molal entropies and Maier-Kelly heat capacity coefficients.

6.11.1 Smectites

Experimental data on the solubilities of clay minerals whose compositions are identical to those of the surrogate phases in SPRONS.JNC are not available, and the accuracy of the estimated thermodynamic data for these phases is therefore difficult to evaluate quantitatively. It is possible, however, to assess whether the estimated data are consistent with phase relations observed in natural systems. In this approach, logarithmic activity diagrams are used to correlate the chemistry of aqueous solutions with the stabilities of coexisting minerals at equilibrium. The idealized stoichiometry assigned in the present study to the smectite clays dictates the intercepts and slopes of boundaries on such diagrams, which in turn define the stability fields of these minerals. The compositions of natural waters plotting within a given stability field, or along one of its boundaries, is necessary, but not sufficient, evidence that the solution has equilibrated with the corresponding minerals.

Stability relations among minerals, including smectites, in the systems

- Na_2O-MgO-Al_2O_3-SiO_2-H_2O,
- K_2O-MgO-Al_2O_3-SiO_2-H_2O,
- Na_2O-K_2O-MgO-Al_2O_3-SiO_2-H_2O, and
- CaO-MgO-Al_2O_3-SiO_2-H_2O

are correlated, for example, with the compositions of deep Japanese groundwaters in Figs. C.55 - C.58, respectively. These diagrams are constructed using the Geochemist's Workbench (Bethke, 1996) and its associated thermodynamic database, which was modified in the present study to ensure that the thermodynamic properties of hydrolysis reactions among minerals and aqueous species are consistent with the data in SPRONS.JNC. The groundwater chemistry database, compiled by JNC, includes analytical data for approximately 15,000 samples from throughout Japan. These data were screened on the basis of sampling depth and temperature, and to discriminate among samples obtained at depths greater than, or less than, 200 m, to derive a database consisting of approximately 1000 samples that characterize the chemistry of "deep" groundwaters in Japan. These data were used with PHREEQE and the H3 TDB (see section 5.3.3) to calculate the logarithms of

activity quotients represented by the axes in Figs. C.55 - C.58. Stability relations among the minerals in these figures are calculated assuming the activity of $SiO_2(aq)$ is controlled by amorphous silica solubility at 19°C, which is the average temperature of the deep groundwater dataset.

As can be seen in Figs. C.55 - C.58, the deep groundwater compositions plot rather consistently in the stability fields of the montmorillonite end members of the smectite clays. Discernable trends in the groundwater data are also revealed suggesting that ion-exchange reactions among these clay minerals control the aqueous activities of Na^+, K^+, Ca^{2+} and Mg^{2+}. These trends are roughly parallel to the slopes of stability-field boundaries between montmorillonite end members, and in some cases are coincident with them (Figs. C.57 and C.58). Small adjustments in log *K* values for the reactions that determine these boundaries in Figs. C.55 and C.56 (< 0.5 log K units) are found by trial and error to generate better agreement with the groundwater data, but these adjustments are arbitrary, and have therefore not been incorporated in SPRONS.JNC.

The observations in Figs C.55 - C.58 that most of the deep groundwaters plot in the stability fields of clay minerals is qualitatively reasonable because reactions among groundwaters and primary aluminosilicate minerals are known to precipitate clay minerals as reaction products at low temperatures (e.g. Drever, 1982; Langmuir, 1997). It is not known, however, if such reactions actually occur in the host rocks from which the groundwater samples were obtained, nor is information available characterizing the mineralogy of these clay minerals, if they exist. Thus, although the thermodynamic data in SPRONS.JNC for the smectites appear to be compatible with known stability relations among minerals in groundwater systems, additional experimentation and field studies are needed to confirm this conclusion. Alternative models of smectite-water equilibria that more realistically account for the solid-solution behavior of these minerals (e.g., Aagaard and Helgeson, 1983) should also be tested using the available data in SPRONS.JNC for end-member components of smectite [e.g., stoichiometrically equivalent to pyrophyllite, margarite, muscovite, paragonite and others (Aagaard and Helgeson, 1983; Ransom and Helgeson, 1993; 1994)].

6.11.2 Illite

The solubility and stability of natural illites have been investigated experimentally by Routson and Kittrick (1971), Sass *et al.* (1987) (later reinterpreted by Aja, 1991), Aja *et al.* (1991a,b), and Yates and Rosenberg (1996). All the studies other than Aja *et al.* (1991b) fail to report Mg concentrations in the experimental solutions, however, and therefore cannot be used to test the reliability of thermodynamic data for illite in SPRONS.JNC.

Aja *et al.* (1991b) measured the compositions of solutions coexisting with illite,

kaolinite, and gibbsite between 25 and 250°C at *Psat*. Their interpretation of phase equilibria in this system is criticized by Essene and Peacor (1995), who assert that equilibrium was either not attained in the experiments, or that the composition of the illite solid-solution controlling aqueous compositions was mis-identified. Aja and Rosenberg (1996) argue that Essene and Peacor (1995) misinterpreted these experimental data, but this is disputed by Essene and Peacor (1997).

Despite these questions of interpretation, the basic experimental data generated by Aja *et al.* (1991b) can be used to test whether the thermodynamic data for illite in SPRONS.JNC are qualitatively reasonable. That is, although our assumption that illite's solid-solution behavior can be approximated using a stoichiometric surrogate phase is a gross simplification, solution compositions at, or near to, equilibrium with the illite surrogate, kaolinite and gibbsite should not conflict severely with solution compositions measured by Aja *et al.* (1991b). The relevant reaction is

$$\text{illite} + 0.9\ H_2O + 1.1\ H^+ = \text{kaolinite} + 0.3\ \text{gibbsite} + 1.5\ SiO_2(aq) + 0.6\ K^+ + 0.25\ Mg^{2+},$$

where thermodynamic data for "stoichiometric" illite in SPRONS.JNC,

$$K_{0.6}(Mg_{0.25}Al_{1.8})(Si_{3.5}Al_{0.5})O_{10}(OH)_2,$$

are estimated by Wolery (1976), as noted above.

Equilibrium constants calculated using SUPCRT and SPRONS.JNC for this reaction between 0 and 250°C at *Psat* are compared in Fig. C.59 with equilibrium constants retrieved from experimental solution compositions by Aja *et al.* (1991b). The solid symbols refer to solutions sampled at the end of the experiments, and their open-symbol counterparts refer to solutions sampled at earlier times. As can be seen, the calculated equilibrium constants at relatively low temperatures are up to 3 log K units lower than their experimental counterparts, but these differences tend to decrease with increasing reaction time. At temperatures greater than 100°C, the calculated equilibrium constants are closely consistent with the experimental values determined at the end of the experiments. It is questionable whether gibbsite is stable, or metastable, in the experiments at temperatures greater than about 100°C (e.g., Pokrovskii and Helgeson, 1995), but accounting for boehmite rather than gibbsite in the above reaction (as shown by the dashed curve in Fig. C.59) does not significantly alter the close correspondence between calculated and experimental equilibrium constants at these temperatures, as can be seen in the figure.

The comparison of calculated and experimental equilibrium constants illustrated in Fig. C.59 suggests that the thermodynamic data for illite in SPRONS.JNC

are reasonably consistent with the limited amount of relevant experimental data over this range of temperatures and pressures. Although discrepancies at temperatures less than about 100°C are significant, they appear to diminish with increasing reaction time and temperature, which supports the contention of Essene and Peacor (1995) that equilibrium was not achieved in these experiments. We emphasize, however, that the reaction considered in this comparison is a gross approximation of illite's true solid-solution behavior, and that alternative modeling approaches that more realistically account for such behavior should be tested in similar comparisons with these experimental data.

6.12 Aqueous Dissociation Reactions

Experimental dissociation constants for Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe^{2+}, and Mn^{2+} complexes with Cl^-, F^-, SO_4^{2-}, $B(OH)_4^-$, $H_3SiO_4^-$ or CH_3COO^- ligands are compared with corresponding dissociation constants calculated using SUPCRT and SPRONS.JNC in Figs. D.27 - D.50. Although most of these diagrams, and numerous others, are similarly described by Sverjensky *et al.* (1997), we include them in the present study because they incorporate experimental dissociation constants that were not considered by these authors. Comments summarized below address instances where these new and additional experimental data compare unfavorably with calculated values, although as can be seen in Figs. D.27 - D.50, calculated dissociation constants generally agree closely with their experimental counterparts.

Experimental dissociation constants for $NaSO_4^-$ and $NaB(OH)_4(aq)$ determined by Pokrovski *et al.* (1995) between 0 and 300°C at *Psat* are compared with values calculated using SUPCRT and SPRONS.JNC in Figs. D.29 and D.30, respectively. Partial molal thermodynamic properties and HKF equation-of-state coefficients for $NaSO_4^-$ and $NaB(OH)_4(aq)$ in SPRONS.JNC were determined by regression of these experimental data, and the close correspondence between calculated and experimental dissociation constants in these figures is therefore expected. Dissociation constants for $NaSO_4^-$ between 150 and 320°C at *Psat* determined in flow-calorimetry experiments by Oscarson *et al.* (1988a) are generally consistent with their calculated counterparts, and with the experimental constants determined by Pokrovski *et al.* (1995).

Dissociation constants for the Na-acetate complex calculated using SUPCRT and SPRONS.JNC between 270 and 330°C at *Psat* are compared with experimental values determined by Oscarson *et al.* (1988b) in Fig. D.31. The partial molal thermodynamic properties of this complex at 25°C and 1 bar in SPRONS.JNC are from Shock and Koretsky (1993), who used the correlation algorithm proposed by Shock and Helgeson (1988) to estimate corresponding equation-of-state coefficients. The poor agreement shown in the figure between calculated and experimental dissociation constants is attributed by Shock and Koretsky (1993) to incorrect dissociation constants for $HCl(aq)$ used by

Oscarson *et al.* (1988b) to retrieve their dissociation constants for Na-acetate.

Dissociation constants for KSO_4^- calculated using SUPCRT and SPRONS.JNC between 0 and 200°C at *Psat* are compared with experimental values for this reaction in Fig. D.33. Sverjensky *et al.* (1997) regressed experimental data from Truesdell and Hostetler (1968), Quist *et al.* (1963) and Bell and George (1953) (not shown) to retrieve partial molal thermodynamic properties and equation-of-state coefficients for this species. Dissociation constants determined by Righellato and Davies (1930) and Jenkins and Monk (1950) at low temperatures are consistent with the calculated curve in Fig. D.33, and the experimental data of Truesdell and Hostetler (1968) and Quist *et al.* (1963).

Dissociation constants for $MgCl^+$ calculated using SUPCRT and SPRONS .JNC are compared with their experimental counterparts from 0 to 300°C at *Psat* in Fig. D.34, and from 300 to 600°C at higher pressures in Fig. D.35. Sverjensky *et al.* (1997) regressed experimental data from Majer and Stulik (1982) and Saccocia and Seyfried (1990) to retrieve partial molal thermodynamic properties and equation-of-state coefficients for this species. Dissociation constants determined by Gillespie *et al.* (1992) and Johnson and Pytkowicz (1978) are consistent with calculated values between 25 and 330°C at *Psat* (Fig. D.34), but dissociation constants retrieved at higher temperatures and pressures from conductance measurements by Frantz and Marshall (1982) differ significantly (Fig. D.35).

Dissociation constants for MgF^+ between 0 and 300°C at *Psat* calculated using SUPCRT and SPRONS.JNC are compared with experimental values in Fig. D.36. Sverjensky *et al.* (1997) regressed experimental data from Richardson and Holland (1979) to retrieve partial molal thermodynamic properties and equation-of-state coefficients for this species. Dissociation constants determined Majer and Stulik (1982) are closely consistent with calculated values at low temperatures, but dissociation constants calculated by Richardson and Holland (1979) using experimental data from Cadek *et al.* (1971) and Tanner *et al.* (1968) are lower by less than 1 log *K* unit than dissociation constants calculated using SUPCRT and SPRONS.JNC.

Dissociation constants for $CaCl^+$ and $CaCl_2(aq)$ calculated using SUPCRT and SPRONS.JNC are compared with experimental values from 0 to 350°C at *Psat* in Figs. D.37 and D.38, respectively, and from 400 to 600°C at higher pressures in Figs. D.39 and D.40, respectively. Sverjensky *et al.* (1997) regressed experimental data from Majer and Stulik (1982), Alakhverdov (1985), Simonson *et al.* (1985), Ramette (1986), Williams-Jones and Seward (1989) and Gillespie *et al.* (1992) to retrieve partial molal thermodynamic properties and equation-of-state coefficients for $CaCl^+$. Experimental data from Ramette (1986) and Williams-Jones and Seward (1989) were used by Sverjensky *et al.* (1997) to retrieve partial molal thermodynamic properties and equation-of-state

coefficients for $CaCl_2(aq)$. Figures D.37 and D.38 confirm that dissociation constants for $CaCl^+$ and $CaCl_2(aq)$ determined in the respective experimental studies are consistent with calculated values between 25 and 360°C at *Psat*, but dissociation constants retrieved at higher temperatures and pressures by Frantz and Marshall (1982) differ significantly (Fig. D.39 and D.40, respectively).

Dissociation constants for CaF^+ between 0 and 300°C at *Psat* calculated using SUPCRT and SPRONS.JNC are compared with their experimental counterparts in Fig. D.41. Sverjensky *et al.* (1997) regressed experimental data from Richardson and Holland (1979) to retrieve partial molal thermodynamic properties and equation-of-state coefficients for this species. Dissociation constants determined Majer and Stulik (1982) are closely consistent with calculated values at low temperatures, but dissociation constants calculated by Richardson and Holland (1979) using experimental data from Tanner *et al.* (1968), Cadek *et al.* (1971) and Aziz and Lyle (1968) differ from values calculated using SUPCRT and SPRONS.JNC by less than 1 log *K* unit. Similar discrepancies are apparent in the solubility of fluorite between 0 and 260°C at *Psat* determined by Richardson and Holland (1979) (Fig. C.54).

Dissociation constants for $MnCl^+$ between 0 and 300°C at *Psat* calculated using SUPCRT and SPRONS.JNC are compared with experimental dissociation constants reported by Wheat and Carpenter (1988) and Gammons and Seward (1996) in Fig. D.49. Sverjensky *et al.* (1997) regressed these experimental data using the partial molal thermodynamic properties and HKF equation-of-state coefficients for Cl- from Shock and Helgeson (1988) to retrieve partial molal thermodynamic properties and equation-of-state coefficients for $MnCl^+$. The source of thermodynamic properties for Mn^{2+} used in this regression procedure is unclear, however, because these data were not determined by Shock and Helgeson (1988). Partial molal thermodynamic properties and equation-of-state parameters for Mn^{2+} from Shock *et al.* (1997a), which are included in SPRONS.JNC, apparently differ from the corresponding data used by Sverjensky *et al.* (1997) because the calculated curve in Fig. D.41 is displaced upward by 0.3 to 0.4 log *K* units relative to the corresponding curve depicted in Fig. 17 of Sverjensky *et al.* (1997). A similar displacement is noted in the calculated curve shown in Fig. D.50 for $MnSO_4(aq)$ dissociation compared with the corresponding curve in Fig. 14 of Sverjensky *et al.* (1997), who used the data from Wheat and Carpenter (1988) as experimental constraints. These observations suggest that the thermodynamic data for $MnCl^+$ and $MnSO_4(aq)$ in SPRONS.JNC should be revised by regression of the experimental data in Figs. D.49 and D.50, using partial molal thermodynamic properties and equation-of-state coefficients for Cl- from Shock and Helgeson (1988), and for Mn^{2+} from Shock *et al.* (1997a).

6.13 Comments on Database Management

We conclude this section with comments on the conditions adopted for a reliable thermodynamic database (Section 3.1) with regard to SPRONS.JNC, and, hence, PHREEQE.JNC.

6.13.1 Internal consistency

SPRONS.JNC is *partially* consistent in the sense defined by Engi (1992), because all the data are compatible with basic thermodynamic definitions and functional relations comprising the SUPCRT model, and fundamental experimental and field observations that constrain these data are consistently evaluated within this modeling framework. The databases are not *fully* consistent, however, because the rationale for selecting certain parameters, such as standard molal or partial molal properties at the reference pressure and temperature, are not generally documented in sufficient detail in original data sources.

The internal consistency of SPRONS.JNC should be maintained as this database is revised. Revisions to the thermodynamic properties of boehmite, diaspore and corundum recommended by Pokrovskii and Helgeson (1995), for example, have resulted in less favorable agreement among calculated and experimental equilibria involving these minerals and various aluminosilicates than were achieved in the original evaluation of these data by Helgeson *et al.* (1978). Similar discrepancies can be expected if the revised partial molal properties of $SiO_2(aq)$ determined by Rimstidt (1997) are incorporated in SPRONS.JNC. Resolving such discrepancies for a given reaction is reasonably straightforward using regression techniques, but matrix analytical methods may be required if multiple reactions are affected by the revised property.

6.13.2 Experimental basis

Additional experimental determination of mineral solubilities at relatively low pressures and temperatures (≈ 0 to 150°C at *Psat*) are needed to improve confidence that the thermodynamic data in SPRONS.JNC are reliable for conditions that are most relevant to the Japanese repository concept. The thermodynamic properties of minerals in this database are constrained primarily by phase-equilibrium studies and a limited amount of calorimetric data. These properties should be integrated with those of aqueous species and gases, and results compared with independent experimental solubility equilibria. Recent studies of this kind, which are remarkably few in number, are described by Sverjensky *et al.* (1991) and Pokrovskii and Helgeson (1995), and provide a useful framework for similar work by JNC and others in the future. Based on the evaluations discussed in preceding sections, similar studies are recommended to revise standard molal thermodynamic properties in SPRONS.JNC for:

- albite,
- strontianite,
- witherite,
- siderite,
- celestite,
- pyrrhotite,
- magnetite, and
- fluorite.

Evaluations of data reliability such as are described in Sections 6.1 - 6.12 should also be undertaken routinely as the results of new solubility and aqueous-speciation studies become available.

Experimental investigations of mineral solubilities at relatively low temperatures are often complicated by sluggish reaction kinetics. To overcome this problem, experiments at higher temperatures are useful because reaction-rates generally increase with increasing temperature, and because thermodynamic relations incorporated in SUPCRT enable extrapolation of the high-temperature data to lower temperatures with reasonable confidence. We also recommend, however, that field investigations of phase relations in natural groundwater systems should be given greater priority for purposes of evaluating the reliability of thermodynamic data. The temperature in such systems is low, but reaction times greatly exceed those that can be accommodated experimentally. Detailed characterization of the mineralogy and groundwater chemistry comprising such systems is required to extract meaningful data that can be used to test the accuracy of thermodynamic data. Such characterization should take into account the effects of metastability, differences in crystallinity and the state of order/disorder in minerals formed under different conditions in different geologic environments, and the effects of solid-solution on mineral compositions.

The minerals in SPRONS.JNC are stoichiometric phases, but as noted above several non-stoichiometric minerals, such as the clays, zeolites and chlorites, are also important in geologic and near-field environments considered in the Japanese repository concept. The compositions of such minerals are variable within limits, and result from ideal or non-ideal mixing of thermodynamic components in solid solution. Helgeson *et al.* (1978), Stoessell (1979), Aagaard and Helgeson (1983) and Giggenbach (1985) describe models of this behavior in which the activities of components computed from site-mixing approximations are correlated with the compositions of the minerals and used as descriptive variables in activity diagrams. The approach is advantageous because it circumvents the need to assign values for the standard Gibbs free energies of formation to one or another solid-solution mineral with a specified composition. SPRONS.JNC includes data for several minerals that are stoichiometrically equivalent to thermodynamic components used in these models to constrain the thermodynamic behavior of solid-solution minerals. This suggests that the reliability of these data could be evaluated by comparing predicted mineral

stability relations in various chemical subsystems with phase relations observed in natural systems.

6.13.3 Documentation

The documentation criteria adopted in the present study are that the selected thermodynamic data are *traceable* to original experimental sources, and that these sources are *scientifically defensible* and *reproducible*. The traceability criterion is met by referencing sources from which the standard molal and partial molal properties in SPRONS.JNC were obtained, and these sources in turn identify sources of primary experimental results that were used to retrieve these data. The sources of thermodynamic data in SPRONS.JNC are summarized in Sections 5.2.2 and 5.2.3, and are referenced in Section 8. The sources of experimental constraints used to retrieve these data are identified in these references, and most are also documented in the present report. The scientific defensibility and reproducibility of the primary experimental results are documented in the original references.

6.13.4 Verification of accuracy

The accuracy of thermodynamic data in SPRONS.JNC is verified in the present study by comparing calculated thermodynamic quantities with their experimental counterparts, which are documented in the various diagrams comprising Appendixes C and D. Similar diagrams, and others, constructed using identical thermodynamic data are documented in the references summarized in Sections 5.2.2 and 5.2.3. It is recommended that a library of such diagrams should also be developed by JNC, and that these should be updated and revised as the results of new experimental investigations become available.

7 Acknowledgements

Enlightening discussions with Drs. Greg Anderson (University of Toronto) and Bill Bourcier (LLNL) clarified various aspects of the SUPCRT model (any inaccuracies in the present report are the sole responsibility of the authors, however). Dr. Everett Shock (Washington University) kindly provided in advance of publication thermodynamic data and equation-of-state coefficients for the actinide ions that are included in SPRONS.JNC, and Dr. Tom Wolery (LLNL) explained the techniques used to estimate the thermodynamic properties of solid-solution surrogate phases included in this database. The efforts of Mr. Makoto Yoshizoe (Mitsubishi Corp.) and Mr. Shinichi Kataoka (Mitsubishi Heavy Industries) in providing contractual and logistical support to this project are gratefully acknowledged.

8 References

Aagaard, P. and Helgeson, H. C. 1983. Activity/composition relations among silicates and aqueous solutions: II. Chemical and thermodynamic consequences of ideal mixing of atoms on homological sites in montmorillonites, illites and mixed-layer clays. *Clays Clay Miner.*, 31(3), 207-217.

Ackerman, T. 1958. Aussagen uber die eigendissoziation des wassers aus molwar messungen geloster elektrolyte. *A. Elektrochem.*, 62, 411-419.

Ahrland, S. and Kullberg, L. 1971. Thermodynamics of metal complex formation in aqueous solution. I. A potentiometric study of fluoride complexes of hydrogen, uranium(VI), and vanadium (IV). *Acta Chim. Scand.*, 25, 3457-3470.

Aja, S. U. 1991. Illite equilibria in solutions. III. A re-interpretation of the data of Sass et al. (1987). *Geochim. Cosmochim. Acta*, 55, 1365-1374.

Aja, S. U. and Rosenberg, P. E. 1996. The thermodynamic status of compositionally-complex clay minerals: Discussion of "clay mineral thermometry-a critical perspective". *Clays Clay Miner.*, 44(4), 560-568.

Aja, S. U., Rosenberg, P. E. and Kittrick, J. A. 1991a. Illite equilibria in solutions. I. Phase relationships in the system K_2O-Al_2O_3-SiO_2-H_2O between 25 and 250°C. *Geochim. Cosmochim. Acta*, 55, 1353-1364.

Aja, S. U., Rosenberg, P. E. and Kittrick, J. A. 1991b. Illite equilibria in solutions. II. Phase relationships in the system K_2O-MgO-Al_2O_3-SiO_2-H_2O. *Geochim. Cosmochim. Acta*, 55, 1365-1374.

Allakhverdov, G. R. 1985. Calculation of the formation constants of singly charged complex ions of bivalent metals in solutions. *Russ. J. Phys. Chem.*, 59, 39-41.

Allred, G. C. and Woolley, E. M. 1981. Heat capacities of aqueous acetic acid, sodium acetate, ammonia and ammonium chloride at 283.15 K, 298.15 K and 313.15 K: ΔC°_{p} for ionization of acetic acid and for dissociation of ammonium ion. *J. Chem. Thermo.*, 13, 155-164.

Alvarez, J., Crovetto, R. and Fernandez-Prini, R. 1988. The dissolution of N_2 and H_2 in water from room temperature to 640 K. *Ber. Bunsenges. Phys. Chem.*, 92, 935-940.

Anderson, G. M. and Burnham, C. W. 1965. The solubility of quartz in supercritical steam. *Am. J. Sci.*, 263, 494-511.

Anderson, G. M. and Burnham, C. W. 1967. Reactions to quartz and corundum with aqueous chloride and hydroxide solutions at high temperatures and pressures. *Am. J. Sci.*, 265, 12-27.

Anderson, G. M. and Crerar, D. A. 1993. *Thermodynamics in Geochemistry*. Oxford University Press, Oxford, U. K. 588p.

Apps, J. A. 1970. The stability field of analcime. Ph.D. Dissertation, Harvard Univ., 347p.

Apps, J. A. and Neil, J. M. 1990. Solubilities of aluminum hydroxides and oxyhydroxides in alkaline solutions. Correlation with the thermodynamic properties of $Al(OH)_4^-$. In. *Chemical modeling of aqueous systems II*, (D.C. Melchior and R.L. Bassett, eds.), Am. Chem. Soc. Symp. Ser., 416, 414-428.

Apps, J. A., Neil, J. M. and Jun, C.-H. 1989. Thermochemical properties of gibbsite, bayerite, boehmite, diaspore, and the aluminate ion between 0 and 350°C. LBL-21482, Lawrence Berkeley Laboratory, Berkeley, California, 98p.

Arthur, R. C. 1994. Equilibria in saturated bentonite. In. *Scientific Basis for Nuclear Waste Management XVII* (A. Barkatt and R. A. Van Konyenburg, eds.), Mat. Res. Soc. Symp., 333, 955-960.

Arthur, R. C., Apted, M.J. and Conca, J. L. 1993. Dealing with uncertainty in the chemical environment of bentonite backfill. In. *Scientific Basis for Nuclear Waste Management XVI* (C.C. Interrante and R. T. Pabalan, eds.), Mat. Res. Soc. Symp., 294, 389-394.

Arthur, R. C., Savage, D., Apted, M. J. and Zhou, W. 1997. Critical evaluation of thermodynamic and kinetic data for non-radioactive minerals, gases and aqueous species. QSCI-9608-4, QuantiSci, Inc., Denver, Colorado.

Aziz, A. and Lyle, S. J. 1969. Applications of the fluoride-sensitive electrode to the study of metal-fluoride ion association constants. *Anal. Chim. Acta*, 47, 49-56.

Azuma, J., Shibata, M., Yui, M., Shibutani, T, Notoya, S. and Yoshida, Y. 1999. Solubility and speciation of radioactive elements of high-level radioactive waste disposal system. Japan Nuclear Cycle Development Institute, Tokai-Mura, Ibaraki, Japan, Technical Report (in preparation).

Barbero, J. A., Hepler, L. G., McCurdy, K. G. and Tremaine, P. R. 1983. Thermodynamics of aqueous carbon dioxide and sulfur dioxide: Heat capacities, volumes and the temperature dependence of ionization. *Can. J. Chem.*, 61, 2509-2519.

Barnes, H. L., Helgeson, H. C. and Ellis, A. J. 1966. Ionization constants in aqueous solutions. In: Handbook of Physical Constants (rev. ed.), *Geol. Soc. America. Mem.* 97, 401-413.

Barta, L. and Hepler, L. G. 1986. Densities and apparent molar volumes of aqueous aluminum chloride. Analysis of apparent molar volumes and heat capacities of aqueous aluminum salts in terms of the Pitzer and Helgeson theoretical models. *Can. J. Chem.*, 64, 353-359.

Barth, T. and Bjorlykke, K. 1993. Organic acids from source rock maturation: generation potentials, transport mechanisms and relevance for mineral diagenesis. *Appl. Geochem.*, 8, 325-337.

Bates, R. G. and Pinching, G. D. 1949. Acidic dissociation constant of ammonium ion at 0° to 50°C, and the base strength of ammonia. *J. Res. Natl. Bur. Stand.*, 42, 419-430.

Bates, R. G., Bower, V. E., Canham, R. G. and Prue, J. E. 1959. The dissociation constant of $CaOH^+$ from 0° to 40°C. *Trans. Faraday Soc.*, 55, 2062-2068.

Becker, K. H., Cemic, L. and Langer, K. E. O. E. 1983. Solubility of corundum in

supercritical water. *Geochim. Cosmochim. Acta*, 47, 1573-1578.

Bell, R. P. and George, J. H. B. 1953. Incomplete dissociation of some thallous and calcium salts at different temperatures. *Trans. Faraday Soc.*, 49, 619-627.

Benes, P. and Selecka, H. 1973. Ion pair formation and solubility of barium carbonate in aqueous solutions. *Radiochem. Radioanal. Lett.*, 13, 339-348.

Benson, B. B. and Krause, D., Jr. 1976. Empirical laws for dilute aqueous solutions of nonpolar gases. *J. Chem. Phys.*, 64, 689-709.

Benson, B. B., Krause, D. and Peterson, M. A. 1979. The solubility and isotopic fractionation of gases in dilute aqueous solution. I. Oxygen. *J. Soln. Chem.*, 8, 655-690.

Berecz, F. and Szita, L. 1970. Electrochemical method for the solubility and dissolution of solid compounds. Some thermodynamic properties of the system $Al(OH)_3$-NaOH-H_2O. *Electrochim. Acta*, 15, 1407-1419.

Berg, R. L. and Vanderzee, C. E. 1978. Thermodynamics of carbon dioxide and carbonic acid: (a) the standard enthalpies of Na_2CO_3*(s)*, $NaHCO_3$*(s)* and CO_2*(g)* in water at 298.15 K; (b) the standard enthalpies of formation, standard Gibbs energies of formation, and standard entropies of CO_2*(aq)*, HCO_3^-*(aq)*, CO_3^{2-}*(aq)*, $NaHCO_3$*(s)*, Na_2CO_3*(s)*, $Na_2CO_3 \cdot H_2O$*(s)*, and $Na_2CO_3 \cdot 10H_2O$ *(s). J. Chem. Thermo.*, 10, 1113-1136.

Berman, R.G. 1988. Internally-consistent thermodynamic data for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. *Journal of Petrology*, 29(2),445-522.

Berman, R.G. and Brown, T.H. 1985. Heat capacity of minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. *Contrib. Mineral. Petrol.*, 89, 168-183.

Berman, R.G. and Greenwood, H.J. 1985. An internally consistent thermodynamic data base for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Atomic Energy Canada, Ltd. Tech. Rep. 377, 62p.

Berman, R. G. and Aranovich, L. Ya. 1996. Optimized standard state and solution properties of minerals. I. Model calibration for olivine, orthopyroxene, cordierite, garnet, and ilmenite in the system FeO-MgO-CaO-Al_2O_3-TiO_2-SiO_2. *Contrib. Mineral. Petrol.*, 126, 1-24.

Berman, R.G., Engi, M. and Greenwood, H.J. 1986. Derivation of internally consistent thermodynamic properties by the technique of mathematical programming: A review with application to the system MgO-SiO_2-H_2O. *Journal of Petrology*, 27(6), 1331-1364.

Berner, R. A. 1967. Thermodynamic stability of sedimentary iron sulfides. *Am. J. Sci.*, 265, 773-785.

Berry, L. G. 1974. Powder diffraction file search manual, minerals. Joint Comm. Powder Diffraction Standards, Pub. M-1-23, 833p.

Bernshtein, V. A. and Matsenok, Ye. A. 1965. Equilibrium in the interaction of diaspore with solutions of sodium hydroxide at temperatures of 250 and 300°C. *J. App. Chem. USSR*, 38,1898-1901.

Bethke, C. M. 1996. *Geochemical Reaction Modeling.* Oxford University Press, Oxford, U. K. 397p.

Beuschlein, W. L. and Simenson, L. O. 1940. Solubility of sulfur dioxide in water. *J. Amer. Chem. Soc.*, 62, 610-612.

Biryukov, A. A. and Shlenskaya, V. I. 1964. Composition and stability constants of chloro-complexes of palladium(II). *Russ. J. Inorg. Chem.*, 9, 450-452.

Bloom, P. R. and Weaver, R. M. 1982. Effect of the removal of reactive surface material on the solubility of synthetic gibbsites. *Clays Clay Miner.*, 30, 281-286.

Bloss, F. D. 1971. *Crystallography and Crystal Chemistry.* Holt, Rinehart and Winston, Inc. New York, 545p.

Blount, C. W. 1977. Barite solubilities and thermodynamic quantities up to 300°C and 1400 bars. *Amer. Mineral.*, 62, 942-957.

Born, M. 1920. Volumen und hydrationswarme der ionen. *Zeit. Physik.*, 1, 45-48.

Bourcier, W. L. 1985. Improvements in the solid solution modeling capabilities of the EQ3/6 geochemical code. UCID 20587, Lawrence Livermore National Laboratory, Livermore, California.

Bourcier W.L., Knauss K.G. and Jackson K.J. 1993. Aluminum hydrolysis constants to 250° from boehmite solubility measurements. *Geochim. Cosmochim. Acta,* 57, 747-762.

Boyle, R. W. 1911. The solubility of radium emanation. Application of Henry's law at low partial pressure. *Phil. Mag.*, 22, 840-854.

Broene, H. H. and DeVries, T. 1947. The thermodynamics of aqueous hydrofluoric acid solutions. *J. Amer. Chem. Soc.*, 69, 1644-1646.

Brown, P. L., Sylva, R. N., Batley, G. E. and Ellis, J. 1985. The hydrolysis of metal ions. Part 8. Aluminum (III). *J. Chem. Soc. Dalton Trans.*, 1967-1970.

Bruno J., Wersin P. and Stumm W. 1992. On the influence of carbonate in mineral dissolution: II. The solubility of $FeCO_3$(s) at 25°C and 1 atm total pressure. *Geochim. Cosmochim. Acta, 56,* 1149-1155.

Burch, T. E. 1993. Albite dissolution and precipitation kinetics at 80°C: The dependence of solution saturation state. Ph.D. Dissertation, Yale University, New Haven, Conn.

Burch, T. E., Nagy, K. L. and Lasaga, A. C. 1993. Free energy dependence of albite dissolution kinetics at 80°C and pH 8.8. *Chem. Geol.*, 105, 137-162.

Burnham, C. W. 1965. Ferrosilite. Carnegie Inst. Washington Year Book, 64, 202-204.

Busey, R. H. and Mesmer, R. E. 1977. Ionization equilibria of silicic acid and

polysilicate formation in aqueous sodium chloride solutions to 300 C. *Inorg. Chem.*, 16, 2444-2450.

Busenberg, E. and Plummer, L. N. 1986. The solubility of $BaCO_3$(cr) (witherite) in CO_2-H_2O solutions between 0 and 90°C, evaluation of the association constants of $BaHCO_3^+$(aq) and $BaCO_3$(aq) between 5 and 80°C, and a preliminary evaluation of the thermodynamic properties of Ba^{2+}(aq). *Geochim. Cosmochim. Acta*, 50, 2225-2233.

Busenberg, E., Plummer, L. N. and Parker, V. B. 1984. The solubility of strontianite ($SrCO_3$) in CO_2-H_2O solutions between 2 and 91°C, the association constants of $SrHCO_3^+$(aq) and $SrCO_3$(aq) between 5 and 80°C, and an evaluation of the thermodynamic properties of Sr^{2+}(aq) and $SrCO_3$(cr) at 25°C and 1 atm total pressure. *Geochim. Cosmochim. Acta*, 48, 2021-2035.

Butler, J. N. and Huston, R. 1970. Potentiometric studies of multicomponent activity coefficients using the lanthanum fluoride membrane electrode. *Anal. Chem.*, 42, 1308-1311.

Cadek, J., Vesely, J. and Sulcek, Z. 1971. Bildung von fluoridkomplexen mit erdalkalimetallen. *Collection Czechoslov. Chem. Commun.*, 36, 3377-3381.

Carmichael, D. M. 1977. Chemical equilibria involving pure crystalline compounds. In *Short course in application of thermodynamics to petrology and ore deposits* (H. J. Greenwood, ed.), Mineral. Assoc. Canada, Toronto, 47-65.

Carothers, W. W. and Kharaka, Y. K. 1978. Aliphatic acid anions in oil-field waters - implications for origin of natural gas. *Am. Assoc. Petrol. Geol. Bull.*, 62, 2441-2453.

Castet, S., Dandurand, J.-L., Schott, J. and Gout, R. 1993. Boehmite solubility and aqueous aluminum speciation in hydrothermal solutions (90-350°C): Experimental study and modeling. *Geochim. Cosmochim. Acta*, 57, 4869-4884.

Chang, B.-T., Pak, L.-H. and Li, Y.-S. 1979. Solubilities and rates of dissolution of diaspore in NaOH aqueous solutions. *Bull. Chem. Soc. Japan*, 52, 1321-1326.

Chatterjee, N. D. 1970. Synthesis and upper stability of paragonite. *Contr. Mineral. Petrol.*, 27, 244-257.

Chen, C-T. A. and Marshall, W. L. 1982. Amorphous silica solubilities. IV. Behavior in pure water and aqueous sodium chloride, sodium sulfate, magnesium chloride, and magnesium sulfate solutions up to 350°C. *Geochim. Cosmochim. Acta*, 46, 279-287.

Chen, X., Izatt, R. M. and Oscarson, J. L. 1994. Thermodynamic data for ligand interaction with protons and metal ions in aqueous solutions at high temperatures. *Chem. Rev.*, 94, 467-517.

Chermak, J. A. and Rimstidt, J. D. 1989. Estimating the thermodynamic properties (ΔG°_f and ΔH°_f) of silicate minerals at 298 K from the sum of polyhedral contributions. *Amer. Mineral., 74*, 1023-1031.

Chernosky J.V. and Berman R.G. 1989. Experimental reversal of the equilibrium: clinochlore + 2 magnesite = 3 forsterite + spinel + 2 CO_2 + 4 H_2O and revised

thermodynamic properties for magnesite. *Am. J. Sci., 289*, 249-266.

Christ, C. L. and Hostetler, P. B. 1973. Studies in the system MgO-SiO_2-CO_2-H_2O: II. The activity product constant of magnesite. *Am. J. Sci.*, 268, 439-453.

Christ, C. L., Hostetler, P. B. and Siebert, R. M. 1973. Studies in the system MgO-SiO_2-CO_2-H_2O: III. The activity product constant of sepiolite. *Am. J. Sci.*, 273, 65-83.

Claussen, W. F. and Polglase, M. F. 1952. Solubilities and structures in aqueous aliphatic hydrocarbon solutions. *J. Am. Chem. Soc.*, 74, 4817-4819.

CODATA. 1978. CODATA recommended key values for thermodynamics 1977. *CODATA Bull. 28*, 17p

Couturier, Y., Michard, G. and Sarazin, G. 1984. Constantes de formation des complexes hydroxydés de l'aluminum en solution aqueuse de 20 a 70°C. *Geochim. Cosmochim. Acta*, 48, 649-659.

Cox, J. D., Wagman, D. D. and Medvedev, V. A. 1989. *CODATA key values for thermodynamics. Final report of the CODATA Task Group on key values for thermodynamics.* Hemisphere Publ. Corp., New York, 271p.

Crerar, D. A. and Anderson, G. M. 1971. Solubility and solvation reactions of quartz in dilute hydrothermal solutions. *Chem. Geol.*, 8, 107-122.

Crerar, D. A. and Barnes, H. L. 1976. Ore solution chemistry V: Solubility of chalcopyrite and chalcocite assemblages in hydrothermal solution at 200 to 350°C. *Econ. Geol.*, 71, 722-794.

Crerar, D. A, Susak, H. J., Borcsik, M. and Schwartz, S. 1978. Solubility of the buffer assemblage pyrite + pyrrhotite + magnetite in NaCl solutions from 200° to 350°C. *Geochim. Cosmochim. Acta*, 42, 1427-1439.

Crovetto, R., Fernandez-Prini, R. and Japas, M. L. 1982. Solubilities of inert gases and methane in H_2O and D_2O in the temperature range of 300 to 600 K. *J. Chem. Phys.*, 86, 1077-1086.

Crozier, T. E. and Yamamoto, S. 1974. Solubility of hydrogen in water, seawater and NaCl solutions. *J. Chem. Eng. Data*, 19(3), 242-244.

Culberson, O. L. and McKetta, J. J. 1951. Phase equilibria in hydrocarbon-water systems. III. The solubility of methane in water at pressures to 10,000 PSIA. *Petrol. Trans. AIME*, 192, 223-226.

Curry, J. and Hazelton, C. L. 1938. The first thermodynamic ionization constant of deuterio-carbonic acid at 25°C. *J. Amer. Chem. Soc.*, 60, 2773-2776.

Cuta, F. and Strafelda, F. 1954. The second dissociation constant of carbonic acid between 60 and 90°C. *Chem. Listy*, 48, 1308-1313.

Deer, W. A., Howie, R. A. and Zussman, J. 1962-1963. *Rock-forming Minerals* (vols. 1-5) John Wiley&Sons, Inc., New York.

Delany, J. M. and Helgeson, H. C. 1978. Calculation of the thermodynamics of

dehydration in subducting oceanic crust to 100 kb and 800°C. *Am. J. Sci.*, 278, 638-686.

Denbigh, K. 1971. *The Principles of Chemical Equilibrium, 3rd ed.* Cambridge University Press, Cambridge, U. K. 494p.

Devidal J-L., Dandurand J-L. and Gout R. 1996. Gibbs free energy of formation of kaolinite from solubility measurement in basic solution between 60 and 170°C. *Geochim. Cosmochim. Acta*, 60(4), 553-564.

Dickson, A. G., Wesolowski, D. J., Palmer, D. A. and Mesmer, R. E. 1990. Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250°C. *J. Phys. Chem.*, 94, 7978-7985.

Donahoe R.J., Liou J.G. and Hemingway B.S. 1990. Thermochemical data for merlinoite: 1. Low-temperature heat capacities, entropies, and enthalpies of formation at 298.15 K of six synthetic samples having various Si/Al and Na/(Na + K) ratios. *Amer. Mineral., 75*, 188-200.

Donnay, J. D. H. and Ondik, H. M. 1973. Crystal data determinative tables, 3rd ed. U.S. Dept. Commerce, Natl. Bur. Standards, Joint Comm. Powder Diff. Standards, 2, 1580p.

Drever, J. I. 1982. *The Geochemistry of Natural Waters.* Prentice-Hall, Englewood Cliffs, N. J. 388p.

Droll, H. A., Block, B. P. and Fernelius, W. C. 1957. Studies on coordination compounds. XV. Formation constants for chloride and acetylacetonate complexes of palladium(II). *Jour. Phys. Chem.*, 61, 1000-1004.

Drummond, S. E., Jr. 1981. Boiling and mixing of hydrothermal fluids: Chemical effects on mineral precipitation. Ph.D dissertation, Penn. State Univ., 357p.

Druzhinina, N. K. 1955. Solubility of diaspore in aluminate solutions. *Tsvetnyye Metally*, 28, 54-56 (in Russian).

Ellis, A. J. 1963. The effect of temperature on the ionization of hydrofluoric acid. *J. Chem. Soc.*, 1963, 4300-4304.

Ellis, A. J. 1968. Partial molal volumes in high-temperature water. Part III. Halide and oxyanion salts. *J. Chem. Soc. (A)*, 1968, 1138-1143.

Ellis, A. J. and Golding, R. M. 1963. The solubility of carbon dioxide above 100°C in water and in sodium chloride solutions. *Am. J. Sci.*, 261, 47-61.

Ellis, A. J. and Giggenbach, W. 1971. Hydrogen sulphide ionization and sulphur hydrolysis in high temperature solution. *Geochim. Cosmochim. Acta*, 35, 247-260.

El-Shazly, A. E. K. 1995. On the thermodynamic data of kaolinite. *Amer. Mineral.*, 80, 1048-1053.

Elmer, T. H. and Nordberg, M. E. 1958. Solubility of silica in nitric acid solutions. *J. Am. Ceram. Soc.*, 41(12), 517-520.

Engi, M. 1992. Thermodynamic data for minerals: a critical assessment. In: *The stability of minerals* (G.D. Price and N.L. Ross, eds.), Chapman & Hall, London, 267-328.

Ernst, W. G. 1968. *Amphiboles.* Springer-Verlag, New York, 125p.

Essene, E. J. and Peacor, D. R. 1995. Clay mineral thermometry - A critical perspective. *Clays Clay Miner.*, 43, 540-553.

Essene, E. J. and Peacor, D. R. 1997. Illite and smectite: Metastable, stable or unstable? Further discussion and a correction. *Clays Clay Miner.*, 45(1), 116-122.

Fein, J. B., Hemley, J. J., D'Angelo, W. M., Komninou, A. and Sverjensky, D. A. 1992. Experimental study of iron-chloride complexing in hydrothermal fluids. *Geochim. Cosmochim. Acta*, 56, 3179-3190.

Felmy, A. R., Rai, D. and Amonette, J. E. 1990. The solubility of barite and celestite in sodium sulfate: Evaluation of thermodynamic data. *J. Soln. Chem.*, 19(2), 175-185.

Fisher, J. R. and Barnes, H. L. 1972. The ion-product constant of water to 350°. *J. Phys. Chem.*, 76(1), 90-99.

Fournier, R. O. 1960. Solubility of quartz in water in the temperature interval from 25°C to300°C. *Geol. Soc. Amer. Bull.*, 71, 1867-1868.

Fournier, R. O. 1973. Silica in thermal waters: Laboratory and field investigation. *Proc. Symp. on Hydrogeochemistry and Biochemistry*, Tokyo, Japan, 1970. Vol. I. Hydrogeochemistry. Clarke, Washington, D. C., 122-138.

Fournier, R. O. 1977. Chemical geothermometers and mixing models for geothermal systems. *Geothermics*, 5, 41-51.

Fournier, R. O. and Rowe, J. J. 1966. Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. *Am. J. Sci*, 264, 685-697.

Fournier, R. O. and Rowe, J. J. 1977. The solubility of amorphous silica in water at high temperatures and pressures. *Amer. Mineral.*, 62, 1052-1056.

Fournier, R. O. and Potter, R. W. 1982. An equation correlating the solubility of quartz in water from 25° to 900°C at pressures up to 10,000 bars. *Geochim. Cosmochim. Acta*, 46, 1969-1973.

Frantz, J. D. and Marshall, W. L. 1982. Electrical conductances and ionization constants of calcium chloride and magnesium chloride in aqueous solutions at temperatures to 600°C and pressures to 4000 bars. *Am. J. Sci.*, 282, 1666-1693.

Fricke, R. and Jucaitis, P. 1930. Untersuchen über die gleichgewichte in den systemen Al_2O_3-Na_2O-H_2O und Al_2O_3-K_2O-H_2O. *Z. Anorg. Allg. Chem.*, 191, 129-149.

Frink, C. R. and Peech, M. 1962. The solubility of gibbsite in aqueous solutions and soil extracts. *Soil Sci. Soc. Amer. Proc.*, 26, 346-347.

Frink, C. R. and Peech, M. 1963. Hydrolysis of the aluminum ion in dilute solutions. *Inorg. Chem.*, 2, 473-478.

Fulda, W. and Ginsberg, H. 1951. *Tonerde und Aluminium*. Walther de Gruyter and Co., Berlin, v.1, 31-32.

Fyfe, W. S., Turner, F. J. and Verhoogen, J. 1958. Metamorphic reactions and metamorphic facies. *Geol. Soc. America Mem.*, 75, 253p.

Gammons, C. H. and Seward, T. M. 1996. Stability of manganese (II) chloride complexes from 25 to 300°C. *Geochim. Cosmochim. Acta*, 60(22), 4295-4311.

Ganor, J., Mogollon, J. L. and Lasaga, A. C. 1995. The effect of pH on kaolinite dissolution rates and on activation energy. *Geochim. Cosmochim. Acta.*, 59(6), 1037-1052.

Garrels, R. M. and Christ, C. L. 1965. *Solutions, Minerals and Equilibria*. Harper & Row, New York, N. Y. 450p.

Garrels, R. M., Thompson, M. E. and Siever, R. 1961. Control of carbonate solubility by carbonate complexes. *Am. J. Sci.*, 259, 24-45.

Giggenbach, W. F. 1985. Construction of thermodynamic stability diagrams involving dioctahedral potassium clay minerals. *Chem. Geol.*, 49, 231-242.

Gillespie, S. E., Oscarson, J. L., Chen, X., Izatt, R. M. and Pando, C. 1992. Thermodynamic quantities for the interaction of Cl^- with Mg^{2+}, Ca^{2+} and H^+ in aqueous solution from 250 to 325°C. *J. Soln. Chem.*, 21(8), 761-788.

Gimblett, F. G. R. and Monk, C. B. 1954. E.M.F. studies of electrolytic dissociation. Part 7. - Some alkali and alkaline earth metal hydroxides in water. *Trans. Faraday Soc.*, 50, 965-972.

Gislason, S. R., Heaney, P. J., Oelkers, E. H. and Schott, J. 1997. Kinetic and thermodynamic properties of moganite, a novel silica polymorph. *Geochim. Cosmochim. Acta*, 61(6), 1193-1204.

Goodman, J. B. and Krase, N. W. 1931. Solubility of nitrogen in water at high pressures and temperatures. *Ind. Eng. Chem.*, 23, 401-404.

Gordon, T. M. 1973. Determination of internally consistent thermodynamic data from phase equilibrium experiments. *Journal of Geology*, 81, 199-208.

Gottschalk, M. 1997. Internally consistent thermodynamic data for rock-forming minerals in the system SiO_2-TiO_2-Al_2O_3-Fe_2O_3-CaO-MgO-FeO-K_2O-Na_2O-H_2O-CO_2. *Eur. J. Mineral.*, 9, 175-223.

Govett, G. J. S. 1961. Critical factors in the colorimetric determination of silica. *Anal. Chim. Acta*, 25, 69-80.

Greenberg, S. A. and Price, E. W. 1957. The solubility of silica in solutions of electrolytes. *J. Phys. Chem.*, 61, 1539-1541.

Greenwald, I. 1941. The dissociation of calcium and magnesium carbonates and bicarbonates. *J. Biol. Chem.*, 141, 789-796.

Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C. and Wanner, H. 1992. *Chemical thermodynamics of uranium*. Elsevier Science Publ., Amsterdam, 715p.

Haar, L., Gallagher, J. S. and Kell, G. S. 1984. *NBS/NRC Steam Tables. Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units*. Hemisphere Pub., Washington, D. C., 320p.

Haas, J. L., Jr. 1974. PHAS20, a program for simultaneous multiple regression of a mathematical model to thermochemical data. NTIS AD-780301. 162p.

Haas, J. L., Jr., and Fisher, J.R. 1976. Simultaneous evaluation and correlation of thermodynamic data. *Am. J. Sci.*, 276, 525-545.

Haas, J. R., Shock, E. L. and Sassani, D. C. 1995. Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. *Geochim. Cosmochim. Acta*, 59, 4329-4350.

Halbach, H. and Chatterjee, N. D. 1984. An internally consistent set of thermodynamic data for twenty one CaO-Al_2O_3-SiO_2-H_2O phases by linear programming. *Contrib. Mineral. Petrol.*, 88, 14-23.

Harman, R. W. 1928. Aqueous solutions of sodium silicates: Part VIII. *J. Phys. Chem.*, 32, 44-60.

Harned, H. S. and Robinson, R. A. 1940. Temperature variation of the ionization constants of weak electrolytes. *Trans. Faraday Soc.*, 36, 973-978.

Harned, H. S. and Scholes, S. R. 1941. The ionization constant of HCO_3^- from 0 to 50°. *J. Amer. Chem. Soc.*, 63, 1706-1709.

Harned, H. S. and Bonner, F. T. 1945. The first ionization of carbonic acid in aqueous solutions of sodium chloride. *J. Amer. Chem. Soc.*, 67, 1026-1031.

Harrison, W. J. and Thyne, G. D. 1992. Prediction of clastic diagenesis in the presence of organic acids. *Geochim. Cosmochim. Acta*, 56, 565-586.

Hasegawa, Y., Kawashiwa, H. and Sekine, T. 1970. Studies of the alkaline earth complexes in various solutions-V. Calcium(II) and strontium(II) complexes with carbonate ions in 1 M sodium chloride media. *Bull. Chem. Soc. Japan*, 43, 1718-1722.

Haselton Jr. A.T., Cygan G.L. and Jenkins D.M. 1995. Experimental study of muscovite stability in pure H_2O and 1 molal KCl-HCl solutions. *Geochim. Cosmochim. Acta, 59:3*, 429-442.

Heaney, P. J. and Post, J. E. 1992. The widespread distribution of a novel silica polymorph in microcrystalline quartz varieties. *Science*, 255, 441-443.

Heinrich, C. A. and Seward, T. M. 1990. A spectrophotometric study of aqueous iron (II) chloride complexing from 25 to 200°C. *Geochim. Cosmochim. Acta*, 54, 2207-2221.

Helgeson, H. C. 1969. Thermodynamics of hydrothermal systems at elevated

temperatures and pressures. *Am. J. Sci.*, 267, 729-804.

Helgeson, H. C. 1981. Prediction of the thermodynamic properties of electrolytes at high pressures and temperatures. In. *Chemistry and geochemistry of solutions at high temperatures and pressures* (D. T. Rickard and F. E. Wickman, eds.), Pergamon Press, New York, 133-177.

Helgeson, H. C. and Kirkham, D. H. 1974a. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. I. Summary of the thermodynamic/electrostatic properties of the solvent. *Am. J. Sci.*, 274, 1089-1198.

Helgeson, H. C. and Kirkham, D. H. 1974b. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. II. Debye-Hückel parameters for activity coefficients and relative partial molal properties. *Am. J. Sci.*, 274, 1199-1261.

Helgeson, H. C. and Kirkham, D. H. 1976. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. III. Equation of state for aqueous species at infinite dilution. *Am. J. Sci.*, 276, 97-240.

Helgeson, H.C., Delany, J.M., Nesbitt, H. W., and Bird, D.K. 1978. Summary and critique of the thermodynamic properties of rock-forming minerals. *Am. J. Sci.*, 278-A, 1-229.

Helgeson, H. C., Kirkham, D. H. and Flowers, G. C. 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb. *Am. J. Sci.*, 281, 1249-1516.

Hemingway, B. S. and Robie, R. A. 1977. Enthalpies of formation of low albite ($NaAlSi_3O_8$), gibbsite ($Al(OH)_3$) and $NaAlO_2$: revised values for $\Delta H^\circ_{f,298}$ and $\Delta G^\circ_{f,298}$ of some alumino-silicate minerals. *U.S. Geol. Survey Jour. Research*, 5, 413-429.

Hemingway, B.S., Hass, J.L., Jr., and Robinson, G.R., Jr. 1982. Thermodynamic properties of selected minerals in the system Al_2O_3-CaO-SiO_2-H_2O at 298.15°K and 1 bar (10^5 pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1544. 70p.

Hemingway B.S., Robie R.A. and Apps, J.A. 1991. Revised values for the thermodynamic properties of boehmite, AlO(OH), and related species and phases in the system Al-H-O. *Amer. Mineral., 76*, 445-457.

Hemley, J. J. 1959. Some mineralogical equilibria in the system K_2O-Al_2O_3-SiO_2-H_2O. *Am. J. Sci.*, 257, 241-270.

Hemley, J. J. and Jones, W. R. 1964. Chemical aspects of hydrothermal alteration with emphasis on hydrogen ion metasomatism. *Econ. Geol.*, 59, 238-369.

Hemley, J. J., Montoya, J. W., Christ, C. L. and Hostetler, P. B. 1977a. Mineral equilibria in the MgO-SiO_2-H_2O system: I. Talc-chrysotile-forsterite-brucite stability relations. *Am. J. Sci*, 277, 322-351.

Hemley, J. J., Montoya, J. W., Shaw, D.R. and Luce, R. W. 1977b. Mineral equilibria in the MgO-SiO_2-H_2O system: II. Talc-antigorite-forsterite-anthophyllite-enstatite stability relations and some geologic implications in the system. *Am. J. Sci*, 277, 353-383.

Hemley, J.J., Montoya, J.W., Marinenko, J.W., and Luce, R.W. 1980. Equilibria in the system Al_2O_3-SiO_2-H_2O and some general implications for alteration/ mineralization processes. *Econ. Geol.*, 75, 210-228.

Hepler, L. G., Stokes, J. M. and Stokes, R. H. 1965. Dilatometric measurements of apparent molar volumes of dilute aqueous electrolytes. *Trans. Faraday Soc.*, 61, 20-29.

Hitch, B. F. and Mesmer, R. E. 1976. The ionization of aqueous ammonia to 300° in KCl media. *J. Soln. Chem.*, 5, 667-680.

Hitchen, C. S. 1935. A method for experimental investigation of hydrothermal solutions, with notes on its application to the solubility of silica. *Trans. Inst. Mining Met.*, 44, 255-280.

Holland, T.J.B. and Powell, R. 1985. An internally consistent thermodynamic dataset with uncertainties and correlations: 2. Data and results. *J. Metamorphic. Geol.*, 3, 343-370.

Holland, T.J.B. and Powell, R. 1990. An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K_2O-Na_2O –CaO –MgO –MnO –FeO –Fe_2O_3 –Al_2O_3 –TiO_2 –SiO_2 –C–H_2–O_2. *J. Metamorphic. Geol.*, 8, 89-124.

Holm, J. L. and Kleppa, O. J. 1966. The thermodynamic properties of the aluminum silicates. *Amer. Mineral.*, 51, 1608-1622.

Holm, J. L., Kleppa, O. J. and Westrum, E. F., Jr. 1967. Thermodynamics of polymorphic transformations in silica. Thermal properties from 5° to 1070°K and pressure-temperature stability fields for coesite and stishovite. *Geochim. Cosmochim. Acta*, 31, 2289-2307.

Hostetler, J. D. 1984. Electrode reactions, aqueous electrons, and redox potentials in natural waters. *Am. J. Sci*, 284, 734-759.

Hostetler, P. B. 1963. The stability and surface energy of brucite in water at 25°C. *Am. J. Sci.*, 261, 238-258.

Huang, W. H. and Keller, W. D. 1973. Gibbs free energy of formation calculated from dissolution data using specific mineral analyses. III. Clay minerals. *Amer. Mineral.*, 58, 1023-1028.

Huang, W. L. 1993. Stability and kinetics of kaolinite to boehmite conversion under hydrothermal conditions. *Chem. Geol.*, 105, 197-214.

Hudson, J. C. 1925. The solubility of sulfur dioxide in water and in aqueous solutions of potassium chloride and sodium sulphate. *J. Chem. Soc.*, 1925, 1332-1347.

Ikkatai, T. and Okada, N. 1962. Viscosity, specific gravity and equilibrium concentrations of sodium aluminate solutions. In: *Extractive metallurgy of*

aluminum (G. Gerhard and P. T. Stroup, eds.), Interscience Publ., 159-173.

Ingri, N. 1959. Equilibrium studies of polyanions IV. Silicate ions in NaCl medium. *Acta Chem. Scand.*, 13, 758-775.

Ipatieff, B. and Teodorovish, B. P. 1934. Solubility of hydrogen in water under pressure at high temperatures. *Zhurnal Obschei Khimii*, 4, 395-399.

Iwatsuki, T. and Yoshida, H. 1999. Groundwater chemistry and fracture mineralogy in the basement granitic rock in the Tono uranium mine area, Gifu Prefecture, Japan - Groundwater composition, Eh evolution analysis by fracture filling minerals. *Geochemical Journal* (in press).

Izatt, R. M., Eatough, D. and Christensen, J. J. 1967. A study of Pd^{2+}(aq) hydrolysis. Hydrolysis constants and the standard potential for Pd, Pd^{2+} couple. *J. Chem. Soc.*, 1967(A), 1301-1304.

Jackson, K. J. and Helgeson, H. C. 1985. Chemical and thermodynamic constraints on the hydrothermal transport and deposition of tin. II. Interpretation of phase relations in the Southeast Asian tin belt. *Econ. Geol.*, 80(5), 1365-1378.

Jacobsen, R. L. and Langmuir, D. 1974. Controls on the quality variations of some carbonate spring waters. *J. Hydrol.*, 23, 247-265.

Jenkins, I. L. and Monk, C. B. 1950. The conductances of sodium, potassium and lanthanum sulfates at 25°. *J. Amer. Chem. Soc.*, 72, 2695-2698.

Jiang, C. 1996. Solubility and solubility constant of barium sulfate in aqueous sodium sulfate solutions between 0 and 80°C. *J. Soln. Chem.*, 25(1), 105-111.

Johnson, G. K. and Bauman, J. E., Jr. 1978. Equilibrium constants for the aquated iron(II) cation. *Inorg. Chem.*, 17, 2774-2779.

Johnson G.K., Tasker I.R., Flotow H.E., O'Hare P.A.G. and Wise W.S. 1992. Thermodynamic studies of mordenite, dehydrated mordenite, and gibbsite. *Amer. Mineral., 77*, 85-93.

Johnson, J. W. and Norton, D. 1991. Critical phenomena in hydrothermal systems: State, thermodynamic, electrostatic, and transport properties of H_2O in the critical region. *Am. J. Sci.*, 291, 541-648.

Johnson, J. W., Oelkers, E. H., and Helgeson, H. C. 1991. SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0° to 1000°C. *Geol. Soc. Am.* short-course manual, San Diego, Ca., Oct. 21-24, 1991.

Johnson, J. W., Oelkers, E. H., and Helgeson, H. C. 1992. SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0° to 1000°C. *Computers and Geosciences*, 18, 899-947.

Johnson, K. S. and Pytkowicz, R. M. 1978. Ion association with H^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} in aqueous solutions at 25°C. *Am. J. Sci.*, 278, 1428-1447.

Kamei, G. 1997. Natural analouge study of waste glass dissolution in bentonite. PNC

TN8410 97-035, Power Reactor and Nuclear Fuel Development Corp., Tokai-Mura, Ibaraki, Japan (in Japanese).

Kelley, K. K. 1960. Contributions to the data on theoretical metallurgy. XIII. High temperature heat content, heat capacity and entropy data for the elements and inorganic compounds. *U.S. Bur. Mines. Bull.*, 584, 232p.

Kelley, K. K., Todd, S. S., Orr, R. L., King, E. G. and Bonnickson, K. R. 1953. Thermodynamic properties of sodium-aluminum and potassium-aluminum silicates. *U.S. Bur. Mines. Rept. Inv.*, 4955, 21p.

Kennedy, G. C. 1950. A portion of the system silica-water. *Econ. Geol.*, 45, 629-653.

Kerrick, D. M. 1987. Cold seal systems. In. *Hydrothermal experimental techniques* (G. C. Ulmer and H. L. Barnes, eds.), John Wiley and Sons, New York, 293-323.

Kharaka, Y. K., Carothers, W. W. and Rosenbauer, R. J. 1983. Thermal decarboxylation of acetic acid: Implications for origin of natural gas. *Geochim. Cosmochim. Acta*, 47, 397-422.

Kharaka, Y. K., Law, L. M., Carothers, W. W. and Goerlitz, D. F. 1986. Role of organic species dissolved in formation waters from sedimentary basins in mineral diagenesis. In: *Roles of organic matter during sediment diagenesis* (D. L. Gautier, ed.), Soc. Econ. Paleontol. Min., SEPM Spec. Pub., 38, 111-122.

Kharaka, Y. K., Lundegard, P. D., Ambats, G., Evans, W. C. and Bischoff, J. L. 1993. Generation of aliphatic acid anions and carbon dioxide by hydrous pyrolysis of crude oils. *Appl. Geochem.*, 8, 317-324.

Khitarov, N. I. 1956. The 400°C isotherm for the system H_2O-SiO_2 at pressures up to 2,000 kg/cm^2. *Geochemistry*, 1956 (1), 55-61.

Khodakovsky, I. L., Katorcha, L. V. and Kuyunko, N. S. 1980. Thermodynamic properties of compounds in the Al_2O_3-H_2O system and their equilibrium relations in the range 25-300°C. *Geokhimia*, 11, 1606-1624 (in Russian).

King, E. G. 1955. Low-temperature heat capacity and entropy at 298.16°K of analcite. *J. Am. Chem. Soc.*, 87, 2192-2193.

King, E. G. and Weller, W. W. 1961. Low-temperature heat capacities and entropies at 298.15°K of diaspore, kaolinite, dickite, and halloysite. *U.S. Bur. Mines Rept. Inv.*, 5810, 6p.

King, E. G., Ferrante, M. J. and Pankratz, L. B. 1975. Thermodynamic data for $Mg(OH)_2$ (brucite). *U.S. Bur. Mines Rept. Inv.*, 8041, 13p.

Kitahara, S. 1960. The solubility of quartz in water at high temperatures and high pressures. *Rev. Phys. Chem. Japan*, 30, 109-114.

Kittrick, J. A. 1966a. The free energy of formation of gibbsite and $Al(OH)_4^-$ from solubility measurements. *Soil Sci. Soc. Amer. Proc.*, 30, 595-601.

Kittrick, J. A. 1966b. Free energy of formation of kaolinite from solubility measurements. *Amer. Mineral.*, 51, 1457-1466.

Kiseleva, I. A., Topor, N. D. and Mel'chakova, L. V. 1972. Experimental determination of the heat content and heat capacity of grossularite, andradite and pyrope [abs.]. *Geochim. Internat.*, 9, p.1087.

Kiseleva, I. A., Topor, N. D. and Andreyenko, E. D. 1974. Thermodynamic parameters of minerals of the epidote group. *Geochim. Internat.*, 11, 389-398.

Klots, C. E. and Benson, B. B. 1963. Solubilities of nitrogen, oxygen and argon in distilled water. *J. Marine Res.*, 21, 48-57.

Kofler, M. 1912. Die löslichkeit der Ra-emanation in wasser in ihrer abhängigkeit von der temperatur. *Sitsungsber. Akad. Wiss. Wien, Math-Naturwiss., Kl*, 121, 2169-2180.

Kolassa, J. E. 1990. Confidence intervals for thermodynamic constants. *Geochim. Cosmochim. Acta*, 55, 3543-3552.

Krupka, K. M., Robie, R. A., and Hemingway, B. S. 1979. High-temperature heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ grossular, and $NaAlSi_3O_8$ glass. *Amer. Mineral.*, 64, 86-101.

Krupka, K. M., Kerrick, D. M. and Robie, R. A. 1977a. High temperature heat capacities of dolomite, talc and tremolite, and implications to equilibrium in the siliceous dolomite system [abs.]. *Geol. Soc. America Abs. with Programs*, 9, p.1060.

Krupka, K. M., Robie, R. A. and Hemingway, B. S. 1977b. The heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular and $NaAlSi_3O_8$ glass between 350 and 1000 K [abs.]. *Am. Geophys. Union Trans.*, 58, p.523.

Kunze, G. 1961. Antigorit. Stuktur, theortische grundlagen und ihre praktische bedeutung für weitere serpentin-forschung. *Fortschr. Mineralogie*, 39, 206-324.

Kuyunko, N. S., Malinin, S. D. and Khodakovsky, I. L. 1983. An experimental study of aluminum ion hydrolysis at 150, 200, and 250°C. *Geochem. Internat.*, 20, 76-86.

Lagerstrom, G. 1959. Equilibrium studies of polyanions III. Silicate ions in $NaClO_4$ medium. *Acta Chem. Scand.*, 13, 722-736.

Langmuir, D. 1968. Stability of calcite based on aqueous solubility measurements. *Geochim. Cosmochim. Acta*, 32(8), 835-851.

Langmuir, D. 1969. The Gibbs free energies in the system $Fe\text{-}O_2\text{-}H_2O\text{-}CO_2$ at 25°C. *USGS Prof. Paper 650-B*, 180-183.

Langmuir, D. 1997. *Aqueous Environmental Geochemistry*. Prentice Hall, Upper Saddle River, N. J. 600p.

Larson, T. E., Sollo, F. W. and McGurk, F. F. 1973. Complexes affecting the solubility of calcium carbonate in water. Research Rept. 68. Univ. Illinois Water Resources Center, Urbana, Ill., 49p.

Lavrova, E. M. and Tudorovskaya, G. L. 1977. Solubility of sulfur dioxide in aqueous hydrochloric acid solutions. *J. App. Chem. USSR*, 50, 1102-1106.

Lemire, R. J., Saluja, P. P. S. and Campbell, A. B. 1992. Aqueous partial molar heat capacities and volumes of $NaTcO_4$ and $NaReO_4$. *J. Soln. Chem.*, 21, 507-523.

Levelt-Sengers, J. M. H., Kamgar-Parsi, B., Balfour, F. W., and Sengers, J. V. 1983. Thermodynamic properties of stream in the critical region. *J. Phys. Chem. Ref. Data*, 12(1), 1-28.

Lietzke, M. H., Stoughton, R. W. and Young, T. F. 1961. The bisulfide acid constant from 25 to 225° as computed from solubility data. *J. Phys. Chem.*, 65, 2247-2249.

Liou, J. G. 1971. P-T stabilities of laumontite, wairakite, lawsonite, and related minerals in the system $CaAl_2Si_2O_8$-SiO_2-H_2O. *Jour. Petrology*, 12(2), 379-411.

Lofgren, G. 1987. Internally heated systems. In. *Hydrothermal experimental techniques* (G. C. Ulmer and H. L. Barnes, eds.), John Wiley and Sons, New York, 324-332.

Loy, H. L. and Himmelblau, P. M. 1961. The first ionization constant of hydrogen sulfide in water. *J. Phys. Chem.*, 65, 264-267.

Lundegard, P. D. and Kharaka, Y. K. 1990. Geochemistry of organic acids in subsurface waters - field data, experimental data, and models. In. *Chemical modeling of aqueous systems II* (D. C. Melchior and R. L. Bassett, eds.), Am. Chem. Soc., Washington, D. C., 169-189.

Lyapunov, A. N., Khodakova, A. G. and Galkina, Z. G. 1964. Solubility of hydrargillite in NaOH solutions containing soda or sodium chloride at 60°C and 95°C. *Tsvetnye Metally*, 37(2), 48-51.

Mackenzie, F. T. and Gees, R. 1971. Quartz: Synthesis at earth-surface conditions. *Science*, 173, 533-535.

Mah, A. D., Pankratz, L. B., Weller, W. W. and King, E. G. 1967. Thermodynamic data for cuprous and cupric oxides. *U.S. Bur. Mines Rept. Inv.*, 7026, 20p.

Maier, C. G. and Kelley, K. K. 1932. An equation for the representation of high temperature heat content data. *J. Am. Chem. Soc.*, 54, 1064-1072.

Majer, V. and Stulik, K. 1982. A study of the stability of alkaline-earth metal complexes with fluoride and chloride ions at various temperatures by potentiometry with ion-selective electrodes. *Talanta*, 29, 145-148.

Malinin, S. D. and Savelyeva, N. I.. 1972. The solubility of CO_2 in NaCl and $CaCl_2$ solutions at 25°, 50° and 75°C under elevated pressures. *Geochem. Internat.*, 9(5), 410-418.

Malinin, S. D. and Kurovskaya, N. A. 1975. Solubility of CO_2 in chloride solutions at elevated temperatures and pressures. *Geochem. Internat.*, 12(2), 199-201.

Malinin, S. D., Uchameyschvili, N. Ye. and Khitarov, N. I. 1969. Application of the theory of strong electrolytes to the solubility of barite in aqueous metal chlorides

under hydrothermal conditions. *Geokhimiya*, 927-938.

Markham, A. E. and Kobe, K. A. 1941. The solubility of carbon dioxide and nitrous oxide in aqueous salt solutions. *J. Am. Chem. Soc.*, 63, 449-454.

Maronny, G. 1959. Constantes der dissociation de l'hydrogenène sulfuré. Electrochim. Acta, 1, 58-69.

Marshall, W. L. and Jones, E. V. 1966. Second dissociation constant of sulfuric acid from 25 to 350° evaluated from solubilities of calcium sulfate in sulfuric acid solutions. *J. Phys. Chem.*, 70, 4028-4040.

Mattigod, S. V. and Sposito, G. 1978. Improved method for estimating the standard free energies of formation ($\Delta G^{\circ}_{f,\,298.15}$) of smectites. *Geochim. Cosmochim. Acta.*, 42, 1753-1762.

May, H. M., Helmke, P. A. and Jackson, M. L. 1979. Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C. *Geochim. Cosmochim. Acta*, 43, 861-868.

May, H. M., Kinniburgh, D. G., Helmke, P. A. and Jackson, M. L. 1986. Aqueous dissolution, solubilities and thermodynamic stabilities of common aluminosilicate clay minerals: Kaolinite and smectites. *Geochim. Cosmochim. Acta.*, 50, 1667-1677.

Markham, A. E. and Kobe, K. A. 1941. The solubility of gases in liquids. *Chem. Rev.*, 28, 519-588.

Marshall, W. L. and Jones, E. V. 1966. Second dissociation constant of sulfuric acid from 25 to 350°C evaluated from solubilities of calcium sulfate in sulfuric acid solutions. *J. Phys. Chem.*, 70, 4028-4040.

McCollough, J. P. and Scott, D.W. 1968. *Experimental Thermodynamics.* Butterworths, London. 606p.

McGee, K. A. and Hostetler, P. B. 1975. Stability constants for $MgOH^{+}$ and brucite below 100°C. *Am. Geophys. Union Trans. (EOS)*, 54, p.487.

Melcher, A. C. 1910. The solubility of silver chloride, barium sulphate and calcium sulphate at high temperature. *J. Am. Chem. Soc.*, 32, 50-66.

Mesmer, R. E. 1971. Hydrolysis of iron(2+) in dilute chloride at 25°. *Inorg. Chem.*, 10, 857-858.

Mesmer, R. E., Baes, C. F., Jr. and Sweeton, F. H. 1972. Acidity measurements at elevated temperatures. VI. Boric acid equilibria. *Inorg. Chem.*, 11, 537-543.

Mesmer, R. E., Patterson, C. S., Busey, R. H. and Holmes, H. F. 1989. Ionization of acetic acid in NaCl(aq) media: A potentiometric study to 573 K and 130 bar. *J. Phys. Chem.*, 93, 7483-7490.

Miller, G. R. and Kester, D. R. 1976. Sodium fluoride ion-pairs in seawater. *Mar. Chem.*, 4, 67-82.

Mills, K. C. 1974. *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides.*

Butterworths, London, 845p.

Montoya, J.W. and Hemley, J. J. 1975. Activity relations and stabilities in alkali feldspar and mica alteration reactions. *Econ. Geol.*, 70, 577-594.

Morey, G. W. 1957. The solubility of solids in gases. *Econ. Geol.*, 52, 225-251.

Morey, G. W. and Hesselgesser, J. M. 1951. The solubility of quartz and some other substances in superheated steam at high pressures. *Amer. Soc. Mech. Eng. Trans.*, 73, 865-875.

Morey, G. W., Fournier, R. O. and Rowe, J. J. 1962. The solubility of quartz in water in the temperature interval from 25° to 300°C. *Geochim. Cosmochim. Acta.*, 26, 1029-1043.

Morey, G. W., Fournier, R. O. and Rowe, J. J. 1964. The solubility of amorphous silica at 25°. *J. Geophys. Res.*, 69(10), 1995-2002.

Morrison, T. J. and Billet, F. 1952. The salting-out of nonelectrolytes. Part II. The effect of variation of the nonelectrolyte. *J. Chem. Soc., London*, 1952, 3819-3822.

Morrison, T. J. and Johnstone, N. B. 1954. Solubilities of the inert gases in water. *J. Chem. Soc., London*, 1954, 3441-3446.

Morss, L. R. 1976. Thermochemical properties of yttrium, lanthanum and lanthanide elements and ions. *Chem. Rev.*, 76, 827-841.

Murphy W.M., Pabalan R.T., Prikryl J.S. and Goulet C.J. 1996. Reaction kinetics and thermodynamics of aqueous dissolution and growth of analcime and Na-clinoptilolite at 25°C. *Am. J. Sci.*, 296, 128-186.

Murray, C. N., Riley, J. P. and Wilson, T. R. S. 1969. The solubility of gases in distilled water and sea water - I. Nitogen. *Deep-Sea Res.*, 16, 297-310.

Nagy, K.L. and Lasaga, A.C. 1992. Dissolution and precipitation kinetics of gibbsite at 80°C and pH 3: The dependence on solution saturation state. *Geochim. Cosmochim. Acta*, 56, 3093-3111.

Nagy, K. L., Blum, A. E. and Lasaga, A. C. 1991. Dissolution and precipitation kinetics of kaolinite at 80°C and pH 3: The dependence on solution saturation state. *Am. J. Sci.*, 291, 649-686.

Nakayama, F. S. 1971a. Thermodynamic functions for the dissociation of $NaHCO_3°$, $NaCO_3^-$, H_2CO_3 and HCO_3^-. *J. Inorg. Nucl. Chem.*, 33, 1287-1291.

Nakayama, F. S. 1971b. Magnesium complex and ion-pair in $MgCO_3$-CO_2 solution system. *J. Chem. Eng. Data*, 16, 178-181.

Näsänen, R. 1946. Zur einwirkung der säure- und basenzusatze auf die fallungskurve von bariumcarbonat.. *Suomen Kemistilehti*, 90, 24-2.

Näsänen, R. 1947. Potentiometric study on the first ionization of carbonic acid in aqueous solutions of sodium chloride. *Acta Chem. Scand.*, 67, 204-209.

Näsänen, R., Merilainen, P. and Leppanen, K. 1961. Potentiometric determination of the solubility product of lead carbonate. *Acta Chem. Scand.*, 15, 913-918.

Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L. 1971. *Handbook of Thermodynamic Data*. Atomizdat, Moscow, 327p.

Navrotsky, A. 1987. Models of crystalline solutions. In. *Thermodynamic modeling of geological materials: Minerals, fluids and melts* (I.S.E. Carmichael and H. P. Eugster, eds.), 17, Reviews in Mineralogy, Mineral. Soc. Amer., 35-69.

Newton, R. C. 1987. Thermodynamic analysis of phase equilibria in simple mineral systems. In. *Thermodynamic modeling of geological materials: Minerals, fluids and melts* (I.S.E. Carmichael and H. P. Eugster, eds.), 17, Reviews in Mineralogy, Mineral. Soc. Amer., 1-33.

Nikolaeva, N. M. and Tolpygina, L. N. 1969. Hydrolysis of aluminum salts at elevated temperatures. *Izvestiya Sibirskogo Otdeleniya AN SSSR, Seriya Khimicheskikh Nauk*, 7, 49-55 (in Russian).

Nordstrom, D.K. and Munoz, J.L. 1985. *Geochemical Thermodynamics*. Benjamin /Cummings, Menlo Park, Ca., 477p.

Nordstrom, D.K., Plummer, L.N., Langmuir, D., Busenberg, E., May, H.M., Jones, B.F. and Parkhurst, D.L. 1990. Revised chemical equilibrium data for major water-mineral reactions and their limitations. In. *Chemical modeling of aqueous systems II*, (D.C. Melchior and R.L. Bassett, eds.), Am. Chem. Soc. Symp. Ser., 416, 399-413.

Noyes, A. A. 1907. The electrical conductivity of aqueous solutions. *Carnegie Inst. Publ. No. 63*, Washington, D. C., 352p.

Oda, C., Yoshikawa, H. and Yui, M. 1996. Effects of aging on the solubility of palladium. In. *Scientific Basis for Nuclear Waste Management XIX* (W. M. Murphy and D.A. Knecht, eds.), Mat. Res. Soc. Symp., 412, 881-887.

Oda, C., Shibata, M. and Yui, M. 1999. Calculation of porewater chemistry in compacted bentonite for the 2nd progress (PA) report. Japan Nuclear Cycle Development Institute, Tokai-Mura, Ibaraki, Japan, Technical Report (in preparation).

Oelkers, E. H. and Helgeson, H. C. 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Dissociation constants for supercritical alkali metal halides at temperatures from 400 to 800°C and pressures from 500 to 4000 bar. *J. Phys. Chem.*, 92, 1631-1639.

Oelkers, E.H., Helgeson, H.C., Shock, E.L., Sverjensky, D.A., Johnson, J.W. and Pokrovskii, V.A. 1995. Summary of the apparent standard molal Gibbs free energies of formation of aqueous species, minerals, and gases at pressures 1 to 5000 bars and temperatures 25 to 1000°C. *J. Phys. Chem. Ref. Data*, 24(4), 1401-1560.

Okamoto, G., Okura, T. and Goto, K. 1957. Properties of silica in water. *Geochim. Cosmochim. Acta*, 12, 123-132.

Olofsson, G., Oshodi, A. A., Qvarnstrom, E. and Wadso, I. 1985. Calorimetric measurements on slightly soluble gases in water. Enthalpies of solution of helium, neon, argon, krypton, xenon, methane, ethane, propane, 1-butane and oxygen at 288.15, 298.15 and 308.15 K. *J. Chem. Thermo.*, 16, 1041-1052.

Onda, K., Sada, E. Kobayashi, T., Kito, S. and Ito, K. 1970. Salting-out parameters of gas solubility in aqueous salt solutions. *J. Chem. Eng. Data*, 3(1), 18-24.

O'Sullivan, T. D. and Smith, N. O. 1970. The solubility and partial molar volume of nitrogen and methane in water and in aqueous sodium chloride from 50 to 125° and 100 to 600 atm. *J. Phys. Chem.*, 74, 1460-1466.

Oscarson, J. L., Izatt, R. M., Brown, P. R., Pawlak, Z., Gillespie, S. E. and Christensen, J. J. 1988a. Thermodynamic quantities for the interaction of SO_4^{2-} with H^+ and Na^+ in aqueous solution from 150 to 320°C. *J. Soln. Chem.*, 17(9), 841-863.

Oscarson, J. L., Gillespie, S. E., Christensen, J. J., Izatt, R. M. and Brown, P. R. 1988b. Thermodynamic quantities for the interaction of H^+ and Na^+ with $C_2H_3O_2^-$ and Cl^- in aqueous solution from 275 to 320°C. *J. Soln. Chem.*, 17(9), 865-885.

Packter, A. 1979. Studies on recrystallized aluminum trihydroxide precipitates: The energetics of dissolution by sodium hydroxide solutions. *Coll. Polymer Sci.*, 257, 977-980.

Palmer, D. A. and van Eldik, R. 1983. The chemistry of metal carbonato and carbon dioxide complexes. *Chem. Rev.*, 83, 651-731.

Palmer, D. A. and Drummond, S. E. 1988. Potentiometric determination of the molal formation constants of ferrous acetate complexes in aqueous solutions to high temperatures. *J. Phys. Chem.*, 92, 6795-6800.

Palmer D.A. and Wesolowski D.J. 1992. Aluminum speciation and equilibria in aqueous solution: II. The solubility of gibbsite in acidic sodium chloride solutions from 30 to 70°C. *Geochim. Cosmochim. Acta*, 56, 1093-1111.

Palmer D.A. and Hyde K.E. 1993. An experimental determination of ferrous chloride and acetate complexation in aqueous solutions to 300°C. *Geochim. Cosmochim. Acta, 57,* 1393-1408.

Palmer D.A. and Wesolowski D.J. 1993. Aluminum speciation and equilibria in aqueous solution: III. Potentiometric determination of the first hydrolysis constant of aluminum (III) in sodium chloride solutions to 125°C. *Geochim. Cosmochim. Acta, 57,* 2929-2938.

Palmer, D. A. and Wesolowski, D. J. 1997. Potentiometric measurements of the first hydrolysis quotient of magnesium (II) to 250°C and 5 molal ionic strength (NaCl). *J. Soln. Chem.*, 26(2), 217-232.

Pankratz, L. B. 1964a. High-temperature heat contents and entropies of andalusite, kyanite, and sillimanite. *U.S. Bur. Mines Rept. Inv.*, 6370, 7p.

Pankratz, L. B. 1964b. High-temperature heat contents and entropies of muscovite and dehydrated muscovite. *U.S. Bur. Mines Rept. Inv.*, 6708, 8p.

Pankratz, L. B. 1968a. High-temperature heat contents and entropies of dehydrated analcite, kaliophilite, and leucite. *U.S. Bur. Mines Rept. Inv.*, 7073, 8p.

Pankratz, L. B. 1968b. High-temperature heat contents and entropies of four crystalline sodium-calcium silicates. *U.S. Bur. Mines Rept. Inv.*, 7201, 8p.

Pankratz, L. B. and Kelley, K. K. 1964. High-temperature heat contents and entropies of akermanite, cordierite, gehlenite, and merwinite. *U.S. Bur. Mines Rept. Inv.*, 6555, 5p.

Pankratz, L. B. and King, E. G. 1965. High-temperature heat contents and entropies of two zinc sulfides and for solid solutions of zinc and iron sulfides. *U.S. Bur. Mines Rept. Inv.*, 6371, 6p.

Pankratz, L. B. and King, E. G. 1970. High-temperature enthalpies and entropies of chalcopyrite and bornite. *U.S. Bur. Mines Rept. Inv.*, 7435, 10p.

Parkhurst, D. L., Plummer, L. N. and Thorstenson, D. C. 1980. PHREEQE - a computer program for geochemical calculations. *U. S. Geol. Surv. Water Resour. Invest. Rept.* 82-14.

Parks, G. A. and Pohl, D. C. 1988. Hydrothermal solubility of uraninite. *Geochim. Cosmochim. Acta*, 52, 836-875.

Patterson, C. S., Slocum, G. H., Busey, R. H. and Mesmer, R. E. 1982. Carbonate equilibria in hydrothermal systems. First ionization of carbonic acid in NaCl media to 300°C. *Geochim. Cosmochim. Acta*, 46, 1653-1663.

Patterson, C. S., Busey, R. H. and Mesmer, R. E. 1984. Second ionization of carbonic acid in NaCl media to 250°C. *J. Soln. Chem.*, 13, 647-661.

Pearson, D., Copeland, C. S. and Benson, S. W. 1963. The electrical conductance of aqueous sodium chloride in the range 300 to 383°. *J. Amer. Chem. Soc.*, 85, 1044-1047.

Perkins, D., III, Essene, E. J., Westrum, E. F., Jr., and Wall, V. J. 1977. Application of new thermodynamic data to grossular phase relations. *Contr. Mineral. Petrol.*, 64, 137-147.

Peryea, F. J. and Kittrick, J. A. 1988. Relative solubility of corundum, gibbsite, boehmite, and diaspore at standard state conditions. *Clays Clay Miner.*, 36, 391-396.

Pierotti, R. A. 1965. Aqueous solutions of nonpolar gases. *J. Phys. Chem.*, 69, 281-288.

Pitzer, K. S., Roy, R. N. and Silvester, L. F. 1977. Thermodynamics of electrolytes. 7. Sulfuric acid. *J. Amer. Chem. Soc.*, 99, 4930-4936.

Plummer, L. N. and Busenberg, E. 1982. The solubilities of calcite, aragonite, and vaterite in CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. *Geochim. Cosmochim. Acta.*, 46, 1011-1040.

PNC. 1992. Research and development on geological disposal of high-level radioactive waste. PNC TN1410 93-059, Power Reactor and Nuclear Fuel Development

Corp., Tokai-Mura, Ibaraki, Japan.

Pokrovski, G. S., Schott, J. and Sergeyev, A. S. 1995. Experimental determination of the stability constants of $NaSO_4^-$ and $NaB(OH)_4$ in hydrothermal solutions using a new high-temperature sodium-selective glass electrode - Implications for boron isotopic fractionation. *Chem. Geol.*, 124, 253-265.

Pokrovskii V.A. and Helgeson H.C. 1995. Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: The system Al_2O_3–H_2O–NaCl. *Am. J. Sci., 295*, 1255-1342.

Pokrovskii, V. A. and Helgeson, H. C. 1997a. Calculation of the standard partial molal thermodynamic properties of KCl° and activity coefficients of aqueous KCl at temperatures and pressures to 1000C and 5 kbar. *Geochim. Cosmochim. Acta*, 61(11), 2175-2183.

Pokrovskii V.A. and Helgeson H.C. 1997b. Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: The system Al_2O_3–H_2O–KOH. *Chem. Geol.*, 137, 221-242.

Pokrovskii V.A. and Helgeson H.C. 1998. Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: A thermodynamic interpretation of mineral equilibria in the system K_2O-Na_2O-Al_2O_3-SiO_2-H_2O–HCl. *Geochim. Cosmochim. Acta* (submitted).

Polzer, W. L. and Hem, J. D. 1965. The dissolution of kaolinite. *J. Geophys. Res.*, 70, 6233-6240.

Potter, R. W. and Clynne, M. A. 1978. The solubility of the noble gases He, Ar, Kr and Xe in water up to the critical point. *J. Soln. Chem.*, 7, 837-844.

Powell, R. and Holland, T.J.B. 1985. An internally consistent thermodynamic dataset with uncertainties and correlations: 1 Methods and a worked example. *J. Metamorphic Geol.*, 3, 327-342.

Pray, H. A., Schweickert, C. E. and Minnich, B. H. 1952. Solubility of hydrogen, oxygen, nitrogen, and helium in water at elevated temperatures. *Ind. Eng. Chem.*, 44, 1146-1151.

Price, L. C. 1979. Aqueous solubility of methane at elevated pressures and temperatures. *AAPG Bull.*, 632, 1527-1533.

Prutton, C. F. and Savage, R. L. 1945. The solubility of carbon dioxide in calcium chloride-water solutions at 75, 100 and 120°C and high pressures. *J. Am. Chem. Soc.*, 67, 1550-1554.

Puigdomenech, I., Rard, J. A., Plyasunov, A. V. and Grenthe, I. 1997. Temperature corrections to thermodynamic data and enthalpy calculations. In: *Modeling in Aquatic chemistry* (I. Grenthe and I. Puigdomenech, eds.), OECD/NEA, Paris, 427-493.

Quist, A. S. and Marshall, W. L. 1968. Ionization equilibria in ammonia-water solutions to 700° and to 4000 bars of pressure. *J. Phys. Chem.*, 72, 3123-3128.

Quist, A. S., Franck, E. U., Jolley, H. R. and Marshall, W.L. 1963. Electrical

conductances of aqueous solutions at high temperature and pressure. I. The conductances of potassium sulfate-water solutions from 25 to 800° and at pressures up to 4000 bars. *J. Phys. Chem.*, 67, 2453-2459.

Raaflaub, J. 1960. Untersuchungen über die magnesium komplex verbindungen von oxalet und carbonat. *Helvetiae Chim. Acta.*, 43, 629-634.

Rabe, A. E. and Harris, J. F. 1963. Vapor liquid equilibrium data for the binary system sulfur dioxide and water. *J. Chem. Eng. Data*, 8, 333-336.

Ragnarsdottir, K. V. and Walther, J. V. 1985. Experimental determination of corundum solubilities in pure water between 400-700°C and 1-3 kbar. *Geochim. Cosmochim. Acta*, 49, 2109-2115.

Ramette, R. W. 1986. Copper (II) complexes with chloride ion. *Inorg. Chem.*, 25, 2481-2482.

Ransom, B. and Helgeson, H. C. 1993. Compositional end members and thermodynamic components of illite and dioctahedral aluminous smectite solid solutions. *Clays Clay Miner.*, 41(5), 537-550.

Ransom, B. and Helgeson, H. C. 1994. Estimation of the standard molal heat capacities, entropies, and volumes of 2:1 clay minerals. *Geochim. Cosmochim. Acta*, 58(21), 4537-4547.

Read, A. J. 1975. The first ionization constant of carbonic acid from 25 to250°C and to 2000 bar. *J. Soln.Chem.*, 4, 53-70.

Read, A. J. 1982. Ionization constants of aqueous ammonia from 25 to 250°C and to 2000 bar. *J. Soln.Chem.*, 11, 649-664.

Read, A. J. 1988. The first ionization constant from 25 to 200°C and 2000 bar for orthophosphoric acid. *J. Soln. Chem.*, 17, 213-224.

Reardon, E. J. and Langmuir, D. 1974. Thermodynamic properties of the ion pairs $MgCO_3°$ and $CaCO_3°$ from 10 to 50°C. *Am. J. Sci.*, 274, 599-612.

Reed, B. L. and Hemley, J. J. 1966. Occurrence of pyrophyllite in the kekituk conglomerate, brooks range, northeastern alaska. *U.S. Geol. Survey Prof. Paper* 550-C, p. C162-C166.

Reesman, A. L. and Keller, W. D. 1968. Aqueous solubility of high-alumina and clay minerals. *Amer. Mineral.*, 53, 929-941.

Reiterer, F., Johannes, W. and Gamsjäger, H. 1981. Semimicro determination of solubility constants: Copper (II) carbonate and iron (II) carbonate. *Mikrochim. Acta*, 1, 63-72.

Richardson, C. K. and Holland, H. D. 1979. The solubility of fluorite in hydrothermal solutions, an experimental study. *Geochim. Cosmochim. Acta*, 43, 1313-1325.

Righellato, E. C. and Davies, C. W. 1930. The extent of dissociation of salts in water. II. Uni-bivalent salts. *Trans. Faraday Soc.*, 26, 592-600

Rimstidt, J. D. 1984. Quartz solubility at low temperatures. *Geol. Soc. Amer. Abstr. Prog.*, 16, 635.

Rimstidt, J. D. 1997. Quartz solubility at low temperatures. *Geochim. Cosmochim. Acta.*, 61(13), 2553-2558.

Rimstidt, J. D. and Barnes, H.L. 1980. The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta.*, 44(11), 1683-1699.

Ringbom, A. 1953. Solubility of sulfides. Report to Anal. Sect. of IUPAC.

Robie, R. A. 1987. Calorimetry. In. *Hydrothermal experimental techniques* (G. C. Ulmer and H. L. Barnes, eds.), John Wiley and Sons, New York, 389-422.

Robie, R. A. and Waldbaum, D. R. 1968. Thermodynamic properties of minerals and related substances at 298.15°K (25°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1259, 256p.

Robie, R. A. and Hemingway, B. S. 1973. The enthalpies of formation of nesquehonite, $MgCO_3 \cdot 3H_2O$, and hydromagnesite, $5MgO \cdot 4CO_2 \cdot 5H_2O$. *U.S. Geol. Survey Jour. Research*, 1, 543-547.

Robie, R. A. and Hemingway, B. S. 1991. Heat capacities of kaolinite from 7 to 380 K and of DMSO-intercalated kaolinite from 20 to 310 K. The entropy of kaolinite $Al_2Si_2O_5(OH)_4$. *Clays Clay Miner.*, 39(4), 362-368.

Robie, R. A., Bethke, P. M., Toulmin, M. S. and Edwards, J. L. 1966. X-ray crystallographic data, densities and molar volumes of minerals. In. *Handbook of Physical Constants* (S. Clark, ed.), Geol. Soc. America Mem., 97, 27-73.

Robie, R.A., Hemingway, B.S. and Fisher, J.R. 1978. Thermodynamic properties of minerals and related substances at 298.15°K and 1 bar (105 pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1452, 456p.

Robinson, G.R., Haas, J.L.Jr, Schafer, C.M. and Hazelton, H.T. 1983. Thermodynamic and thermophysical properties of selected phases in the MgO-SiO_2-H_2O-CO_2,CaO-Al_2O_3-SiO_2-H_2O-CO_2, and Fe-FeO-Fe_2O_3-SiO_2 chemical systems, with special emphasis on the properties of basalts and their mineral components. *U.S. Geol. Surv. Open-File Rept.* 83-79, 429p.

Roller, P. S. and Ervin, G. 1940. The system calcium oxide-silica-water at 30 C. The association of silicate ion in dilute alkaline solution. *J. Amer. Chem. Soc.*, 62, 461-471.

Roselle, G. T. and Baumgartner, L. P. 1995. Experimental determination of anorthite solubility and calcium speciation in supercritical chloride solutions at 2 kb from 400 to 600°C. *Geochim. Cosmochim. Acta*, 59(8), 1539-1549.

Routson, R. C. and Kittrick, J. A. 1971. Illite solubility. *Soil Sci. Soc. Amer. Proc.*, 35, 714-718.

Rumyantsev, V. N. 1993. Some specific features of quartz solubility in aqueous chloride solutions at increased temperatures and pressures. *Russ. J. Inorg. Chem.*, 38(6), 897-901.

Rumyantsev, V. N. 1995. Solubility of quartz in NaOH aqueous solutions at elevated temperatures and pressures. *Russ. J. Inorg. Chem.*, 40(1), 40-45.

Russel, A. S., Edwards, J. D. and Taylor, C. S. 1955. Solubility and density of hydrated aluminas in NaOH solutions. *J. Metals*, 7, 1123-1128.

Ryzhenko, B. N. 1963. Determination of the dissociation constants of carbonic acid and the degree of hydrolysis of the CO_3^{--} and HCO_3^- ions in solutions of alkali carbonates and bicarbonates at elevated temperatures. *Geochemistry*, 1963, 151-164.

Ryzhenko, B. N. 1965. Determination of the dissociation constant of hydrofluoric acid and the conditions for replacement of calcite by fluorite. *Geochem. Int.*, 2, 196-199.

Saccocia, P. J. and Seyfried, W. E., Jr. 1990. Talc-quartz equilibria and the stability of magnesium chloride complexes in NaCl-$MgCl_2$ solutions at 300, 350, and 400°C, 500 bars. *Geochim. Cosmochim. Acta*, 54, 3283-3294.

Saccocia P.J. and Seyfried, Jr. W.E. 1993. A resolution of discrepant thermodynamic properties for chamosite retrieved from experimental and empirical techniques. *Amer. Mineral.*, 78, 607-611.

Saddington, A. W. and Krase, N. W. 1934. Vapor-liquid equilibria in the system nitrogen-water. *J. Amer. Chem. Soc.*, 56, 353-361.

Sasaki, Y., Shibata, M., Yui, M. and Ishikawa, H. 1995. Experimental studies on the interaction of groundwater with bentonite. In. *Scientific Basis for Nuclear Waste Management XVIII* (T. Murakami and R.C. Ewing, eds.), Mat. Res. Soc. Symp., 353, 337-344.

Sasamoto, H., Yui, M. and Arthur, R. C. 1999a. Status of geochemical modeling of groundwater evolution at the Tono in-situ test site, Japan. Japan Nuclear Cycle Development Institute, Tokai-Mura, Ibaraki, Japan, Technical Report (in preparation).

Sasamoto, H., Yui, M. and Arthur, R. C. 1999b. Hydrochemical investigation and status of geochemical modeling of groundwater evolution at the Kamaishi in-situ test site, Japan. Japan Nuclear Cycle Development Institute, Tokai-Mura, Ibaraki, Japan, Technical Report (in preparation).

Sasamoto, H., Yui, M. and Arthur, R. C. 1999c. Modeling studies of saline type groundwater evolution - A test case for Mobara groundwater chemistry, Japan. Japan Nuclear Cycle Development Institute, Tokai-Mura, Ibaraki, Japan, Technical Report (in preparation).

Sass, B. M., Rosenberg, P. E. and Kittrick, J. A. 1987. The stability of illite/smectite during diagenesis: An experimental study. *Geochim. Cosmochim. Acta*, 51, 2103-2115.

Sassani, D. C. and Shock, E. L. 1990. Speciation and solubility of palladium in aqueous magmatic-hydrothermal solutions. *Geology*, 18, 925-928.

Sassani, D.C. and Shock, E.L. 1992. Estimation of standard partial molal entropies of aqueous ions at 25°C and 1 bar. *Geochim. Cosmochim. Acta*, 56, 3895-3908.

Sassani, D.C. and Shock, E.L. 1994. Errata to Sassani & Shock (1992). *Geochim. Cosmochim. Acta*, 58, 2756-2758.

Sassani, D. C. and Shock, E. L. 1999. Solubility and transport of platinum-group elements in supercritical fluids: Thermodynamic properties of Ru, Rh, Pd and Pt solids, aqueous ions and aqueous complexes to 5 kbar and 1000 C. *Geochim. Cosmochim. Acta*, (in press).

Saxena, S. K. 1997. Systematization and estimation of thermochemical data on silicates. In: *Modeling in aquatic chemistry* (I. Grenthe and I. Puigdomenech, eds.). OECD/NEA, Paris, 289-323.

Saxena, S. K., Chatterjee, N., Fei, Y. and Shen, G. 1993. *Thermodynamic Data Base for Silicates and Oxides*. Springer Verlag, Heidelberg, 428p.

Schofield, R. K. and Taylor, A. W. 1954. The hydrolysis of aluminum salt solutions. *J. Chem. Soc.*, 4445-4448.

Schwarz, V. R. and Muller, W. D. 1958. Die wasserlosliche monokieselsaure. *Z. Anorg. Allg. Chemie*, 2296, 273-279.

Seewald, J. S. and Seyfried, W. E., Jr. 1991. Experimental determination of portlandite solubility in H_2O and acetate solutions at 100-350°C and 500 bars: constraints on calcium hydroxide and calcium acetate complex stability. *Geochim. Cosmochim. Acta*, 55, 659-669.

Seward, T. M. 1974. Determination of the first ionization constant of silicic acid from quartz solubility in borate buffer solutions to 350°C. *Geochim. Cosmochim. Acta*, 38, 1657-1664.

Sheppard, R. A. and Gude, A. J., III. 1970. Chemical composition and physical properties of phillipsite from the Pacific and Indian oceans. *Amer. Mineral.*, 55, 2053-2063.

Shock, E. L. 1995. Organic acids in hydrothermal solutions: Standard molal thermodynamic properties of carboxylic acids, and estimates of dissociation constants at high temperatures and pressures. *Amer. J. Sci.*, 295, 496-580.

Shock, E.L. and Helgeson, H.C., 1988, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000 C. *Geochim. Cosmochim. Acta*, 52, 2009-2036.

Shock, E.L., and Helgeson, H.C. 1990. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. *Geochim. Cosmochim. Acta*, 54, 915-945.

Shock, E. L. and Koretsky, C. M. 1993. Metal-organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures. *Geochim. Cosmochim. Acta*, 57, 4899-4922.

Shock, E. L. and Koretsky, C. M. 1995. Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of

aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. *Geochim. Cosmochim. Acta*, 59, 1497-1532.

Shock, E.L. Helgeson H.C. and Sverjensky D.A. 1989. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta, 53,* 2157-2183.

Shock E.L., Oelkers, E.H., Johnson, J.W., Sverjensky, D.A. and Helgeson, H.C. 1992. Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures. *J. Chem. Soc. Faraday Trans.*, 88(6), 803-826.

Shock, E. L., Sassani, D. C., Willis, M. and Sverjensky, D. A. 1997a. Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta*, 61(5), 907-950.

Shock, E. L., Sassani, D. C. and Betz, H. 1997b. Uranium in geologic fluids: Estimates of standard partial molal properties, oxidation potentials, and hydrolysis constants at high temperatures and pressures. *Geochim. Cosmochim. Acta*, 61(20), 4245-4266.

Shock, E. L., Sassani, D. C. and Betz, H. 1999. Actinide ions in aqueous solution: Summary of standard state properties and estimates at high temperatures and pressures. *Appl. Geochem.* (submitted).

Siebert, R. M. and Hostettler, P. B. 1977. The stability of the magnesium carbonate ion pair from 10° to 90°C. *Am. J. Sci.*, 277, 716-734.

Siever, R. 1962. Silica solubility, 0-200°C, and the diagenesis of siliceous sediments. *J. Geol.*, 70, 127-150.

Silva, R. J., Bidoglio, G., Rand, M., Robouch, P. B., Wanner, H. and Puigdomenech, I. 1995. *Chemical thermodynamics of americium*. Elsevier Science Publ., Amsterdam, 374p.

Simonson, J. M., Busey, R. H. and Mesmer, R. E. 1985. Enthalpies of dilution of aqueous calcium chloride to low molalities at high temperatures. *J. Phys. Chem.*, 89(4), 557-560.

Singer, P. C. and Stumm, W. 1970. The solubility of ferrous iron in carbonate-bearing waters. *J. Amer. Water Works Assoc.*, 62, 198-202.

Singh, S. S. 1974. The solubility product of gibbsite at 15°, 25°, and 35°C. *Soil Sci. Soc. Amer. Proc.*, 38, 415-417.

Smith, H. J. 1918. On equilibrium in the system ferrous iron in carbonate-bearing waters. *J. Am. Chem. Soc.*, 40, 879.

Steinfink, H. 1958. The crystal structure of chlorite. I. A monoclinic polymorph. *Acta Cryst.*, 11, 191-195.

Stephan, E. F., Hatfield, N. S., Peoples, R. S. and Pray, H. A. H. 1956. The solubility of gases in water and in aqueous uranyl salt solutions at elevated temperatures and pressures. BMI 1067, p. 54, Battelle Mem. Inst., Columbus, Ohio.

Stoessell, R. K. 1979. A regular solution site-mixing model for illites. *Geochim. Cosmochim. Acta*, 43, 1151-1159.

Strübel, G. 1965. Quantitative untersuchungen über die hydrothermale löslichkeit von flusspat (CaF_2). *Neues Jahrb. Mineral. Monatsh.*, 3, 83-95.

Strübel, G. 1967. Zur kenntnis und genetischen bedeutung des systems $BaSO_4$-NaCl-H_2O. *Neues Jahrb. Mineral. Monatsh.*, 223-234.

Stull, D. R. and Prophet, H. 1971. JANAF thermochemical tables, 2nd ed. *Natl. Bur. Standards*, Natl. Standards Ref. Data Ser., NBS37, 1141p.

Su C. and Harsh J.B. 1994. Gibbs free energies of formation at 298 K for imogolite and gibbsite from solubility measurements. *Geochim. Cosmochim. Acta*, 58(6), 1667-1677.

Suleimenov, O. M. and Krupp, R. E. 1994. Solubility of hydrogen sulfide in pure water and in NaCl solutions, from 20 to 320°C and at saturation pressures. *Geochim. Cosmochim. Acta*, 58(11), 2433-2444.

Sullivan, T. O. and Smith, N. O. 1970. The solubility and partial molar volume of nitrogen and methane in water and aqueous sodium chloride from 50° to 125°C and 100 to 600 atm. *J. Phys. Chem.*, 74(7), 1460-1466.

Sverjensky, D.A., 1987, Calculations of the thermodynamic properties of aqueous species and the solubilities of minerals in supercritical electrolyte solutions. In. *Thermodynamic modeling of geologic materials: Minerals, fluids and melts* (I.S.E. Carmichael and H.P. Eugster, eds.), Mineral. Soc. Amer., Reviews in Mineralogy, 17, 177-209.

Sverjensky D.A., Hemley J.J. and D'Angelo W.M. 1991. Thermodynamic assessment of hydrothermal alkali feldspar-mica-aluminosilicate equilibria. *Geochim. Cosmochim. Acta, 55*, 989-1004.

Sverjensky, D.A., Shock, E.L. and Helgeson, H.C. 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000C and 5kb. *Geochim. Cosmochim. Acta*, 61(7), 1359-1412.

Sweeton, F. H. and Baes, C. F., Jr. 1970. The solubility of magnetite and hydrolysis of ferrous ion in aqueous solutions at elevated temperatures. *J. Chem. Thermodynamics*, 2, 479-500.

Szeparowicz, M. 1920. Untersuchungen über die verteilung von radiumemanation in verschiedenen phasen. *Sitsungsber. Akad. Wiss. Wien, Math-Naturwiss., Kl Abt. IIa*, 129, 437-454.

Tagirov, B. R., Zotov, A. V. and Akinfiev, N. N. 1997. Experimental study of dissociation of HCl from 350 to 500 C and from 500 to 2500 bars: Thermodynamic properties of HCl(*aq*). *Geochim. Cosmochim. Acta*, 61(20), 4267-4280.

Tanger, J. C. and Helgeson, H. C. 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes. *Am. J. Sci.*, 288, 19-98.

Tanner, S. P., Walker, J. B. and Choppin, G. R. 1968. Thermodynamic parameters of the alkaline earth mono-fluorides. *J. Inorg. Nucl. Chem.*, 30, 2067-2070.

Tardy, Y. and Garrels, R. M. 1974. A method of estimating the Gibbs energies of formation of layer silicates. *Geochim. Cosmochim. Acta*, 38, 1101-1116.

Templeton, C. C. 1960. Solubility of barium sulfate in sodium chloride solutions from 25° to 95°C. *J. Chem. Eng. Data*, 5, 514-516.

Tiepel, E. W. and Gubbins, K. E. 1972. Partial molal volumes of gases dissolved in electrolyte solutions. *J. Phys. Chem.*, 76, 3044-3049.

Thompson, A. B. 1970. A note on the kaolinite-pyrophyllite equilibrium. *Am. J. Sci.*, 268, 454-458.

Thompson, J. B., Jr., Waldbaum, D. R. and Holvis, G. L. 1974. Thermodynamic properties related to ordering in end-member alkali feldspars. In. *The Feldspars* (W. S. MacKenzie and J. Zussman, eds.), Crane, Russack and Co., New York, 218-248.

Tremaine, P. R. and LeBlanc, J. C. 1980. The solubility of magnetite and the hydrolysis and oxidation of Fe^{2+} in water to 300°C. *J. Soln. Chem.*, 9, 415-442.

Truesdell, A. H. and Hostetler, P. B. 1968. Dissociation constants of KSO_4^- from 10° - 50°C. *Geochim. Cosmochim. Acta*, 32, 1019-1022.

Tsirlina, S. M. 1936. The solubility of aluminum hydroxide in sodium hydroxide solutions (the system $Al(OH)_3$-$NaOH$-H_2O). *Legie Metally*, 5(3), 28-37 (in Russian).

Ulmer, G. C. and Barnes, H. L. 1987. *Hydrothermal experimental techniques*, John Wiley and Sons, New York, 293-323.

van Lier, J. A., de Bruyn, P. L. and Overbeek, J. T. G. 1960. The solubility of quartz. *J. Phys. Chem.*, 64, 1675-1682.

Verdes, G., 1990. Solubilité des hydroxydes d'aluminum entre 20 et 300°C. Propriétés thermodynamiques des principales espéces naturelles du systémes Al_2O_3-H_2O. Ph.D. dissertation, Paul Sabatier Univ., Toulouse, France, 267p.

Verdes, G., Gout, R. and Castet, S. 1992. Thermodynamic properties of the aluminate ion and of bayerite, boehmite, diaspore and gibbsite. *Eur. J. Mineral.*, 4, 767-792.

Volokhov, Yu. A., Pavlov, L. N., Eremin, N. I. and Mironov, V. E. 1971. Hydrolysis of aluminium salts. *J. Appl. Chem.*, 44, 243-246.

Volosov, A. G., Khodakovsky, I. L. and Ryzhenko, B. N. 1972. Equilibria in the system SiO_2-H_2O at elevated temperatures along the lower three-phase curve. *Geochem. Int.*, 9, 362-377.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M., and Schumm, R. H. 1968. Selected values of chemical thermodynamic properties, Part 3. Natl. Bur. Standards Tech. Note 270-3, 264p.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M., and Schumm, R. H. 1969. Selected values of chemical thermodynamic properties, Part 4. Natl. Bur. Standards Tech. Note 270-4, 141p.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L and Nuttall, R.L. 1982. The NBS Tables of Chemical and Thermodynamic Properties. *Jour. Phys. Chem. Ref. Data*, 11 (suppl. 2), 392 p.

Walther, J. V. and Helgeson, H. C. 1977. Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *Am. J. Sci.*, 277, 1315-1351.

Walther, J. V. and Orville, P. M. 1983. The extraction-quench technique for determination of the thermodynamic properties of solute complexes: application to quartz solubility in fluid mixtures. *Amer. Mineral.*, 68, 731-741.

Walther, J. V. and Woodland, A. B. 1993. Experimental determination and interpretation of the solubility of the assemblage microcline, muscovite, and quartz in supercritical H_2O. *Geochim. Cosmochim. Acta.*, 57, 2431-2437.

Weast, R. C. 1979. *CRC handbook of chemistry and physics, 60th ed.* CRC Press, Inc., Boca Raton, Florida.

Wefers, K. 1967. Zur chemischen technologie des bauxitaufschlusses. Teil 1: Das system Na_2O-Al_2O_3-H_2O. *Metall*, 25, 422-431.

Weill, D. F. and Fyfe, W. S. 1964. The solubility of quartz in H_2O in the range 1000-4000 bars and 400-500°C. *Geochim. Cosmochim. Acta.*, 28, 1243-1255.

Wheat, C. G. and Carpenter, R. 1988. $MnCl^+$ and $MnSO_4$ association constants to 170°C. *J. Soln. Chem.*, 17(5), 467-480.

Wilkin, R. T. and Barnes, H. L. 1998. Solubility and stability of zeolites in aqueous solution: I. Analcime, Na-, and K-clinoptilolite. *Amer. Mineral.*, 83, 746-761.

Williams-Jones, A. E. and Seward, T. M. 1989. The stability of calcium chloride ion pairs in aqueous solutions at temperatures between 100 and 360°C. *Geochim. Cosmochim. Acta*, 53, 313-318.

Wesolowski D.J. 1992. Aluminum speciation and equilibria in aqueous solution: I. The solubility of gibbsite in the system Na–K–Cl–OH–$Al(OH)_4$ from 0 to 100°C. *Geochim. Cosmochim. Acta*, 56, 1065-1091.

Wesolowski D.J. and Palmer, D. A. 1994. Aluminum speciation and equilibria in aqueous solution: V. Gibbsite solubility at 50°C and pH 3-9 in 0.1 molal NaCl solutions (a general model for aluminum speciation; analytical methods). *Geochim. Cosmochim. Acta*, 58(14), 2947-2969.

Wiebe, R., Gaddy, V. L. and Heins, C., Jr. 1933. The solubility of nitrogen in water at 50, 75 and 100° from 25 to 1000 atmospheres. *J. Amer. Chem. Soc.*, 55, 947-953.

Wolery, T.J. 1976. Some chemical aspects of hydrothermal processes at mid-oceanic ridges: A theoretical study. I) Basalt-sea water reaction and chemical cycling between the oceanic crust and the oceans. II) Calculation of chemical

equilibrium between aqueous solutions and minerals. Unpublished Ph.D. thesis, Northwestern University, Ill.

Wolery, T.J. 1992. EQ3/6, a software package for geochemical modeling of aqueous systems: package overview and installation guide (Version 7.0). Lawrence Livermore National Laboratory Report UCRL-MA-110662 PT I, Livermore, CA.

Wolery, T. J., Jackson, K. J., Bourcier, W. L., Bruton, C. J., Viani, B. E., Knauss, K. G. and Delany, J. M.. 1990. Current status of the EQ3/6 software package for geochemical modeling. In. *Chemical modeling of aqueous systems II* (D.C. Melchior and R.L. Bassett, eds.), Am. Chem. Soc. Symp. Ser., 416, 104-116.

Wood, B. J. 1987. Thermodynamics of multicomponent systems containing several solid solutions. In. *Thermodynamic modeling of geological materials: Minerals, fluids and melts* (I.S.E. Carmichael and H. P. Eugster, eds.), 17, Reviews in Mineralogy, Mineral. Soc. Amer., 71-95.

Wood, S. A. and Crerar, D. A. 1985. A numerical method for obtaining multiple linear regression parameters with physically realistic signs and magnitudes: Applications to the determination of equilibrium constraints from solubility data. *Geochim. Cosmochim. Acta*, 49, 165-172.

Wright, J. M., Lindsay, W. T., Jr. and Druga, T. R. 1961. The behavior of electrolytic solutions at elevated temperatures as derived from conductance measurements. WAPD-TM-204, AEC Research and Development Report.

Wright, R. H. and Maas, O. 1932. The electrical conductivity of aqueous solutions of hydrogen sulphide and the state of the dissolved gas. *Can. J. Res.*, 6, 588-595.

Yamamoto, S., Alcauskas, J. B. and Crozier, T. E. 1976. Solubility of methane in distilled water and seawater. *J. Chem. Eng. Data*, 21(1), 78-80.

Yasunishi, A. and Yoshida, F. 1979. Solubility of carbon dioxide in aqueous electrolyte solutions. *J. Chem. Eng. Data*, 24(1), 11-14.

Yates, D. M. and Rosenberg, P. E. 1996. Formation and stability of endmember illite: I. Solution equilibration experiments at 100-250°C and $P_{v,soln}$. *Geochim. Cosmochim. Acta*, 60(11), 1873-1883.

Yeatts, L. B. and Marshall, W. L. 1969. Apparent invariance of activity coefficients of calcium sulfate at constant ionic strength and temperature in the system $CaSO_4$-Na_2SO_4-$NaNO_3$-H_2O to the critical temperature of water. Association equilibria. *J. Phys. Chem.*, 73(1), 81-90.

Yui, M., Makino, H., Ashida, T., Umeki, H., Ishiguro, K. and Neyama, A. 1992a. Dissolution behavior of vitrified waste and evaluation of radionuclide solubilities in near-field porewater chemistry. PNC TN8410 92-161, Power Reactor and Nuclear Fuel Development Corp., Tokai-Mura, Ibaraki, Japan.

Yui, M., Takeda, S., Komuro, M., Makino, H., Shibutani, T., Umeki, H., Ishiguro, K., Takase, H. and Neyama, A. 1992b. Modelling of groundwater evolution for performance assessment of high-level radioactive waste isolation (in Japanese). PNC TN8410 92-166, Power Reactor and Nuclear Fuel Development Corp., Tokai-Mura, Ibaraki, Japan (in Japanese).

Yui, M., Sasamoto, H. and Arthur, R. C. 1999. Groundwater evolution modeling for the 2nd progress (PA) report. Japan Nuclear Cycle Development Institute, Tokai-Mura, Ibaraki, Japan, Technical Report (in preparation).

Zotov, A., Mukhamet-Galeev, A. and Schott, J. 1998. An experimental study of kaolinite and dickite relative stability at 150-300°C and the thermdynamic properties of dickite. *Amer. Mineral.*, 83, 516-524.

Appendix A: Listing of the SPRONS.JNC Database

(see Tables 5.1_1 - 5.1_3 for formatting and unit conventions)

```
***     sprons.jnc -s[sequential acccess] pro[perties of] n[atural
***     s[ubstances] database developed for the Japan Nuclear Cycle
***     Development Institute (JNC).
***     Sequential-access thermodynamic datafile to be used as input
***     to program cprons,a code that converts sprons.jnc into its direct
***     -access equivalent(dprons.jnc), which is used by program supert.
***     NOTE: species can be added, deleted, or modified using program
***     mprons.

***     last updated: 20.Jan.98 by r. arthur

***     1.Apr.98:   s2o3-2 data corrected (r. arthur)

***     14.Apr.98: corrected names of species HBO2,aq, BO2- and NaH2BO3,aq to
***     B(OH)3,aq B(OH)4- and NaB(OH)4,aq,respectively, in accordance
***     ref 39 (r. arthur)

*******************************************************************************
***
***         REFERENCES: cited below as "ref:#,#,..."
***
*
*  1 ... Helgeson, H.C., Delany, J.M, Nesbitt, H.W., and Bird, D.K.,
*          1978, Summary and Critique of the Thermodynamic
*          Properties of Rock-Forming Minerals: Amer. Jour. Sci.,
*          278A, 229p.
*
*  2 ... Shock, E.L., and Helgeson, H.C., 1988, Calculation of the
*          thermodynamic and transport properties of aqueous
*          species at high pressures and temperatures: Correlation
*          algorithms for ionic species and equation of state
*          predictions to 5 kb and 1000 C: Geochim. Cosmochim. Acta,
*          52, 2009-2036.
*
*  3 ... Shock, E.L., Helgeson, H.C., and Sverjensky, D.A., 1989,
*          Calculation of the thermodynamic and transport
*          properties of aqueous species at high pressures and
*          temperatures: Standard partial molal properties of
*          inorganic neutral species: Geochim. Cosmochim. Acta, 53,
*          pp. 2157-2183.
*
*  4 ... Shock, E.L., and Helgeson, H.C., 1990, Calculation of the
*          thermodynamic and transport properties of aqueous
*          species at high pressures and temperatures: Standard
*          partial molal properties of organic species.
*          Geochim. Cosmochim. Acta, 54, 915-945.
*
*  5 ... Sverjensky, D.A., 1990, Thermodynamic properties of aqueous
*          inorganic metal complexes: Geochim. Cosmochim. Acta
*          (see ref 22).
*
*  6 ... Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H.,
*          Halow, I., Bailey, S.M., Churney, K.L., Nuttall, R.L.,
*          1982, The NBS Tables of Chemical and Thermodynamic
*          Properties: Jour. Phys. Chem. Ref. Data, v. 11,
*          supplement no. 2, 392 p.
*
*  7 ... Robie, R.A., Hemingway, B.S., and Fisher, J.S., 1979,
*          Thermodynamic Properties of Minerals and Related
*          Substances at 298.15 K and 1 Bar (10**5 Pascals)
*          Pressure and at Higher Temperatures: U.S. Geol. Surv.
*          Bull. 1452, 456 p.
*
*  8 ... Kelley, K.K., 1960, Contributions to the Data in Theoretical
*          Metallurgy XIII: High Temperature Heat Content, Heat
*          Capacities and Entropy Data for the Elements and
*          Inorganic Compounds.  U.S. Bureau of Mines Bulletin
*          584, 232 p.
*
*  9 ... Bowers, T.S., and Helgeson, H.C., 1983, Calculation of the
*          thermodynamic and geochemical consequences of nonideal
*          mixing in the system H2O-CO2-NaCl on phase relations
*          in geologic systems: Equation of state for H2O-CO2-NaCl
*          fluids at high pressures and temperatures: Geochim.
*          Cosmochim. Acta, 47, 1247-1275.
*
* 10 ... Sverjensky, D.A., 1987, Calculations of the thermodynamic
*          properties of aqueous species and the solubilities of
*          minerals in supercritical electrolyte solutions, in
*          Carmichael, I.S.E. and H.P. Eugster, eds., Thermodynamic
*          Modeling of Geologic Materials: Minerals, Fluids and
*          Melts: Mineral. Soc. Amer., Reviews in Mineralogy,
*          17, 177-209.
*
* 11 ... Shock, E.L., Personal calculation, Laboratory of Theoretical
*          Geochemistry, Dept. Geol. Geophys., Univ. CA,
*          Berkeley, CA.
*
* 12 ... Jackson, K.J., and Helgeson, H.C., 1985, Chemical and
*          thermodynamic constraints on the hydrothermal transport
*          and deposition of tin: II. Interpretation of phase
*          relations in the Southeast Asian tin belt: Econ. Geol.,
*          80 (5), 1365-1378.
*
* 13 ... Helgeson, H.C., 1985, Errata II. Thermodynamics of minerals,
*          reactions, and aqueous solutions at high pressures and
*          temperatures: Amer. Jour. Sci., 285, 845-855.
*
* 14 ... Shock, E.L., and Helgeson, H.C., 1989, Corrections to Shock
*          and Helgeson (1988) [ref:2 above]: Geochim. Cosmochim.
*          Acta, 53, 215.
*
* 15 ... Pankratz, L.B., 1970, Thermodynamic Data for Silver Chloride
*          and Silver Bromide: U.S. Bureau of Mines Report of
*          Investigations #7430, 12 p.
*
* 16 ... Pankratz, L.B., and King, E.G., 1970, High-Temperature
*          Enthalpies and entropies of chalcopyrite and bornite:
*          U.S. Bureau of Mines Report of Investigations #7435,
*          10 p.
*
* 17 ... Johnson, J.W., Personal calculation, Earth Sciences Dept.,
*          Lawrence Livermore National Lab., Livermore, CA.
*          Parameters given provide smooth metastable
*          extrapolation of one-bar steam properties predicted
*          by the Haar et al. (1984) equation of state to
*          temperatures < the saturation temperature (99.632 C).
*
* 18 ... Gibbs free energies calculated from solubility data reported by
*          Plummer, L.N. and Busenberg, E., 1982. The Solubilities
*          of Calcite, Aragonite, and Vaterite in CO2-H2O Solutions
*          Between 0 and 90 C and an Evaluation of the Aqueous
*          Model of the System CaCO3-CO2-H2O. Geochim. Cosmochim.
*          Acta, 46, 1011-1040. Enthalpies adjusted for the
*          correction in the Gibbs free energy.
*
* 19 ... Gibbs free energies and enthalpies were corrected to be
*          consistant with updated values of Gibbs free
*          energies of Ca++ and CO3-- (Shock and Helgeson [ref:2
*          above]) together with the solubilities of calcite and
*          aragonite reported by Busenberg and Plummer [ref:18
*          above]
*
* 20 ... Pokrovskii, V. A. and Helgeson, H. C.  1995. Thermodynamic
*          properties of aqueous species and the solubilities of
*          minerals at high pressures and temperatures: The system
*          Al2O3-H2O-NaCl.  Am. Jour. Sci., 295, 1255-1342.
*
* 21 ... Shock, E. L., Sassani, D. C., Willis, M. and Sverjensky,
*          D. A.  1997.  Inorganic species in geologic fluids:
*          Correlations among standard molal thermodynamic
*          properties of aqueous ions and hyroxide complexes.
*          Geochim. Cosmochim. Acta, 61(5), 907-950.
*
* 22 ... Sverjensky, D.A., Shock, E.L. and Helgeson, H.C.  1997.
*          Prediction of the thermodynamic properties of aqueous
*          metal complexes to 1000C and 5kb. Geochim. Cosmochim.
*          Acta, 61(7), 1359-1412.
*
* 23 ... Pokrovskii, V. A. and Helgeson, H. C. 1997a. Calculation
*          of the standard partial molal thermodynamic properties
*          of KCl° and activity coefficients of aqueous KCl at
*          temperatures and pressures to 1000C and 5 kbar. Geochim.
*          Cosmochim. Acta, 61(11), 2175-2183.
*
* 24 ... Pokrovskii, V. A. and Helgeson, H. C.  1997b. Thermodynamic
*          properties of aqueous species and the solubilities of
*          minerals at high pressures and temperatures: the system
*          Al2O3-H2O-KOH. Chem. Geol., 137, 221-242.
*
* 25 ... Haas, J. R., Shock, E. L. and Sassani, D. C. (1995) Rare earth
*          elements in hydrothermal systems: Estimates of standard
*          partial molal thermodynamic properties of aqueous complexes
*          of the rare earth elements at high pressures and temperatures.
*          Geochim. Cosmochim. Acta, 59, 4329-4350.
*
* 26 ... Shock, E. L. (1995) Organic acids in hydrothermal solutions: Standard
*          molal thermodynamic properties of carboxylic acids, and estimates
```

of dissociation constants at high temperatures and pressures. Amer. J. Sci., 295, 496-580.

27 ... Shock, E. L. and Koretsky, C. M. (1995) Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochim. Cosmochim. Acta, 59, 1497-1532.

28 ... Standard molal Gibbs free energy and enthalpy of formation from ref (7) included with original data from ref (1). CAUTION: These data may not be internally consistent with the ref (1) database.

29 ... Standard molal Gibbs free energy and enthalpy of formation from Saccocia, P. J. and Seyfried, W. E., Jr. (1993) A resolution of discrepant thermodynamic properties for chamosite retrieved from experimental and empirical techniques. Am. Mineral., 78, 607-611. Values are consistent with thermodynamic data for minerals from ref (1). The nomenclature for trioctahedral chlorites adopted by the authors requires that the terms chamosite, daphnite and 14A-daphnite all refer to Fe5Al2Si3O10(OH)8 and are synonymous.

30 ... Standard molal Gibbs free energy and enthalpy of formation from Wolery, T.J. (1976) Some chemical aspects of hydrothermal processes at mid-oceanic ridges: A theoretical study. I) Basalt-sea water reaction and chemical cycling between the oceanic crust and the oceans. II) Calculation of chemical equilibrium between aqueous solutions and minerals. Unpublished Ph.D. thesis, Northwestern University, Ill. CAUTION: the reliability of these data are uncertain and the data may not be internally consistent with the ref (1) database.

31 ... Standard molal Gibbs free energy and enthalpy of formation, and third law entropy (muscovite), adjusted from ref (1) values according to recommendations by Sverjensky, D. A., Hemley, J. J. and D'Angelo, W. M. (1991)Thermodynamic assessment of hydrothermal alkali feldspar-mica-aluminosilicate equilibria. Geochim. Cosmochim. Acta, 55, 989-1004.

32 ... Standard molal Gibbs free energy and enthalpy of formation, third-law entropy, standard molal volume, and Maier-Kelley heat capacity coefficients and corresponding temperature range from ref (30). CAUTION: the reliability of these data are uncertain, and the data may not be internally consistent with the ref (1) database.

33 ... Shock, E. L. and Koretsky, C. M. (1993) Metal-organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures. Geochim. Cosmochim. Acta, 57, 4899-4922.

34 ... Database development group iii/3 (1988) Errors in computation of estimated delh298 for montmor-x endmembers of smectite-di solid solution: Internal memo 88db 3 Lawrence Livermore National Laboratory,Livermore, CA.

35 ... Oelkers, E. H., Helgeson, H. C., Shock, E. L., Sverjensky, D. A., Johnson, J. W. and Pokrovskii, V. A. (1995) Summary of apparent standard partial molal Gibbs free energies of formation of aqueous species, minerals, and gases at pressures 1 to 5000 bars and temperatures 25 to 1000 C. J. Phys.Chem. Ref. Data, 24(4), 1401-1560.

36 ... Shock, E. L., Sassani, D. C. and Betz, H.(in revision) Actinide ions in aqueous solution: Summary of standard state properties and estimates at high temperatures and pressures. Appl. Geochem.

37 ... Shock, E. L., Sassani, D. C. and Betz, H. (1997) Uranium in geologic fluids: Estimates of standard partial molal properties, oxidation potentials, and hydrolysis constants at high temperatures and pressures. Geochim. Cosmochim. Acta, 61(20), 4245-4266.

38 ... Sassani, D. C. and Shock, E. L. (1990) Speciation and solubility of palladium in aqueous magmatic-hydrothermal solutions. Geology, 18, 925-928. CAUTION These data may be revised by Sassani, D. C. and Shock, E. L. Solubility and transport of platinum-group elements in supercritical fluids: Thermodynamic properties of Ru, Rh, Pd and Pt solids,aqueous ions and aqueous complexes to 5 kbar and 1000 C. Geochim. Cosmochim. Acta, (in press).

39 ... Pokrovski, G. S., Schott, J. and Sergeyev, A. S. (1995) Experimental determination of the stability constants of NaSO4- and NaB(OH)4 in hydrothermal solutions using a new high-temperature sodium-selective glass electrode - Implications for boron isotopic fractionation. Chem. Geol., 124, 253-265.

40 ... Tagirov, B. R., Zotov, A. V. and Akinfiev, N. N. (1997) Experimental study of dissociation of HCl from 350 to 500 C and from 500 to 2500 bars: Thermodynamic properties of HCl(aq). Geochim. Cosmochim. Acta, 61(20),4267-4280.

****

MINERAL ABBREVIATIONS ARE CONSISTENT WITH THOSE RECOMMENDED BY THE AMERICAN MINERALOGIST AND PUBLISHED BY

Kretz, R., 1983, Symbols for Rock-Forming Minerals: Amer. Mineral., v. 68, pp. 277-279.

****

```
**********************************************************
        minerals that do not undergo phase transitions
**********************************************************
AKERMANITE              Ca2MgSi2O7
Ak                      Ca(2)Mg(1)Si(2)O(7)
ref:1,19                15.Mar.90
        -879362.0       -926497.0       50.030      92.810
         60.090000       11.400000      -11.400000
        1700.00
ALABANDITE              MnS
Alb                     Mn(1)S(1)
ref:1                   5.May.78
         -52178.0        -51000.0       19.200      21.460
        11.400000        1.800000         .000000
        1803.00
ALBITE,LOW              NaAlSi3O8
Lo-Ab                   Na(1)Al(1)Si(3)O(8)
ref:1                   5.May.78
        -886308.0       -939680.0       49.510     100.070
         61.700000       13.900000      -15.010000
        1400.00
ALUNITE                 KAl3(OH)6(SO4)2
Alu                     K(1)Al(3)S(2)O(14)H(6)
ref:1                   5.May.78
       -1113600.0      -1235600.0       78.400     293.600
        153.450000         .000000      -54.950000
         650.00
AMESITE,7A              Mg2Al(AlSi)O5(OH)4
Ams-7A                  Mg(2)Al(2)Si(1)O(9)H(4)
ref:1                   5.May.78
         999999.0        999999.0       52.000     103.000
         81.030000       24.738000      -20.230000
        1000.00
AMORPHOUS-SILICA        SiO2*NH2O
Amor-Sl                 Si(1)O(2)H(2N)O(N)
ref:1                   5.May.78
        -202892.0       -214568.0       14.340      29.000
         5.930000        47.200000      -22.780000
         622.00
ANALCIME                NaAlSi2O6*H2O
Anl                     Na(1)Al(1)Si(2)O(7)H(2)
ref:1                   5.May.78
        -738098.0       -790193.0       56.000      97.100
         53.490000       24.140000       -8.880000
        1000.00
ANALCIME,DEHYDRATED     NaAlSi2O6
Dhyd-Anl                Na(1)Al(1)Si(2)O(6)
ref:1                   5.May.78
        -674989.0       -714678.0       41.900      89.100
         42.090000       24.140000       -8.880000
        1000.00
ANDALUSITE              Al2SiO5
And                     Al(2)Si(1)O(5)
ref:1                   5.May.78
        -580587.0       -615866.0       22.200      51.530
         41.310833        6.292556      -12.392063
        1043.00
ANDRADITE               Ca3Fe2Si3O12
Adr                     Ca(3)Fe(2)Si(3)O(12)
ref:1,19                15.Mar.90
       -1296819.0      -1380345.0       70.130     131.850
        113.532000      15.636000       -30.889000
        1100.00
ANGLESITE               PbSO4
Ang                     Pb(1)S(1)O(4)
ref:1                   5.May.78
        -194353.0       -219870.0       35.510      47.950
         10.960000       31.000000        4.200000
        1100.00
ANHYDRITE               CaSO4
Anh                     Ca(1)S(1)O(4)
ref:1                   5.May.78
        -315925.0       -342760.0       25.500      45.940
         16.780000       23.600000         .000000
        1453.00
ANNITE                  KFe3(AlSi3)O10(OH)2
Ann                     K(1)Fe(3)Al(1)Si(3)O(12)H(2)
ref:1                   5.May.78
       -1147156.0      -1232195.0       95.200     154.320
        106.430000      29.770000       -19.310000
        1000.00
ANORTHITE               Ca(Al2Si2)O8
An                      Ca(1)Al(2)Si(2)O(8)
ref:1,19                15.Mar.90
        -954078.0       -1007552.0       49.100     100.790
         63.311000       14.794000       -15.440000
        1700.00
ARAGONITE               CaCO3
Arg                     Ca(1)C(1)O(3)
ref:1,18                9.Mar.90
        -269683.0       -288531.0       21.560      34.150
         20.130000       10.240000        -3.340000
         600.00
ARTINITE                Mg2(OH)2(CO3)*3H2O
Art                     Mg(2)C(1))O(8)H(8)
ref:1                   5.May.78
        -613915.0       -698043.0       55.670      96.900
         70.870000       27.660000        -7.430000
        1000.00
AZURITE                 Cu3(OH)2(CO3)2
Azr                     Cu(3)C(2)O(8)H(2)
ref:1                   5.May.78
        -334417.0       -390100.0       66.970      91.010
         36.880000       77.440000         -.920000
         780.00
BARITE                  BaSO4
Brt                     Ba(1)S(1)O(4)
ref:1                   5.May.78
        -325563.0       -352100.0       31.600      52.100
         33.800000          .000000       -8.430000
        1422.00
BEIDELLITE,CA           Ca0.165Al2.33Si3.67O10(OH)2
Ca-Bei                  Ca(0.165)Al(2.33)Si(3.67)O(12)H(2)
ref:32                  14.Jan.98
        -1280909.0      -1370654.0       58.300     129.530
         82.191000       37.150000       -18.030000
         600.00
BEIDELLITE,K            K0.33Al2.33Si3.67O10(OH)2
K-Bei                   K(0.33)Al(2.33)Si(3.67)O(12)H(2)
ref:32                  14.Jan.98
        -1281773.0      -1371891.0       60.510     133.700
         83.319000       38.400000       -17.920000
         600.00
BEIDELLITE,MG           Mg0.165Al2.33Si3.67O10(OH)2
Mg-Bei                  Mg(0.165)Al(2.33)Si(3.67)O(12)H(2)
ref:32                  14.Jan.98
        -1277064.0      -1366883.0       57.700     123.190
         81.945000       37.260000       -18.020000
         600.00
BEIDELLITE,NA           Na0.33Al2.33Si3.67O10(OH)2
Na-Bei                  Na(0.33)Al(2.33)Si(3.67)O(12)H(2)
ref:32                  14.Jan.98
        -1279688.0      -1369757.0       59.620     130.540
         83.277000       37.780000       -18.250000
         600.00
BERNDTITE               SnS2
Brn                     Sn(1)S(2)
ref:12                  5.May.78
         -34750.0        -36700.0       20.900      40.960
         15.510000        4.200000         .000000
        1000.00
BOEHMITE                AlO(OH)
Bhm                     Al(1)O(2)H(1)
ref:20                  29.Apr.97
        -219599.0       -238240.0        8.890      19.535
         12.902000       12.421000       -3.228000
         900.00
BROMELLITE              BeO
Brm                     Be(1)O(1)
ref:1                   5.May.78
         999999.0        999999.0        3.380       8.309
         8.450000        4.000000       -3.170000
        1200.00
BRUCITE                 Mg(OH)2
Brc                     Mg(1)O(2)H(2)
ref:1                   5.May.78
        -199646.0       -221390.0       15.090      24.630
         24.147000       4.012400        -6.110000
         900.00
CA-AL-PYROXENE          CaAl(AlSi)O6
Ca-Al-Px                Ca(1)Al(2)Si(1)O(6)
ref:1,19                15.Mar.90
        -742067.0       -783793.0       35.000      63.500
         54.130000       6.420000       -14.900000
        1400.00
CALCITE                 CaCO3
Cal                     Ca(1)C(1)O(3)
ref:1,18                9.Mar.90
        -269880.0       -288552.0       22.150      36.934
         24.980000       5.240000        -6.200000
        1200.00
CASSITERITE             SnO2
Cst                     Sn(1)O(2)
ref:12                  5.May.78
        -124260.0       -138800.0       12.500      21.550
         17.246000       2.802600        -4.900100
        1500.00
CELADONITE              K(MgAl)Si4O10(OH)2
Cln                     K(1)Mg(1)Al(1)Si(4)O(12)H(2)
ref:1,30                9.Jan.98
       -1305895.0      -1394899.0       74.900     157.100
         80.250000       25.300000       -18.540000
        1000.00
CELESTITE               SrSO4
Cls                     Sr(1)S(1)O(4)
ref:1                   5.May.78
        -320435.0       -347300.0       28.000      46.250
         21.800000       13.300000          .000000
        1500.00
CERUSSITE               PbCO3
Cer                     Pb(1)C(1)O(3)
ref:1                   5.May.78
        -150370.0       -168000.0       31.300      40.590
         12.390000       28.600000          .000000
         800.00
CHABAZITE               Ca(Al2Si4)O12*6H2O
Cbz                     Ca(1)Al(2)Si(4)O(18)H(12)
ref:1                   5.May.78
         999999.0        999999.0      152.900     247.760
        146.000000       44.470000      -16.430000
        1000.00
CHALCEDONY              SiO2
Cha                     Si(1)O(2)
ref:1                   5.May.78
        -204276.0       -217282.0        9.880      22.688
         11.220000        8.200000       -2.700000
         848.00
CHAMOSITE,7A            Fe2Al(AlSi)O5(OH)4
Chm-7A                  Fe(2)Al(2)Si(1)O(9)H(4)
ref:1,30                9.Jan.98
```

```
       -828026.0     -902403.0     64.700    106.200
         84.910000     25.400000   -18.770000
       1000.00
CHLORARGYRITE          AgCl
Crg                    Ag(1)Cl(1)
ref:7,15               5.May.78
        -26247.0      -30370.0      23.000     25.727
         14.330000      1.821000     -2.430000
        728.00
CHLORITOID             FeAl2SiO5(OH)2
Cld                    Fe(1)Al(2)Si(1)O(7)H(2)
ref:1                  5.May.78
         999999.0      999999.0      42.100     69.800
         60.630000     17.130000    -13.630000
       1000.00
CHRYSOTILE             Mg3Si2O5(OH)4
Ctl                    Mg(3)Si(2)O(9)H(4)
ref:1                  5.May.78
        -964871.0     -1043123.0     52.900    108.500
         75.820000     31.600000    -17.580000
       1000.00
CINNABAR               HgS
Cin                    Hg(1)S(1)
ref:1                  5.May.78
        -10940.0      -12750.0      19.700     28.416
         10.460000      3.720000       .000000
        618.00
CLINOCHLORE,14A        Mg5Al(AlSi3)O10(OH)8
14A-Cnc                Mg(5)Al(2)Si(3)O(18)H(8)
ref:1                  5.May.78
       -1961703.0     -2116964.0    111.200    207.110
        166.500000     42.100000    -37.470000
        900.00
CLINOZOISITE           Ca2Al3Si3O12(OH)
Czo                    Ca(2)Al(3)Si(3)O(13)H(1)
ref:1,19               15.Mar.90
       -1549240.0     -1643781.0     70.640    136.200
        106.118000     25.214000    -27.145000
        700.00
COPPER,NATIVE          Cu
Cu                     Cu(1)
ref:1                  5.May.78
              .0             .0      7.923      7.113
         5.410000      1.500000       .000000
       1357.00
CORDIERITE             Mg2Al3(AlSi5)O18
Crd                    Mg(2)Al(4)Si(5)O(18)
ref:1                  5.May.78
       -2061279.0     -2183199.0     97.330    233.220
        143.830000     25.800000    -38.600000
       1700.00
CORDIERITE,HYDROUS     Mg2Al3(AlSi5)O18*H2O
Hyd-Crd                Mg(2)Al(4)Si(5)O(19)H(2)
ref:1                  5.May.78
       -2121350.0     -2255676.0    111.430    241.220
        155.230000     25.800000    -38.600000
       1700.00
CORUNDUM               Al2O3
Crn                    Al(2)O(3)
ref:20                 05.May.98
        -378167.0      -400500.0     12.170     25.575
         29.321000      1.644000    -12.0070000
       1200.00
COVELLITE              CuS
Cv                     Cu(1)S(1)
ref:1                  5.May.78
         -12612.0      -12500.0      15.900     20.420
         10.600000      2.640000       .000000
       1273.00
CRISTOBALITE,ALPHA     SiO2
A-Crs                  Si(1)O(2)
ref:1                  5.May.78
       -203895.0     -216755.0     10.372     25.740
         13.980000      3.340000     -3.810000
       1000.00
CRISTOBALITE,BETA      SiO2
B-Crs                  Si(1)O(2)
ref:1                  5.May.78
       -203290.0     -215675.0     11.963     27.380
         17.390000       .310000     -9.890000
       2000.00
CUMMINGTONITE          Mg7Si8O22(OH)2
Cum                    Mg(7)Si(8)O(24)H(2)
ref:1                  5.May.78
         999999.0      999999.0    127.500    271.900
        185.240000     58.610000    -44.660000
        800.00
CUPRITE                Cu2O
Cpr                    Cu(2)O(1)
ref:1                  5.May.78
        -35384.0      -40830.0      22.080     23.437
         14.080000      5.880000      -.760000
       1515.00
DAPHNITE,14A           Fe5Al(AlSi3)O10(OH)8
Dph-14A                Fe(5)Al(2)Si(3)O(18)H(8)
ref:1,29               9.Jan.98
       -1551548.0     -1696591.0    142.500    213.420
        176.210000     43.760000    -33.820000
       1000.00
DIASPORE               AlO(OH)
Dsp                    Al(1)O(2)H(1)
ref:20                 29.Apr.97
        -220150.0      -238924.0      8.446     17.760
         12.273000     13.070000     -2.903000
        900.00
DICKITE                Al2Si2O5(OH)4
Dck                    Al(2)Si(2)O(9)H(4)
ref:1,7                5.May.78
         999999.0      999999.0     47.100     99.300
         72.770000     29.200000    -21.520000
       1000.00
DIOPSIDE               CaMg(SiO3)2
Di                     Ca(1)Mg(1)Si(2)O(6)
ref:1,19               15.Mar.90
        -723780.0      -765378.0     34.200     66.090
         52.870000      7.840000    -15.740000
       1600.00
DOLOMITE               CaMg(CO3)2
Dol                    Ca(1)Mg(1)C(2)O(6)
ref:1,19               15.Mar.90
        -517760.0      -556631.0     37.090     64.365
         41.557000     23.952000     -9.884000
       1000.00
DOLOMITE,DISORDERED    CaMg(CO3)2
Dis-Dol                Ca(1)Mg(1)C(2)O(6)
ref:1,19               15.Mar.90
        -515653.0      -553704.0     39.840     64.390
         44.711000     17.779000    -10.948000
       1000.00
DOLOMITE,ORDERED       CaMg(CO3)2
Ord-Dol                Ca(1)Mg(1)C(2)O(6)
ref:1,19               15.Mar.90
        -517760.0      -556631.0     37.090     64.340
         44.711000     17.779000    -10.948000
       1000.00
EPIDOTE                Ca2FeAl2Si3O12(OH)
Ep                     Ca(2)Fe(1)Al(2)Si(3)O(13)H(1)
ref:1,19               15.Mar.90
       -1450906.0     -1543992.0     75.280    139.200
        117.622000     12.816000    -31.864000
       1100.00
EPIDOTE,ORDERED        Ca2FeAl2Si3O12(OH)
Ord-Ep                 Ca(2)Fe(1)Al(2)Si(3)O(13)H(1)
ref:1,19               15.Mar.90
       -1450906.0     -1544016.0     75.200    139.200
        113.780000     14.690000    -28.920000
       1100.00
FAYALITE               Fe2SiO4
Fa                     Fe(2)Si(1)O(4)
ref:1                  5.May.78
        -330233.0      -354119.0     35.450     46.390
         36.510000      9.360000     -6.700000
       1490.00
FERROPARGASITE         Na(Ca2Fe4Al)(Al2Si6)O22(OH)2
Fe-Prg                 Na(1)Ca(2)Fe(4)Al(3)Si(6)O(24)H(2)
ref:1                  5.May.78
         999999.0      999999.0    185.500    279.890
        213.570000     42.990000    -47.290000
       1000.00
FERROTREMOLITE         (Ca2Fe5)Si8O22(OH)2
Fe-Tr                  Ca(2)Fe(5)Si(8)O(24)H(2)
ref:1                  5.May.78
         999999.0      999999.0    163.500    282.800
        197.930000     58.950000    -41.170000
        800.00
FERROUS-OXIDE          FeO
Frs-Ox                 Fe(1)O(1)
ref:1                  5.May.78
         -60097.0      -65020.0     14.520     12.000
         12.122000      2.072000       -.750000
       1600.00
FLUORITE               CaF2
Fl                     Ca(1)F(2)
ref:1                  5.May.78
        -280493.0      -293000.0     16.390     24.542
         14.300000      7.280000       .470000
       1424.00
FLUORPHLOGOPITE        KMg3(AlSi3)O10(F)2
F-Phl                  K(1)Mg(3)Al(1)Si(3)O(10)F(2)
ref:1,7                5.May.78
         999999.0      999999.0     80.380    146.370
         96.130000     26.740000    -20.410000
       1000.00
FLUORTREMOLITE         (Ca2Mg5)Si8O22(F)2
F-Tr                   Ca(2)Mg(5)Si(8)O(22)F(2)
ref:1                  5.May.78
         999999.0      999999.0    129.400    270.450
        183.740000     55.250000    -43.730000
        800.00
FORSTERITE             Mg2SiO4
Fo                     Mg(2)Si(1)O(4)
ref:1                  5.May.78
        -491564.0      -520000.0     22.750     43.790
         35.810000      6.540000     -8.520000
       1800.00
GALENA                 PbS
Gn                     Pb(1)S(1)
ref:1                  5.May.78
         -23115.0       -23500.0     21.800     31.490
         11.170000      2.200000       .000000
       1388.00
GEHLENITE              Ca2(Al2Si)O7
Gh                     Ca(2)Al(2)Si(1)O(7)
ref:1,19               15.Mar.90
        -903148.0      -951225.0     48.100     90.240
         63.740000      8.000000    -15.120000
       1800.00
GIBBSITE               Al(OH)3
Gbs                    Al(1)O(3)H(3)
ref:20                 29.Apr.97
        -276025.0      -309065.0     16.360     31.956
         13.073000     40.696000     -2.920000
        600.00
GLAUCOPHANE            Na2(Mg3Al2)Si8O22(OH)2
Gln                    Na(2)Mg(3)Al(2)Si(8)O(24)H(2)
ref:1                  5.May.78
```

```
        999999.0      999999.0    130.000    269.700
        190.260000     59.360000   -50.010000
         800.00
GOLD,NATIVE           Au
Au                    Au(1)
ref:1                 5.May.78
                 .0           .0    11.330     10.215
           5.660000      1.240000      .000000
        1336.00
GRAPHITE              C
Gr                    C(1)
ref:1                 5.May.78
                 .0           .0     1.372      5.298
           4.030000      1.140000     -2.040000
        2500.00
GREENALITE            Fe3Si2O5(OH)4
Grn                   Fe(3)Si(2)O(9)H(4)
ref:1,30              9.Jan.98
        -716501.0     -787774.0     72.600    115.000
         81.650000     32.600000    -15.390000
        1000.00
GROSSULAR             Ca3Al2Si3O12
Grs                   Ca(3)Al(2)Si(3)O(12)
ref:1,19              15.Mar.90
       -1496307.0    -1582737.0     60.870    125.300
         104.017000    17.013000    -27.318000
        1000.00
GRUNERITE             Fe7Si8O22(OH)2
Gru                   Fe(7)Si(8)O(24)H(2)
ref:1                 5.May.78
        999999.0      999999.0    163.300    256.670
        198.830000     60.930000    -39.550000
         800.00
HALITE                NaCl
Hl                    Na(1)Cl(1)
ref:1                 5.May.78
         -91807.0      -98260.0     17.240     27.015
         10.980000      3.900000      .000000
        1073.00
HALLOYSITE            Al2Si2O5(OH)4
Hal                   Al(2)Si(2)O(9)H(4)
ref:1,7,28            9.Jan.98
         -903628.2     -980294.7     48.520     99.300
         72.770000     29.200000    -21.520000
        1000.00
HEDENBERGITE          CaFe(SiO3)2
Hd                    Ca(1)Fe(1)Si(2)O(6)
ref:1,19              5.Mar.90
         -638998.0     -678276.0     40.700     68.270
         54.810000      8.170000    -15.010000
        1600.00
HUNTITE               CaMg3(CO3)4
Hun                   Ca(1)Mg(3)C(4)O(12)
ref:1                 5.May.78
       -1004710.0    -1082600.0     71.590    122.900
         84.170000     42.860000    -20.440000
        1000.00
HYDROMAGNESITE        Mg5(OH)2(CO3)4*4H2O
Hydro-Mgs             Mg(5)C(4)O(18)H(10)
ref:1                 5.May.78
       -1401687.0    -1557090.0    129.380    208.800
        141.460000     65.280000    -21.670000
        1000.00
ILLITE                K0.6Mg0.25Al1.8Al0.5Si3.5O10(OH)2
Ill                   K(0.6)Mg(0.25)Al(2.3)Si(3.5)O(12)H(2)
ref:32                14.Jan.98
       -1303971.0    -1394709.0     63.590    138.940
         86.044000     38.570000    -17.820000
        600.00
JADEITE               NaAl(SiO3)2
Jd                    Na(1)Al(1)Si(2)O(6)
ref:1                 5.May.78
```

```
        -679445.0     -722116.0     31.900     60.400
         48.160000     11.420000    -11.870000
        1400.00
K-FELDSPAR            K(AlSi3)O8
K-Fs                  K(1)Al(1)Si(3)O(8)
ref:1,31              9.Jan.98
         -895610.0     -949424.0     51.130    108.870
         76.617000      4.311000    -29.945000
        1400.00
KAOLINITE             Al2Si2O5(OH)4
Kln                   Al(2)Si(2)O(9)H(4)
ref:1                 5.May.78
         -905614.0     -982221.0     48.530     99.520
         72.770000     29.200000    -21.520000
        1000.00
KYANITE               Al2SiO5
Ky                    Al(2)Si(1)O(5)
ref:1                 5.May.78
         -580956.0     -616897.0     20.000     44.090
         41.393132      6.816463    -12.882104
         466.00
LAUMONTITE            Ca(Al2Si4)O12*4H2O
Lmt                   Ca(1)Al(2)Si(4)O(16)H(8)
ref:1,19              15.Mar.90
       -1596823.0    -1728664.0    116.100    207.550
        123.200000     44.470000    -16.430000
        1000.00
LEONHARDITE           Ca2(Al4Si8)O24*7H2O
Lnr                   Ca(2)Al(4)Si(8)O(31)H(14)
ref:1                 5.May.78
        999999.0      999999.0    220.400    407.860
        235.000000     88.940000    -32.860000
        1000.00
LIME                  CaO
Lim                   Ca(1)O(1)
ref:1                 5.May.78
         -144366.0     -151790.0      9.500     16.764
         11.670000      1.080000     -1.560000
        2000.00
MAGNESITE             MgCO3
Mgs                   Mg(1)C(1)O(3)
ref:1                 5.May.78
         -245658.0     -265630.0     15.700     28.018
         19.731000     12.539000     -4.748000
        1000.00
MALACHITE             Cu2(OH)2(CO3)
Mal                   Cu(2)C(1)O(5)H(2)
ref:1                 5.May.78
         -214204.0     -251900.0     44.500     54.860
         27.760000     43.780000     -1.340000
         780.00
MANGANOSITE           MnO
Mng                   Mn(1)O(1)
ref:1,6               5.May.78
          -86735.0      -92070.0     14.270     13.221
         11.110000      1.940000      -.880000
        1800.00
MERWINITE             Ca3Mg(SiO4)2
Mer                   Ca(3)Mg(1)Si(2)O(8)
ref:1,19              15.Mar.90
       -1036526.0    -1090796.0     60.500    104.400
         72.970000     11.960000    -14.440000
        1700.00
METACINNABAR          HgS
Met-Cin               Hg(1)S(1)
ref:1                 5.May.78
          -10437.0      -11800.0     21.200     30.169
         10.520000      3.630000      .000000
        1000.00
MICROCLINE,MAXIMUM    K(AlSi3)O8
Max-Mc                K(1)Al(1)Si(3)O(8)
ref:1,31              9.Jan.98
```

```
         -895610.0     -949424.0     51.130    108.741
          63.830000     12.900000    -17.050000
        1400.00
MINNESOTAITE          Fe3Si4O10(OH)2
Mnn                   Fe(3)Si(4)O(12)H(2)
ref:1,30              9.Jan.98
        -1070048.0    -1153366.0     83.500    147.860
          88.310000     42.610000    -11.150000
         800.00
MONTICELLITE          CaMgSiO4
Mtc                   Ca(1)Mg(1)Si(1)O(4)
ref:1                 5.May.78
         -512829.0     -540800.0     26.400     51.470
          36.820000      5.340000     -8.000000
        1400.00
MONTMORILLONITE,CA    Ca0.165Mg0.33Al1.67Si4O10(OH)2
Ca-Mon                Ca(0.165)Mg(0.33)Al(1.67)Si(4)O(12)H(2)
ref:34                14.Jan.98
        -1272340.0    -1361490.0     59.893    133.264
          80.180000     39.500000    -16.650000
         600.00
MONTMORILLONITE,K     K0.33Mg0.33Al1.67Si4O10(OH)2
K-Mon                 K(0.33)Mg(0.33)Al(1.67)Si(4)O(12)H(2)
ref:34                15.Jan.98
        -1273300.0    -1362823.0     62.103    137.432
          84.320000     40.750000    -16.530000
         600.00
MONTMORILLONITE,MG    Mg0.495Al1.67Si4O10(OH)2
Mg-Mon                Mg(0.495)Al(1.67)Si(4)O(12)H(2)
ref:34                15.Jan.98
        -1268590.0    -1357862.0     59.131    131.247
          79.940000     39.610000    -16.630000
         600.00
MONTMORILLONITE,NA    Na0.33Mg0.33Al1.67Si4O10(OH)2
Na-Mon                Na(0.33)Mg(0.33)Al(1.67)Si(4)O(12)H(2)
ref:34                15.Jan.98
        -1271210.0    -1360684.0     61.213    134.271
          81.270000     40.130000    -16.870000
         600.00
MUSCOVITE             KAl2(AlSi3)O10(OH)2
Ms                    K(1)Al(3)Si(3)O(12)H(2)
ref:1,31              9.Jan.98
        -1335667.0    -1427644.0     70.000    140.710
          97.560000     26.380000    -25.440000
        1000.00
NEPHELINE             Na(AlSi)O4
Ne                    Na(1)Al(1)Si(1)O(4)
ref:1                 5.May.78
         -472872.0     -500241.0     29.720     54.160
          35.908062      6.457918     -7.327965
        1500.00
NONTRONITE,CA         Ca0.165Fe2Al0.33Si3.67O10(OH)2
Ca-Non                Ca(0.165)Fe(2)Al(0.33)Si(3.67)O(12)H(2)
ref:32                14.Jan.98
        -1079492.0    -1166692.0     66.350    131.100
          78.191000     52.930000    -13.200000
         600.00
NONTRONITE,K          K0.33Fe2Al0.33Si3.67O10(OH)2
K-Non                 K(0.33)Fe(2)Al(0.33)Si(3.67)O(12)H(2)
ref:32                14.Jan.98
        -1080356.0    -1167926.0     68.570    135.270
          79.319000     54.180000    -13.090000
         600.00
NONTRONITE,MG         Mg0.165Fe2Al0.33Si3.67O10(OH)2
Mg-Non                Mg(0.165)Fe(2)Al(0.33)Si(3.67)O(12)H(2)
ref:32                14.Jan.98
        -1075647.0    -1162924.0     65.740    129.760
          77.945000     53.040000    -13.190000
         600.00
NONTRONITE,NA         Na0.33Fe2Al0.33Si3.67O10(OH)2
Na-Non                Na(0.33)Fe(2)Al(0.33)Si(3.67)O(12)H(2)
ref:32                14.Jan.98
```

```
       -1078271.0    -1165798.0     67.660    132.110
        79.277000     53.560000    -13.420000
        600.00
PALLADIUM             Pd
Pd                    Pd(1)
ref:38                20.Jan.98
              .0            .0      8.990      8.850
         5.800000      1.380000       .000000
        973.00
Pd-OXIDE              PdO
Pd-OX                 Pd(1)O(1)
ref:38                20.Jan.98
        -14400.0      -20400.0     13.200     14.070
         3.300000      14.200000       .000000
        973.00
PARAGONITE            NaAl2(AlSi3)O10(OH)2
Pg                    Na(1)Al(3)Si(3)O(12)H(2)
ref:1                 5.May.78
       -1326012.0     -1416963.0     66.400    132.530
        97.430000      24.500000    -26.440000
       1000.00
PARGASITE             Na(Ca2Mg4Al)(Al2Si6)O22(OH)2
Prg                   Na(1)Ca(2)Mg(4)Al(3)Si(6)O(24)H(2)
ref:1,19              15.Mar.90
       -2846728.0     -3016624.0    160.000    273.500
        205.800000     41.660000    -50.210000
       1000.00
PERICLASE             MgO
Per                   Mg(1)O(1)
ref:1                 5.May.78
        -136086.0      -143800.0      6.440     11.248
         10.180000      1.740000     -1.480000
       2100.00
PHLOGOPITE            KMg3(AlSi3)O10(OH)2
Phl                   K(1)Mg(3)Al(1)Si(3)O(12)H(2)
ref:1,31              9.Jan.98
       -1396423.0     -1488303.0     76.100    149.660
        100.610000     28.780000    -21.500000
       1000.00
POTASSIUM-OXIDE       K2O
K-Ox                  K(2)O(1)
ref:1                 5.May.78
         -77056.0       -86800.0     22.500     40.380
         18.510000       8.650000      -.880000
       1100.00
PYRITE                FeS2
Py                    Fe(1)S(2)
ref:1                 5.May.78
         -38293.0       -41000.0     12.650     23.940
         17.880000       1.320000     -3.050000
       1000.00
PYROPHYLLITE          Al2Si4O10(OH)2
Prl                   Al(2)Si(4)O(12)H(2)
ref:1                 5.May.78
       -1255997.0     -1345313.0     57.200    126.600
        79.432000      39.214000    -17.282000
        800.00
RHODOCHROSITE         MnCO3
Rds                   Mn(1)C(1)O(3)
ref:1                 5.May.78
        -195045.0      -212521.0     23.900     31.075
         21.990000       9.300000     -4.690000
        700.00
RICHTERITE            Na2(CaMg5)Si8O22(OH)2
Rct                   Na(2)Ca(1)Mg(5)Si(8)O(24)H(2)
ref:1                 5.May.78
        999999.0       999999.0    137.600    272.800
       194.800000      61.100000    -46.150000
        800.00
ROMARCHITE            SnO
Sn-Ox                 Sn(1)O(1)
ref:12                5.May.78
         -61459.0       -68340.0     13.660     20.895
          9.550000       3.500000       .000000
       1237.00
RUTILE                TiO2
Ru                    Ti(1)O(2)
ref:7,9               Mar.83
        -212883.0      -226101.0     12.020     18.820
         15.014420       2.720501     -2.365364
       1800.00
SANIDINE,HIGH         K(AlSi3)O8
Hi-Sa                 K(1)Al(1)Si(3)O(8)
ref:1,31              9.Jan.98
        -893974.0      -946774.0     54.530    109.008
         63.830000      12.900000    -17.050000
       1400.00
SEPIOLITE             Mg4Si6O15(OH)2(H2O)2*4H2O
Sep                   Mg(4)Si(6)O(23)H(14)
ref:1                 5.May.78
       -2211192.0     -2418000.0    146.600    285.600
        157.920000     104.300000    -18.680000
        800.00
SIDERITE              FeCO3
Sd                    Fe(1)C(1)O(3)
ref:1,13              5.May.78
        -162414.0      -179173.0     25.100     29.378
         11.630000      26.800000       .000000
        885.00
SILLIMANITE           Al2SiO5
Sil                   Al(2)Si(1)O(5)
ref:1                 5.May.78
        -580091.0      -615099.0     23.130     49.900
         40.023988       7.390511    -11.674053
       1200.00
SILVER,NATIVE         Ag
Ag                    Ag(1)
ref:1                 5.May.78
              .0            .0     10.170     10.272
         5.090000      2.040000       .360000
       1234.00
SMITHSONITE           ZnCO3
Smt                   Zn(1)C(1)O(3)
ref:1                 5.May.78
        -174850.0      -194260.0     19.700     28.275
          9.300000      33.000000       .000000
        780.00
SODIUM-OXIDE          Na2O
Na-Ox                 Na(2)O(1)
ref:1                 5.May.78
         -89883.0       -99140.0     17.935     25.000
         18.250000       4.890000     -2.890000
       1000.00
SPHALERITE            ZnS
Sp                    Zn(1)S(1)
ref:1                 5.May.78
         -47947.0       -49000.0     14.019     23.830
         11.770000       1.260000     -1.160000
       1300.00
SPINEL                MgAl2O4
Spn                   Mg(1)Al(2)O(4)
ref:1                 5.May.78
        -517006.0      -546847.0     19.270     39.710
         36.772808       6.415456     -9.708792
       2000.00
STAUROLITE            Fe2Al9Si4O23(OH)
St                    Fe(2)Al(9)Si(4)O(24)H(1)
ref:1                 5.May.78
        999999.0       999999.0    117.100    224.400
       207.120000      36.940000    -57.220000
       1000.00
STRONTIANITE          SrCO3
Str                   Sr(1)C(1)O(3)
ref:1                 5.May.78
         -275470.0      -294600.0     23.200     39.010
          23.520000       6.320000     -5.080000
       1197.00
SYLVITE               KCl
Sy                    K(1)Cl(1)
ref:1                 5.May.78
          -97735.0      -104370.0     19.730     37.524
          9.890000       5.200000       .770000
       1043.00
TALC                  Mg3Si4O10(OH)2
Tcl                   Mg(3)Si(4)O(12)H(2)
ref:1                 5.May.78
       -1320188.0     -1410920.0     62.340    136.250
         82.482000      41.614000    -13.342000
        800.00
TENORITE              CuO
Tn                    Cu(1)O(1)
ref:1                 5.May.78
          -30568.0       -37200.0     10.180     12.220
         11.530000       1.880000     -1.760000
       1600.00
TITANITE              CaTiSiO5
Ti                    Ca(1)Ti(1)Si(1)O(5)
ref:7,9,19            Mar.90
         -587129.0      -620960.0     30.880     55.650
         42.234220       5.703951     -9.525038
       1670.00
TREMOLITE             (Ca2Mg5)Si8O22(OH)2
Tr                    Ca(2)Mg(5)Si(8)O(24)H(2)
ref:1,19              15.Mar.90
       -2770245.0     -2944038.0    131.190    272.920
        188.222000      57.294000    -44.822000
        800.00
WAIRAKITE             Ca(Al2Si4)O12*2H2O
Wai                   Ca(1)Al(2)Si(4)O(14)H(4)
ref:1,19              15.Mar.90
       -1477432.0     -1579333.0    105.100    186.870
        100.400000      44.470000    -16.430000
       1000.00
URANINITE             UO2
Uran                  U(1)O(2)
ref:37                18.Jan.98
        -246610.0      -259320.0     18.400     24.638
         15.003000       7.586000     -1.839000
        573.15
WITHERITE             BaCO3
Wth                   Ba(1)C(1)O(3)
ref:1                 5.May.78
        -278400.0      -297500.0     26.800     45.810
         21.500000      11.060000     -3.910000
       1079.00
WOLLASTONITE          CaSiO3
Wo                    Ca(1)Si(1)O(3)
ref:1,19              15.Mar.90
        -369225.0      -389590.0     19.600     39.930
         26.640000       3.600000     -6.520000
       1400.00
WURTZITE              ZnS
Wur                   Zn(1)S(1)
ref:1                 5.May.78
         -44810.0       -45850.0     14.064     23.846
         11.820000       1.160000     -1.040000
       1300.00
ZINCITE               ZnO
Znc                   Zn(1)O(1)
ref:1                 5.May.78
          999999.0       999999.0     10.430     14.338
         11.710000       1.220000     -2.180000
       2000.00
ZOISITE               Ca2Al3Si3O12(OH)
Zo                    Ca(2)Al(3)Si(3)O(13)H(1)
ref:1,19              15.Mar.90
```

```
      -1549179.0    -1643691.0    70.740   135.900
      106.118000     25.214000   -27.145000
       700.00
************************************************************
        minerals that undergo one phase transition
************************************************************
ALBITE                Na(AlSi3)O8
Ab                    Na(1)Al(1)Si(3))O(8)
ref:1                 5.May.78
        -886308.0     -939680.0    49.510   100.250
        61.700000     13.900000   -15.010000
        473.00  999999.0  999999.000  999999.000
        81.880000      3.554000   -50.154000
       1200.00
ALBITE,HIGH           NaAlSi3O8
Hi-Ab                 Na(1)Al(1)Si(3)O(8)
ref:1                 5.May.78
        -884509.0     -937050.0    52.300   100.430
        61.700000     13.900000   -15.010000
        623.00  999999.0  999999.000  999999.000
        64.170000     13.900000   -15.010000
       1400.00
ALMANDINE             Fe3Al2Si3O12
Alm                   Fe(3)Al(2)Si(3)O(12)
ref:1                 5.May.78
         999999.0      999999.0    75.600   115.280
        97.520000     33.640000   -18.730000
        848.00  999999.0  999999.000  999999.000
       107.090000     14.860000   -10.630000
       1600.00
AMESITE,14A           Mg4Al2(Al2Si2)O10(OH)8
14A-Am                Mg(4)Al(4)Si(2)O(18)H(8)
ref:1                 5.May.78
         999999.0      999999.0   108.900   205.400
       172.590000     34.980000   -41.670000
        848.00  999999.0  999999.000  999999.000
       169.400000     41.240000   -44.370000
       1000.00
ANTIGORITE            Mg48Si34O85(OH)62
Atg                   Mg(48)Si(34)O(147)H(62)
ref:1                 5.May.78
      -15808020.0   -17070891.0   861.360  1749.130
      1228.450000    513.760000   -286.680000
        848.00  999999.0  999999.000  999999.000
      1234.830000    501.240000   -281.280000
       1000.00
CLINOCHLORE,7A        Mg5Al(AlSi3)O10(OH)8
7A-Cnc                Mg(5)Al(2)Si(3)O(18)H(8)
ref:1                 5.May.78
      -1957101.0    -2113197.0   106.500   211.500
       162.820000     50.620000   -40.880000
        848.00  999999.0  999999.000  999999.000
       166.010000     44.360000   -38.180000
        900.00
COESITE               SiO2
Cos                   Si(1)O(2)
ref:1                 5.May.78
       -203541.0     -216614.0     9.650    20.641
        11.000000      8.200000    -2.700000
        848.00  999999.0  999999.000  999999.000
        14.190000      1.940000      .000000
       2000.00
CRISTOBALITE          SiO2
Crs                   Si(1)O(2)
ref:1                 5.May.78
       -203895.0     -216755.0    10.372    25.740
        13.980000      3.340000    -3.810000
        543.00     321.0  999999.000  999999.000
        17.390000       .310000    -9.890000
       2000.00
DAPHNITE,7A           Fe5Al(AlSi3)O10(OH)8
7A-Dph                Fe(5)Al(2)Si(3)O(18)H(8)
ref:1,30              9.May.98
      -1544331.0    -1689504.0   138.900   221.200
       172.530000     52.280000   -37.230000
        848.00  999999.0  999999.000  999999.000
       175.720000     46.020000   -34.630000
       1000.00
EDENITE               Na(Ca2Mg5)(AlSi7)O22(OH2)
Ed                    Na(1)Ca(2)Mg(5)Al(1)Si(7)O(24)H(2)
ref:1                 5.May.78
         999999.0      999999.0   161.000   271.000
       199.710000     48.780000   -46.010000
        848.00  999999.0  999999.000  999999.000
       202.900000     42.520000   -43.310000
       1000.00
EPISTILBITE           Ca(Al2Si6)O16*5H2O
Eps                   Ca(1)Al(2)Si(6)O(21)H(10)
ref:1                 5.May.78
         999999.0      999999.0   152.900   267.560
       157.040000     60.870000   -21.830000
        848.00  999999.0  999999.000  999999.000
       163.420000     48.350000   -16.430000
       1000.00
FERROEDENITE          Na(Ca2Fe5)(AlSi7)O22(OH)2
Fe-Ed                 Na(1)Ca(2)Fe(5)Al(1)Si(7)O(24)H(2)
ref:1                 5.May.78
         999999.0      999999.0   193.700   280.900
       209.420000     50.440000   -42.360000
        848.00  999999.0  999999.000  999999.000
       212.610000     44.180000   -39.660000
       1000.00
FERROSILITE           FeSiO3
Fs                    Fe(1)Si(1)O(3)
ref:1,13              5.May.78
       -267588.0     -285658.0    21.630    32.952
        26.490000      5.070000    -5.550000
        413.00    37.0       .056      67.000
        23.865000      8.780000    -4.700000
       1400.00
FLUOREDENITE          Na(Ca2Mg5)(AlSi7)O22(F)2
Fl-Ed                 Na(1)Ca(2)Mg(5)Al(1)Si(7)O(22)F(2)
ref:1                 5.May.78
         999999.0      999999.0   146.700   272.500
       195.230000     46.740000   -44.920000
        848.00  999999.0  999999.000  999999.000
       198.420000     40.480000   -42.220000
       1000.00
HERZENBERGITE         SnS
Hrz                   Sn(1)S(1)
ref:12                5.May.78
        -25023.0      -25464.0    18.360    29.010
         8.530000      7.480000      .900000
       875.00     160.0  999999.000  999999.000
         9.780000      3.740000      .000000
       1153.00
HEULANDITE            Ca(Al2Si7)O18*6H2O
Hul                   Ca(1)Al(2)Si(7)O(24)H(12)
ref:1                 5.May.78
         999999.0      999999.0   182.400   316.370
       179.660000     69.070000   -24.530000
        848.00  999999.0  999999.000  999999.000
       189.230000     50.290000   -16.430000
       1000.00
KALSILITE             K(AlSi)O4
Kls                   K(1)Al(1)Si(1)O(4)
ref:1                 5.May.78
        -481750.0     -509408.0    31.850    59.890
        29.430000     17.360000    -5.320000
       810.00     160.0  999999.000  999999.000
        42.500000       .000000      .000000
       1800.00
LAWSONITE             CaAl2Si2O7(OH)2*H2O
Lws                   Ca(1)Al(2)Si(2)O(10)H(4)
ref:1,19              15.Mar.90
      -1073408.0    -1158104.0    55.800   101.320
        81.800000     23.360000   -16.260000
        848.00  999999.0  999999.000  999999.000
        84.990000     17.100000   -13.560000
       1000.00
MAGNETITE             Fe3O4
Mag                   Fe(3)O(4)
ref:1                 5.May.78
       -242574.0     -267250.0    34.830    44.524
        21.880000     48.200000      .000000
        900.00  999999.0  999999.000  999999.000
        48.000000       .000000      .000000
       1800.00
MARGARITE             CaAl2(Al2Si2)O10(OH)2
Mrg                   Ca(1)Al(4)Si(2)O(12)H(2)
ref:1,19              15.Mar.90
      -1394150.0    -1485803.0    63.800   129.400
       102.500000     16.350000   -28.050000
        848.00  999999.0  999999.000  999999.000
         99.310000     22.610000   -30.750000
       1000.00
NATROLITE             Na2(Al2Si3)O10*2H2O
Ntr                   Na(2)Al(2)Si(3)O(12)H(4)
ref:1                 5.May.78
         999999.0      999999.0   101.600   169.720
        95.760000     40.080000   -15.060000
        848.00  999999.0  999999.000  999999.000
        92.570000     46.340000   -17.760000
       1000.00
NESQUEHONITE          MgCO3*3H2O
Nsh                   Mg(1)C(1)O(6)H(6)
ref:1                 5.May.78
       -412035.0     -472576.0    46.760    74.790
     -1574.804000   3899.173000  -417.325000
        306.50     184.0  999999.000  999999.000
        25.246000     91.289000    -4.222000
        340.00
NICKEL                Ni
Ni                    Ni(1)
ref:1                 5.May.78
              .0            .0     7.140     6.588
         4.060000      7.040000      .000000
       633.00        .0  999999.000  999999.000
         6.000000      1.800000      .000000
       1725.00
PHILLIPSITE,CA        Ca(Al2Si5)O14*5H2O
Ca-Php                Ca(1)Al(2)Si(5)O(19)H(10)
ref:1                 5.May.78
         999999.0      999999.0   166.600   265.000
       145.820000     52.670000   -19.130000
        848.00  999999.0  999999.000  999999.000
       149.010000     46.410000   -16.430000
       1000.00
PHILLIPSITE,K         K2(Al2Si5)O14*5H2O
K-Php                 K(2)Al(2)Si(5)O(19)H(10)
ref:1                 5.May.78
         999999.0      999999.0   172.100   265.000
       152.660000     60.240000   -18.450000
        848.00  999999.0  999999.000  999999.000
       155.850000     53.980000   -15.750000
       1000.00
PHILLIPSITE,NA        Na2(Al2Si5)O14*5H2O
Na-Php                Na(2)Al(2)Si(5)O(19)H(10)
ref:1                 5.May.78
         999999.0      999999.0   172.400   265.000
       152.400000     56.480000   -20.460000
        848.00  999999.0  999999.000  999999.000
       155.590000     50.220000   -17.760000
       1000.00
PREHNITE              Ca2Al2Si3O10(OH)2
Prh                   Ca(2)Al(2)Si(3)O(12)H(2)
```

```
ref:1,19              15.Mar,90
       -1390097.0     -1481649.0     65.000    140.330
        91.600000      37.820000     -19.600000
        848.00  999999.0  999999.000  999999.000
       101.170000      19.040000     -11.500000
       1000.00
PYROPE                Mg3Al2Si3O12
Prp                   Mg(3)Al(2)Si(3)O(12)
ref:1,7               5.May.78
         999999.0       999999.0     62.300    113.270
        91.690000      32.640000     -20.920000
        848.00  999999.0  999999.000  999999.000
       101.260000      13.860000     -12.820000
       1800.00
QUARTZ                SiO2
Qtz                   Si(1)O(2)
ref:1                 5.May.78
        -204646.0      -217650.0      9.880     22.688
        11.220000       8.200000     -2.700000
        848.00      290.0       .372      38.500
        14.410000       1.940000       .000000
       2000.00
QUICKSILVER           Hg
Hg                    Hg(1)
ref:1                 5.May.78
                .0             .0     18.170    14.822
         6.440000       .000000       .190000
        629.00   14140.0  999999.000  999999.000
         4.970000       .000000       .000000
       3000.00
SPESSARTINE           Mn3Al2Si3O12
Sps                   Mn(3)Al(2)Si(3)O(12)
ref:1                 5.May.78
         999999.0       999999.0     74.500    117.900
        94.480000      33.240000     -19.120000
        848.00  999999.0  999999.000  999999.000
       104.050000      14.460000     -11.020000
       1800.00
STILBITE              NaCa2(Al5Si13)O36*14H2O
Stb                   Na(1)Ca(2)Al(5)Si(13)O(50)H(28)
ref:1                 5.May.78
         999999.0       999999.0    399.300    649.910
       390.550000     137.680000     -49.840000
        848.00  999999.0  999999.000  999999.000
       400.120000     118.900000     -41.740000
       1000.00
TIN,NATIVE            Sn
Sn                    Sn(1)
ref:12                Aug.85
                .0             .0     12.240    16.289
         4.420000       6.300000       .000000
        505.06   1680.0  999999.000  999999.000
         7.300000       .000000       .000000
       3000.00
**********************************************************
        minerals that undergo two phase transitions
**********************************************************
ACANTHITE             Ag2S
Acn                   Ag(2)S(1)
ref:1                 5.May.78
          -9446.0       -7550.0     34.300     34.200
        15.630000       8.600000       .000000
        450.00      950.0  999999.000  999999.000
         1.819000      53.000000       .000000
        620.00      600.0  999999.000  999999.000
        21.600000       .000000       .000000
       1000.00
AEGERINE              NaFe(SiO3)2
Agt                   Na(1)Fe(1)Si(2)O(6)
ref:1                 5.May.78
         999999.0       999999.0     36.700     64.370
        46.160000      19.310000      -9.460000
        950.00  999999.0  999999.000  999999.000
         52.420000      10.010000      -7.680000
        1050.00  999999.0  999999.000  999999.000
         50.270000      10.890000      -7.680000
        1400.00
ANTHOPHYLLITE         Mg7Si8O22(OH)2
Ath                   Mg(7)Si(8)O(24)H(2)
ref:1                 5.May.78
       -2715430.0     -2888749.0    128.600    264.400
        180.682000      60.574000     -38.462000
        903.00  999999.0  999999.000  999999.000
        197.542000      41.614000     -13.342000
        1258.00  999999.0  999999.000  999999.000
        199.522000      41.614000     -13.342000
        1800.00
BORNITE               Cu5FeS4
Bn                    Cu(5)Fe(1)S(4)
ref:1,16              5.May.78
         -86704.0       -79922.0     99.290     98.600
        49.760000       35.080000     -1.350000
        485.00    1430.0  999999.000  999999.000
       -34.310000      247.000000       .000000
        540.00        .0  999999.000  999999.000
         80.330000      -2.040000       .000000
        1200.00
BUNSENITE             NiO
Bsn                   Ni(1)O(1)
ref:1                 5.May.78
         -50573.0       -57300.0      9.080     10.970
        -4.990000       37.580000      3.890000
        525.00        .0  999999.000  999999.000
         13.880000        .000000       .000000
        565.00        .0  999999.000  999999.000
         11.180000       2.020000       .000000
        2000.00
CHALCOCITE            Cu2S
Cc                    Cu(2)S(1)
ref:1                 5.May.78
         -20626.0       -19000.0     28.900     27.480
        12.630000       18.820000       .000000
        376.00      920.0  999999.000  999999.000
        26.780000       -7.350000       .000000
        717.00      287.0  999999.000  999999.000
         20.320000        .000000       .000000
        1400.00
CHALCOPYRITE          CuFeS2
Ccp                   Cu(1)Fe(1)S(2)
ref:1,16              5.May.78
         -44900.0       -44453.0     31.150     42.830
        20.790000       12.800000      -1.340000
        830.00     2405.0  999999.000  999999.000
       -141.400000      210.000000       .000000
        930.00        .0  999999.000  999999.000
         41.220000        .000000       .000000
        1200.00
CRONSTEDTITE,7A       Fe2Fe(FeSi)O5(OH)4
7A-Csd                Fe(4)Si(1)O(9)H(4)
ref:1                 5.May.78
         999999.0       999999.0     73.500    110.900
        84.790000       41.840000     -12.476000
        950.00  999999.0  999999.000  999999.000
        97.300000       23.240000      -8.930000
        1050.00  999999.0  999999.000  999999.000
        93.010000       25.000000      -8.930000
        1500.00
ENSTATITE             MgSiO3
En                    Mg(1)Si(1)O(3)
ref:1                 5.May.78
       -348930.0      -369686.0     16.200     31.276
        24.550000       4.740000      -6.280000
        903.00      166.0       .020     384.615
        28.765000        .000000       .000000
        1258.00      390.0       1.090      11.900
         29.260000        .000000       .000000
        1800.00
FERROGEDRITE          (Fe5Al2)(Al2Si6)O22(OH)2
Fe-Ged                Fe(5)Al(4)Si(6)O(24)H(2)
ref:1                 5.May.78
         999999.0       999999.0    153.500    265.900
        196.270000      58.390000     -39.010000
        903.00  999999.0  999999.000  999999.000
        204.700000      48.910000     -26.450000
        1258.00  999999.0  999999.000  999999.000
        205.690000      48.910000     -26.450000
        1500.00
HASTINGSITE           Na(Ca2Fe4Fe)(Al2Si6)O22(OH)2
Hs                    Na(1)Ca(2)Fe(5)Al(2)Si(6)O(24)H(2)
ref:1                 5.May.78
         999999.0       999999.0    189.200    280.300
        211.570000      50.880000     -44.880000
        950.00  999999.0  999999.000  999999.000
        217.820000      41.580000     -43.100000
        1050.00  999999.0  999999.000  999999.000
        215.680000      42.460000     -43.100000
        1500.00
HEMATITE              Fe2O3
Hem                   Fe(2)O(3)
ref:1                 5.May.78
         -178155.0      -197720.0     20.940     30.274
        23.490000       18.600000      -3.550000
        950.00      160.0  999999.000  999999.000
         36.000000       .000000       .000000
        1050.00        .0  999999.000  999999.000
         31.710000       1.760000       .000000
        1800.00
LARNITE               Ca2SiO4
Lrn                   Ca(2)Si(1)O(4)
ref:1,8               5.May.78
         999999.0       999999.0     30.500     51.600
        34.870000       9.740000      -6.260000
        970.00      440.0  999999.000  999999.000
         32.160000      11.020000       .000000
        1710.00    3390.0  999999.000  999999.000
         49.000000       .000000       .000000
        2000.00
MAGNESIOHASTINGSITE   Na(Ca2Mg4Fe)(Al2Si6)O22(OH)2
Mg-Hs                 Na(1)Ca(2)Mg(4)Fe(1)Al(2)Si(6)O(24)H(2)
ref:1                 5.May.78
         999999.0       999999.0    163.800    273.800
        203.800000      49.550000     -47.800000
        950.00  999999.0  999999.000  999999.000
        210.060000      40.250000     -46.020000
        1050.00  999999.0  999999.000  999999.000
        207.910000      41.130000     -46.020000
        1500.00
MAGNESIORIEBECKITE    Na2(Mg3Fe2)Si8O22(OH)2
Mg-Rbk                Na(2)Mg(3)Fe(2)Si(8)O(24)H(2)
ref:1                 5.May.78
         999999.0       999999.0    138.000    271.300
        186.260000      75.140000     -45.180000
        950.00  999999.0  999999.000  999999.000
        198.770000      56.540000     -41.630000
        1050.00  999999.0  999999.000  999999.000
        194.480000      58.300000     -41.630000
        1500.00
PYRRHOTITE            FeS
Po                    Fe(1)S(1)
ref:1                 5.May.78
         -24084.0       -24000.0     14.410     18.200
        5.190000       26.400000       .000000
        411.00      570.0  999999.000  999999.000
         17.400000       .000000       .000000
        598.00      120.0  999999.000  999999.000
         12.200000      2.380000       .000000
```

```
      1468.00
RIEBECKITE            Na2(Fe3Fe2)Si8O22(OH)2
Rbk                   Na(2)Fe(5)Si(8)O(24)H(2)
ref:1                 5.May.78
        999999.0      999999.0    156.600    274.900
       192.090000     76.140000    -42.990000
        950.00  999999.0  999999.000  999999.000
       204.600000     57.540000    -39.440000
        1050.00  999999.0  999999.000  999999.000
       200.310000     59.300000    -39.440000
       1500.00
*************************************************************
        minerals that undergo three phase transitions
*************************************************************
IRON                  Fe
Fe                    Fe(1)
ref:7,8               5.May.78
              .0              .0      6.520      7.092
         3.040000       7.580000      .600000
         1033.00      326.0  999999.000  999999.000
         11.130000        .000000       .000000
         1183.00      215.0  999999.000  999999.000
          5.800000       1.980000       .000000
         1673.00      165.0  999999.000  999999.000
          6.740000       1.600000       .000000
        1812.00
PD-OXYANNITE          KFe3(AlSi3)O10(OH)O-
Pd-Oxn                K(1)Fe(3)Al(1)Si(3)O(12)H(1)
ref:1                 5.May.78
         999999.0       999999.0     68.500    143.200
        88.340000      54.120000    -18.060000
        848.00  999999.0  999999.000  999999.000
        97.910000      35.340000     -9.960000
        950.00  999999.0  999999.000  999999.000
       116.680000       7.440000     -4.630000
        1050.00  999999.0  999999.000  999999.000
       110.240000      10.080000     -4.630000
       1100.00
*************************************************************
        gases
*************************************************************
Ar,g                  ARGON
Ar(g)                 Ar(1)
ref:6,8               27.Dec.89
              .0              .0     37.008       .000
         4.968000        .000000       .000000
        8000.00
CH4,g                 METHANE
CH4(g)                C(1)H(4)
ref:6,8               15.Dec.87
        -12122.4        -17880.0     44.518       .000
         5.650000       11.440000      -.460000
        1500.00
CO2,g                 CARBON-DIOXIDE
CO2(g)                C(1)O(2)
ref:6,8               27.Dec.89
         -94254.0        -94051.0     51.085       .000
         10.570000        2.100000     -2.060000
        2500.00
H2,g                  HYDROGEN
H2(g)                 H(2)
ref:6,8               27.Dec.89
              .0              .0     31.234       .000
         6.520000        .780000       .120000
        3000.00
H2O,g                 STEAM
H2O(g)                H(2)O
ref:17                24.Mar.90
        -54524.8        -57935.1     44.763       .000
        12.664700       -10.404100       .013078
        2523.15
H2S,g                 HYDROGEN-SULFIDE
H2S(g)                H(2)S(1)

ref:6,8               27.Dec.89
         -8021.0         -4931.0     49.185       .000
         7.810000        2.960000      -.460000
        2300.00
He,g                  HELIUM
He(g)                 He(1)
ref:6,8               27.Dec.89
              .0              .0     30.151       .000
         4.968000        .000000       .000000
        8000.00
Kr,g                  KRYPTON
Kr(g)                 Kr(1)
ref:6,8               27.Dec.89
              .0              .0     39.217       .000
         4.968000        .000000       .000000
        8000.00
N2,g                  NITROGEN
N2(g)                 N(2)
ref:6,8               27.Dec.89
              .0              .0     45.796       .000
         6.830000        .900000      -.120000
        3000.00
NH3,g                 AMMONIA
NH3(g)                N(1)H(3)
ref:6,8               26.Jul.89
         -3932.0        -11021.0     46.000       .000
         7.110000        6.000000      -.370000
        1800.00
Ne,g                  NEON
Ne(g)                 Ne(1)
ref:6,8               27.Dec.89
              .0              .0     34.973       .000
         4.968000        .000000       .000000
        8000.00
O2,g                  OXYGEN
O2(g)                 O(2)
ref:6,8               27.Dec.89
              .0              .0     49.029       .000
         7.160000        1.000000      -.400000
        3000.00
Rn,g                  RADON
Rn(g)                 Rn(1)
ref:6,8               27.Dec.89
              .0              .0     42.120       .000
         4.968000        .000000       .000000
        3000.00
S2,g                  SULFUR
S2(g)                 S(2)
ref:6,8               27.Dec.89
          18953.0         30681.0     54.540       .000
          8.720000        .160000      -.900000
        3000.00
SO2,g                 SULFUR-DIOXIDE
SO2(g)                S(1)O(2)
ref:6,8               27.Dec.89
         -71748.0        -70944.0     59.330       .000
         11.040000       1.880000     -1.840000
        2000.00
Xe,g                  XENON
Xe(g)                 Xe(1)
ref:6,8               27.Dec.89
              .0              .0     40.555       .000
         4.968000        .000000       .000000
        8000.00
*************************************************************
        aqueous species
*************************************************************
FORMIC-ACID,aq        H2CO2
FOAC(aq)              C(1)H(2)O(2)+(0)
ref:26                17.Jun.92
        -88982.         -101680.      38.900
         6.3957          7.7713       2.8318     -3.1002
        26.1000          3.1000      -0.3300           0.
FORMATE               HCO2-
FOR-                  H(1)C(1)O(2)-(1)
ref:26                28.Feb.92
        -83862.         -101680.      21.700
         5.7842          4.7242       7.3630     -2.9742
        17.0000        -12.4000       1.3003           -1.
ACETIC-ACID,aq        C2H4O2
ACAC(aq)              C(2)H(4)O(2)+(0)
ref:26                6.Mar.92
        -94760.         -116100.      42.700
        11.6198          5.2180       2.5088     -2.9946
        42.0760         -1.5417      -0.1500           0.
ACETATE               C2H3O2-
AE-                   C(2)H(3)O(2)-(1)
ref:26                28.Feb.92
        -88270.         -116160.      20.600
         7.7525          8.6996       7.5825     -3.1385
        26.3000         -3.8600       1.3182           -1.
PROPANOIC-ACID,aq     C3H6O2
PRAC(aq)              C(3)H(6)O(2)+(0)
ref:26                6.Mar.92
        -93450.         -122470.      49.400
        11.0057         18.7077      -0.7792     -3.5523
        62.9700         -1.1900      -0.1500           0.
PROPANOATE            C3H5O2-
PRO-                  C(3)H(5)O(2)-(1)
ref:26                28.Feb.92
        -86780.         -122630.      26.500
         9.6992         12.1344       9.0612     -3.2805
        52.3000         -4.2000       1.2276           -1.
BUTANOIC-ACID,aq      C4H8O2
BUAC(aq)              C(4)H(8)O(2)+(0)
ref:26                6.Mar.92
        -91210.         -127950.      56.100
        13.2702         23.3487      -0.6985     -3.7441
        72.4342          2.9924      -0.2155           0.
BUTANOATE             C4H7O2-
BUT8                  C(4)H(7)O(2)-(1)
ref:26                17.Jun.92
        -84650.         -128630.      31.800
        11.7724         17.0492       7.4458     -3.4837
        62.3135         -3.5666       1.1469           -1.
PENTANOIC-ACID,aq     C5H10O2
PEAC(aq)              C(5)H(10)O(2)+(0)
ref:26                6.Mar.92
        -89240.         -133690.      62.800
        15.4596         28.3156      -1.8374     -3.9495
        91.0659          5.2450      -0.1710           0.
PENTANOATE            C5H9O2-
N-PEN8-               C(5)H(9)O(2)-(1)
ref:26                17.Jun.92
        -82630.         -134380.      38.300
        13.9304         24.8456      -1.0403     -3.8060
        86.5816         -3.2539       1.0496           -1.
GLYCOLIC-ACID,aq      C2H4O3
glyac                 C(2)H(4)O(3)+(0)
ref:26                16.Jun.92
        -126400.        -154890.      43.100
         8.7445         12.1496       4.0222     -3.2812
        43.6669         -0.4655      -0.3017           0.
GLYCOLATE             C2H3O3-
C2H3O3-               C(2)H(3)O(3)-(1)
ref:26                17.Jun.92
        -121170.        -154700.      26.200
         7.6349         11.0570       0.9834     -3.2360
        26.0463         -4.0271       1.2334           -1.
LACTIC-ACID,aq        C3H6O3
lacac                 C(3)H(6)O(3)+(0)
ref:26                16.Jun.92
```

```
      -127800.     -164000.       49.800
      11.1720      17.2432       3.8083      -3.4917
      61.0199       1.6290      -0.2572            0.
LACTATE                 C3H5O3-
lac8                    C(3)H(5)O(3)-(1)
ref:26                  17.Jun.92
      -122530.     -164070.       31.900
       9.8498      12.8244        8.0990     -3.3091
      44.9518      -3.7823        1.1469           -1.
OXALIC-ACID,aq          C2H2O4
OXAC                    C(2)H(2)O(4)+(0)
ref:26                  28.FEB.92
      -168640.     -194580.       44.000
       8.4291      12.3793        1.7866     -3.2907
      25.4994      -2.7181       -0.2957            0.
H-OXALATE               C2HO4-
Hoxa-                   C(2)H(1)O(4)-(1)
ref:26                  17.JUN.92
      -166907.     -195600.       36.000
       7.9276      11.2406        2.0500     -3.2436
       6.5915      -6.3548        1.0831           -1.
OXALATE                 C2O4-2
Ox-2                    C(2)O(4)-(2)
ref:26                  17.JUN.92
      -161100.     -197200.       10.900
       6.9414       9.6716        0.8669     -3.1787
     -10.7618     -18.6787        3.0480           -2.
SUCCINIC-ACID,aq        C4H6O4
SUCAC                   C(4)H(6)O(4)+(0)
ref:26                  28.FEB.92
      -177800.     -218000.       62.300
      12.9872      22.7109       -0.5623     -3.7178
      51.0740       0.3050       -0.1744            0.
H-SUCCINATE             C4H5O4-
Hsuc-                   C(4)H(5)O(4)-(1)
ref:26                  16.JUN.92
      -172060.     -217350.       45.200
      11.6617      19.7057        0.1226     -3.5935
      26.117       -3.9932        0.9446           -1.
SUCCINATE               C4H4O4-2
Suc-2                   C(4)H(4)O(4)-(2)
ref:26                  17.JUN.92
      -164380.     -217350.       19.500
      10.4577      15.8622        3.5716     -3.4346
     -14.0383      -4.7180        2.9170           -2.
GLYCINE,aq              C2H5NO2
GLY(aq)                 C(2)H(5)O(2)N(1)+(0)
ref:4                   4.Sep.87
       -88618.     -122846.       37.840
       7.6046       7.0825       10.9119     -3.0717
      14.1998      -3.4185        -.2330            0.
ALANINE,aq              C3H7NO2
ALA(aq)                 C(3)H(7)O(2)N(1)+(0)
ref:4                   4.Sep.87
       -88800.     -132130.       40.000
       9.9472      11.7629       11.3023     -3.2652
      34.9465      -1.7690        -.2658            0.
Ac+2                    Ac(+2)
Ac+2                    Ac(1)+(2)
ref:36                  16.Jan.98
       -79200.      -73200.        4.000
       0.1865       -7.3171        8.6064     -2.4764
       7.9173       -5.6215        0.9979           2.
Ac+3                    Ac(+3)
Ac+3                    Ac(1)+(3)
ref:36                  16.Jan.98
      -153200.     -155300.      -39.000
      -2.5931      -14.1059       11.2780     -2.1958
       3.9756      -10.7344        2.1668           3.
Ag+                     Ag(+)
Ag+                     Ag(1)+(1)
ref:2                   1.Jul.87
       18427.       25275.        17.540
      1.7285       -3.5608        7.1496     -2.6318
     12.7862       -1.4254         .2160           1.
AgOH,aq                 AgOH(0)
AgOH(aq)                Ag(1)O(1)H(1)+(0)
ref:21                  12.Dec.97
      -21900.      -31800.        17.200
      2.2885       -2.1912        6.6063     -2.6883
     -0.3221       -5.1937        -.0300            0.
AgO-                    AgO(-1)
AgO-                    Ag(1)O(1)-(1)
ref:21                  12.Dec.97
       -5500.      -16300.        13.900
      1.4640       -4.1994        7.3839     -2.6053
      0.8786       -9.4103        1.4171           -1.
AgCl,aq                 AgCl(0)
AgCl(aq)                Ag(1)Cl(1)+(0)
ref:22                  17.Sep.97
      -17450.      -18270.        34.100
       5.2088       4.9399        3.8015     -2.9832
       9.8168       -1.6698        -.0300            0.
AgCl2-                  AgCl2(-)
AgCl2-                  Ag(1)Cl(2)-(1)
ref:40                  20.Jan.98
      -51350.      -55438.        49.780
       7.1327       9.8065        1.8947     -3.1844
       4.8953       -6.7789        0.6667           -1.
AgCl3-2                 AgCl3(-2)
AgCl3-2                 Ag(1)Cl(3)-(2)
ref:22                  17.Sep.97
      -82710.     -105613.        44.500
      14.5040      27.6363       -5.1192     -3.9214
      35.8339       -.8570        2.5402           -2.
AgCl4-3                 AgCl4(-3)
AgCl4-3                 Ag(1)Cl(4)-(3)
ref:22                  17.Sep.97
      -112280.     -150616.        35.000
      20.0386      41.1504      -10.4309     -4.4801
      55.0238       .243         4.2796           -3.
AgF,aq                  AgF(0)
AgF(aq)                 Ag(1)F(1)+(0)
ref:22                  6.Jan.98
       -49459.      -54722.        16.740
       2.5788       -1.4818        6.3255     -2.7177
      12.1829       -0.8218        -0.0380           0.
AgCO3-                  AgCO3(-)
AgCO3-                  Ag(1)C(1)O(3)-(1)
ref:22                  17.Sep.97
      -111430.     -142490.         0.000
       2.2588       -2.2632        6.6326     -2.6854
      15.2147       -5.1123        1.6310           -1.
Ag(CO3)2-3              Ag(CO3)2(-3)
Ag(CO3)2-3              Ag(1)C(2)O(6)-(3)
ref:22                  17.Sep.97
      -236890.     -304200.       -19.000
       3.7128       1.2872        5.2371     -2.8322
      36.5589       -8.7993        5.0992           -3.
AgNO3,aq                AgNO3(0)
AgNO3(aq)               Ag(1)N(1)O(3)+(0)
ref:22                  17.Sep.97
        -7738.      -23320.        49.000
       6.7660        8.7423        2.3069     -3.1404
      24.1485        3.3372        -.0380            0.
Ag(HS)2-                Ag(HS)2(-)
Ag(HS)2-                Ag(1)H(2)S(2)-(1)
ref:22                  6.Jan.98
           0.           -8200.        44.680
      10.3654      17.5311       -1.1475     -3.5037
      37.2753       4.7273        0.9527           -1.
Ag(Ae),aq               AgCH3COO
Ag(Ae),aq               Ag(1)C(2)H(3)O(2)
ref:33                  17 Aug 92
       -70840.      -91650.        38.900
       8.3987       12.7257        0.7485     -3.3050
      48.3694       11.7300        -0.0300           0.
Ag(Ae)2-                Ag(CH3COO)2-
Ag(Ae)2-                Ag(1)C(4)H(6)O(4)-(1)
ref:33                  17 Aug 92
      -158990.     -210560.        49.900
      16.2287       31.8418        -6.7592     -4.0952
     110.8373       30.5473         0.8741           -1.
Ag+2                    Ag(+2)
Ag+2                    Ag(1)+(2)
ref:2                   16.Feb.88
       64300.       64200.        -21.000
       -.4299       -8.8310         9.2210     -2.4139
      15.2224       -4.1142         1.3201           2.
Al+3                    Al(+3)
Al+3                    Al(1)+(3)
ref:20                  29.Apr.97
      -116543.     -128681.        -80.800
      -3.3404      -17.1108        14.9917     -2.0716
      10.7000       -8.0600         2.8711           3.
AlOH+2                  AlOH(+2)
AlOH+2                  Al(1)O(1)H(1)+(2)
ref:20                  30.Apr.97
      -166468.     -185096.        -46.820
        .2580       -9.6965         9.6000     -2.5767
      38.0000       -2.6000         1.7666           2.
AlO+                    AlO(+)
AlO+                    Al(1)O(1)+(1)
ref:20                  29.Apr.97
      -215465.     -241825.        -17.000
       3.5000       -2.4600         6.3000     -2.8100
      46.7000       -1.5000          .8089           1.
AlO2-                   AlO2(-)
AlO2-                   Al(1)O(2)-(1)
ref:20                  29.Apr.97
      -198700.     -222079.         -7.000
       3.7280        3.9800        -1.5170     -2.9435
      19.1000       -6.2000         1.7595           -1.
Al(Ae)+2                AlCH3COO+2
Al(Ae)+2                Al(1)C(2)H(3)O(2)+(2)
ref:33,35               15.Jan.98
      -208564.     -249130.        -32.770
       2.1643       -2.4961         6.7288     -2.6757
      63.2437       11.8151         1.5579           2.
Al(Ae)2+                Al(CH3COO)2+
Al(Ae)2+                Al(1)C(4)H(6)O(4)+(1)
ref:33,35               15.Jan.98
      -299359.     -372080.          8.520
       8.5167       13.0156         0.6302     -3.3170
     109.3239       31.4722         0.4210           1.
Am+2                    Am(+2)
Am+2                    Am(1)+(2)
ref:36                  16.Jan.98
       -89600.      -85100.         -3.000
       0.0294       -7.7042         8.7663     -2.4604
       9.6780       -5.3363         1.1000           2.
Am+3                    Am(+3)
Am+3                    Am(1)+(3)
ref:36                  16.Jan.98
      -142900.     -147400.        -48.900
       -2.9531      -14.9848        11.6223     -2.1594
        6.5235      -10.3270         2.3161           3.
Am+4                    Am(+4)
Am+4                    Am(1)+(4)
ref:36                  16.Jan.98
       -82900.      -99200.        -104.000
       -4.3164      -18.3144        12.9330     -2.0218
       40.0550       -3.2586         3.7484           4.
AmO2+                   AmO2(+)
AmO2+                   Am(1)O(2)+(1)
ref:36                  18.Jan.98
```

```
      -177100.     -192400.       -4.900
       3.4121       0.5496        5.5350      -2.8016
      -2.3999      -8.0048        0.6223            1.
AmO2+2                AmO2(+2)
AmO2+2                Am(1)O(2)+(2)
ref:36                18.Jan.98
      -140400.     -155800.      -20.800
       3.1185      -0.1662        5.8139      -2.7720
      23.6816      -1.3438        1.3732            2.
Ar,aq                 Ar(0)
Ar(aq)                Ar(1)+(0)
ref:3                 26.Jun.87
         3900.        -2870.        14.300
       6.0003       6.8698        3.0499      -3.0630
      35.6471       7.3160        -.3073            0.
AsO2-                 AsO2(-)
AsO2-                 As(1)O(2)-(1)
ref:21                12.Dec.97
       -83650.      -102540.        9.700
       3.2101       0.0554        5.7305      -2.7812
       3.4104      -8.7381        1.4820            -1.
AsO4-3                AsO4(-3)
AsO4-3                As(1)O(4)-(3)
ref:21                12.Dec.97
      -154970.     -212270.      -38.900
       1.0308      -5.2609        7.8091      -2.5614
     -12.1352     -26.6841        5.3990            -3.
Au+                   Au(+)
Au+                   Au(1)+(1)
ref:21                5.Jan.98
         39000.       47900.        25.600
       3.5312       0.8428        5.4139      -2.8137
       7.5089      -3.0956        0.1648            1.
AuCl,aq               AuCl(0)
AuCl(aq)              Au(1)Cl(1)+(0)
ref:22                5.Jan.98
        -3184.       -2140.        41.470
       7.0357       9.4008        2.0481      -3.1676
       0.0551      -5.0371       -0.0380            0.
AuCl2-                AuCl2(-)
AuCl2-                Au(1)Cl(2)-(1)
ref:22                5.Jan.98
       -36781.      -44725.        53.600
      11.5192      20.3482       -2.2547      -3.6201
      -0.6764      -8.0300        0.8173            -1.
AuCl3-2               AuCl3(-2)
AuCl3-2               Au(1)Cl(3)-(2)
ref:22                5.Jan.98
       -67811.      -86023.        61.390
      16.6878      32.9687       -7.2151      -4.1419
       1.7155     -11.8910        2.2827            -2.
Au(HS)2-              Au(HS)2(-)
Au(HS)2-              Au(1)H(2)S(2)-(1)
ref:22                6.Jan.98
         2429.        -2509.        56.770
      12.3420      22.3572       -3.0443      -3.7032
      16.8038      -1.8007        0.7693            -1.
Au(Ae),aq             AuCH3COO
Au(Ae),aq             Au(1)C(2)H(3)O(2)
ref:33                10 Sept 92
       -49870.      -68310.        48.000
      10.2130      17.1576       -0.9969      -3.4882
      38.7432       8.3843       -0.0300            0.
Au(Ae)2-              Au(CH3COO)2-
Au(Ae)2-              Au(1)C(4)H(6)O(4)-(1)
ref:33                10 Sept 92
      -138240.     -186750.       61.300
      18.1917      36.6392       -8.6534      -4.2936
      90.4610      24.0193        0.7010            -1.
Au+3                  Au(+3)
Au+3                  Au(1)+(3)
ref:21                5.Jan.98
       103600.      97800.       -54.800
      -1.7167     -11.9654       10.4352      -2.2843
      23.5775      -4.7048        2.4115            3.
AuCl4-                AuCl4(-)
AuCl4-                Au(1)Cl(4)-(1)
ref:22                5.Jan.98
         35332.       23573.       -32.720
       -0.5361      -9.0876        9.3148      -2.4033
      19.7251      -3.3107        1.5579            -1.
B(OH)3,aq             BOH3(0)
B(OH)3(aq)            B(1)O(3)H(3)+(0)
ref:39                20.Jan.98
       -231540.     -256820.       38.790
       8.0000       7.5000       15.0000      -6.4400
      40.0000      -6.8500        0.0450            0.
B(OH)4-               BOH4(-)
B(OH)4-               B(1)O(4)H(4)-(1)
ref:39                20.Jan.98
       -275610.     -321230.       24.500
       5.5200       6.3300        3.8000      -3.2500
      45.0000     -19.3300        0.9000            -1.
BF4-                  BF4(-)
BF4-                  B(1)F(4)-(1)
ref:2                 16.Feb.88
       -355400.     -376400.       43.000
       7.9796      11.7027        1.1504      -3.2628
      11.8941      -4.1753         .9779            -1.
Ba+2                  Ba(+2)
Ba+2                  Ba(1)+(2)
ref:2                 1.Jul.87
       -134030.     -128500.        2.300
       2.7383     -10.0565        -.0470      -2.3633
       3.8000      -3.4500         .9850            2.
BaOH+                 BaOH(+1)
BaOH+                 Ba(1)O(1)H(1)+(1)
ref:21                12.Sep.97
       -172300.     -175900.       27.500
       3.0700       -.2825        5.8541      -2.7672
      -5.7064      -7.5974         .1362            1.
BaCl+                 BaCl(+)
BaCl+                 Ba(1)Cl(1)+(1)
ref:22                17.Sep.97
       -164730.     -165323.       24.000
       3.4534        .6537        5.4861      -2.8060
      11.8213      -1.6759         .1895            1.
BaF+                  BaF(+)
BaF+                  Ba(1)F(1)+(1)
ref:22(tab. 3)        15.Sep.97
       -201120.     -206510.        5.500
         .9652      -5.4218        7.8740      -2.5548
      16.7505       -.8529         .4675            1.
BaCO3,aq              BaCO3(0)
BaCO3(aq)             Ba(1)C(1)O(3)+(0)
ref:22                17.Sep.97
       -263830.     -285850.       16.000
         .1361      -7.4461        8.6697      -2.4711
     -14.3440     -10.0418        -.0380            0.
Ba(Ae)+               BaCH3COO+
Ba(Ae)+               Ba(1)C(2)H(3)O(2)+(1)
ref:33                17 Aug 92
       -223650.     -242850.       33.500
       6.6253       8.3926        2.4574      -3.1259
      48.9806      11.6995        0.0459            1.
Ba(Ae)2,aq            Ba(CH3COO)2
Ba(Ae)2,aq            Ba(1)C(4)H(6)O(4)
ref:33                10 Sept 92
       -312620.     -358010.       59.700
      13.9186      26.2066       -4.5556      -3.8623
     103.6344      30.9388       -0.0300            0.
Ba(Ala)+              Ba(C3H6NO2)+
Ba(Ala)+              Ba(1)C(3)H(6)N(1)O(2)+(1)
ref:27                14.Aug.93
       -210013.     -243703.       56.097
       9.4348      15.2528        -.2391      -3.4095
      58.4325      16.0850       -0.2977            1.
Ba(Ala)2,aq           Ba(C3H6NO2)2
Ba(Ala)2,aq           Ba(1)C(6)H(12)N(2)O(4)
ref:27                14.Aug.93
       -285287.     -359051.      107.026
      20.1040      41.3073      -10.4865      -4.4865
     133.7647      41.4112       -0.0300            0.
Ba(But)+              BaCH3(CH2)2CO2+
Ba(But)+              Ba(1)C(4)H(7)O(2)+(1)
ref:27                14.Aug.93
       -218640.     -253285.       44.647
      10.6454      18.2150       -1.4160      -3.5319
      89.0694      26.1794       -0.1247            1.
Ba(But)2,aq           Ba(CH3CH2CH2CO2)2
Ba(But)2,aq           Ba(1)C(8)H(14)O(4)
ref:27                14.Aug.93
       -302827.     -378066.       85.592
      22.5399      47.2556      -12.8248      -4.7324
     203.1160      65.5159       -0.0300            0.
Ba(For)+              BaCHO2+
Ba(For)+              Ba(1)C(1)H(1)O(2)+(1)
ref:27                26.Aug.93
       -219775.     -228918.       34.547
       4.6569       3.5906        4.3358      -2.9273
      18.1411       1.0380        0.0279            1.
Ba(For)2,aq           Ba(CHO2)2
Ba(For)2,aq           Ba(1)C(2)H(2)O(4)
ref:27                26.Aug.93
       -304769.     -329933.       62.275
       9.7700      16.0719       -0.5623      -3.4433
      30.3870       5.4799       -0.0300            0.
Ba(Gly)+              Ba(C2H4NO2)+
Ba(Gly)+              Ba(1)C(2)H(4)N(1)O(2)+(1)
ref:27                27.Aug.93
       -211341.     -235808.       54.327
       6.9656       9.2295        2.1164      -3.1604
      32.1389       6.8602       -0.2709            1.
Ba(Gly)2,aq           Ba(C2H4NO2)2
Ba(Gly)2,aq           Ba(1)C(4)H(8)N(2)O(4)
ref:27                27.Aug.93
       -287819.     -343302.      102.940
      14.8647      28.5140       -5.4575      -3.9577
      70.3874      19.3830       -0.0300            0.
Ba(Glyc)+             BaCH3OCO2+
Ba(Glyc)+             Ba(1)C(2)H(3)O(3)+(1)
ref:27                30.Aug.93
       -256564.     -282924.       34.000
       6.5329       8.1729        2.5314      -3.1168
      49.2137      11.8129        0.0358            1.
Ba(Glyc)2,aq          Ba(CH3OCO2)2
Ba(Glyc)2,aq          Ba(1)C(4)H(6)O(6)
ref:27                30.Aug.93
       -378689.     -436833.       66.059
      13.7306      25.7444       -4.3677      -3.8432
     104.4137      31.2096       -0.0300            0.
Ba(Lac)+              BaCH3CH2OCO2+
Ba(Lac)+              Ba(1)C(3)H(5)O(3)+(1)
ref:27                30.Aug.93
       -257433.     -291416.       41.000
       8.7414      13.5626        0.4195      -3.3396
      70.2142      19.4498       -0.0697            1.
Ba(Lac)2,aq           Ba(CH3CH2OCO2)2
Ba(Lac)2,aq           Ba(1)C(6)H(10)O(6)
ref:27                30.Aug.93
       -380522.     -453654.       80.919
      18.4752      37.3316       -8.9265      -4.3222
     156.8818      49.4461       -0.0300            0.
Ba(Pent)+             BaCH3(CH2)3CO2+
Ba(Pent)+             Ba(1)C(5)H(9)O(2)+(1)
ref:27                31.Aug.93
```

```
      -216357.    -259492.      51.147
      12.8030     23.4822     -3.4843     -3.7497
     125.4720     39.1471     -0.2231          1.
Ba(Pent)2,aq       Ba(CH3CH2CH2CH2CO2)2
Ba(Pent)2,aq       Ba(1)C(10)H(18)O(4)
ref:27             31.Aug.93
      -298289.    -389909.     100.598
      27.1717     58.5642    -17.2675     -5.1999
     292.2076     96.4819     -0.0300          0.
Ba(Prop)+          BaCH3CH2CO2+
Ba(Prop)+          Ba(1)C(3)H(5)O(2)+(1)
ref:27             15.Sep.93
      -221005.    -248190.      39.347
       8.5720     13.1515       0.5756     -3.3226
      75.0141     21.0377      -0.0446          1.
Ba(Prop)2,aq       Ba(CH3CH2CO2)2
Ba(Prop)2,aq       Ba(1)C(6)H(10)O(4)
ref:27             15.Sep.93
      -307529.    -368336.      73.356
      18.0991     36.4138      -8.5671     -4.2842
     167.7909     53.2379      -0.0300          0.
Be+2               Be(+2)
Be+2               Be(1)+(2)
ref:21             15.Sep.97
       -90550.     -91500.     -32.100
        -.5718     -9.1742       9.3462     -2.3996
      17.0245      -4.2160       1.5475          2.
BeOH+              BeOH(+1)
BeOH+              Be(1)O(1)H(1)+(1)
ref:21             16.Sep.97
      -139900.    -153200.     -17.900
        2.3302     -2.0945       6.5792     -2.6923
       30.9714      2.9542        .8222          1.
BeO,aq             BeO(0)
BeO(aq)            Be(1)O(1)+(0)
ref:21             16.Sep.97
      -128600.    -144100.     -25.100
        1.8917     -3.1609       6.9887     -2.6482
       13.5675      -.3660       -.0300          0.
BeO2-2             BeO2(-2)
BeO2-2             Be(1)O(2)-(2)
ref:21             16.Sep.97
      -152900.    -189700.     -41.000
        3.2657       .1906       5.6788     -2.7868
       34.0366     -5.6215       3.8330          -2.
BeCl+              BeCl(+1)
BeCl+              Be(1)Cl(1)+(1)
ref:22             13.Sep.97
      -115316.    -124998.      92.310
        1.1974     -4.8548       7.6512     -2.5783
       16.6475      3.3197      -0.8467          1.
BeCl2,aq           BeCl2(0)
BeCl2(aq)          Be(1)Cl(2)+(0)
ref:22             13.Sep.97
      -145521.    -156432.     130.440
        5.0297      4.5026       3.9733     -2.9651
       39.6530      8.7262      -0.0380          0.
BeF+               BeF(+1)
BeF+               Be(1)F(1)+(1)
ref:22             15.Sep.97
      -158493.    -177322.      59.200
       -1.2603    -10.8560      10.0098     -2.3302
       23.7740      4.1893       -.3447          1.
BeF2,aq            BeF2(0)
BeF2(aq)           Be(1)F(2)+(0)
ref:22             15.Sep.97
      -231386.    -258350.      71.720
        -.5250     -9.0604       9.3042     -2.4044
       45.6271     10.8026       -.0380          0.
BeF3-              BeF3(-1)
BeF3-              Be(1)F(3)-(1)
ref:22             15.Sep.97
      -302532.    -331512.     104.780
         .2052     -7.2776       8.6034     -2.4781
       62.8555     16.5406        .0401          -1.
BeF4-2             BeF4(-2)
BeF4-2             Be(1)F(4)-(2)
ref:22             15.Sep.97
      -370691.    -386096.     190.120
        1.0882     -5.1214       7.7560     -2.5672
       79.5432     21.4033        .3329          -2.
Be(Ae)+            BeCH3COO+
Be(Ae)+            Be(1)C(2)H(3)O(2)+(1)
ref:33             11 Mar 93
      -174020.    -213040.     -45.600
        5.0795      4.6238       3.9264     -2.9700
       74.5470     16.7410       1.2465          1.
Be(Ae)2,aq         Be(CH3COO)2
Be(Ae)2,aq         Be(1)C(4)H(6)O(4)
ref:33             11 Mar 93
      -263740.    -336230.     -43.800
       11.7442     20.8961      -2.4661     -3.6427
      131.9355     40.7754      -0.0300          0.
Bi+3               Bi(+3)
Bi+3               Bi(1)+(3)
ref:21             11.Sep.97
        22880.      19360.      -45.000
       -1.0957    -10.4536       9.8506     -2.3467
       27.5027     -2.8715       2.2651          3.
BiOH+2             BiOH(+2)
BiOH+2             Bi(1)O(1)H(1)+(2)
ref:21             16.Sep.97
      -32300.     -44800.     -19.500
        2.4693     -1.7539       6.4433     -2.7064
        9.8610     -6.0900       1.3552          2.
BiO+               BiO(+)
BiO+               Bi(1)O(1)+(1)
ref:21             16.Sep.97
      -29300.     -30300.      19.100
        2.9487      -.5825       5.9810     -2.7548
      -39.8159    -19.8601       .2634          1.
BiO2-              BiO2(-)
BiO2-              Bi(1)O(2)-(1)
ref:21             16.Sep.97
      -61700.     -71600.      45.100
        5.2319      4.9920       3.7909     -2.9853
      -59.7858    -28.9859       .9456          -1.
Bi(Ae)+2           BiCH3COO+2
Bi(Ae)+2           Bi(1)C(2)H(3)O(2)+(2)
ref:33             26 Sept 92
      -67750.     -96420.     -15.200
        5.1690      4.8386       3.8508     -2.9789
      107.9465     28.2236       1.2860          2.
Bi(Ae)2+           Bi(CH3COO)2+
Bi(Ae)2+           Bi(1)C(4)H(6)O(4)+(1)
ref:33             26 Sept 92
      -157070.    -212380.       9.600
       11.9760     21.4619      -2.6877     -3.6661
      201.6950     63.6303       0.4046          1.
Bi(Ae)3,aq         Bi(CH3COO)3
Bi(Ae)3,aq         Bi(1)C(6)H(9)O(6)
ref:33             26 Sep.92
      -245540.    -329240.      28.600
       19.7454     40.4309     -10.1406     -4.4503
      313.6160    103.9230      -0.0300          0.
Br-                Br(-)
Br-                Br(1)-(1)
ref:2              1.Jul.87
      -24870.     -29040.      19.800
        5.2690      6.5940       4.7450     -3.1430
       -3.8000     -6.8110       1.3858          -1.
Br3-               Br3(-)
Br3-               Br(3)-(1)
ref:2              12.Jul.87
      -25590.     -31170.      51.500
        9.0992     14.4364       .0759     -3.3758
       17.2705     -1.8939       .8490          -1.
BrO-               BrO(-)
BrO-               Br(1)O(1)-(1)
ref:21             11.Sep.97
         -8000.     -22500.       9.700
        2.3206     -2.1131       6.5758     -2.6915
        3.4104     -8.7381       1.4820          -1.
BrO3-              BrO3(-)
BrO3-              Br(1)O(3)-(1)
ref:2              12.Jul.87
          4450.     -16030.      38.650
        6.9617      9.2173       2.1272     -3.1600
        3.7059     -7.2308       1.0433          -1.
BrO4-              BrO4(-)
BrO4-              Br(1)O(4)-(1)
ref:21             30.Apr.97
         28200.       3100.      47.600
        8.7361     13.5515       .4200     -3.3391
       11.4884     -4.0937       .9085          -1.
CH4,aq             CH4(0)
CH4(aq)            C(1)H(4)+(0)
ref:4              31.Aug.87
         -8234.     -21010.      20.990
        6.7617      8.7279       2.3212     -3.1397
       42.0941     10.4707       -.3179          0.
CN-                CN(-1)
CN-                C(1)N(1)-(1)
ref:21             11.Sep.97
         41200.      36000.      22.500
        5.4714      5.5813       3.5497     -3.0096
        7.6773     -6.6400       1.2900          -1.
CO2,aq             CO2(0)
CO2(aq)            C(1)O(2)+(0)
ref:3              26.Jun.87
        -92250.     -98900.      28.100
        6.2466      7.4711       2.8136     -3.0879
       40.0325      8.8004       -.0200          0.
CO3-2              CO3(-2)
CO3-2              C(1)O(3)-(2)
ref:2              1.Jul.87
      -126191.    -161385.     -11.950
        2.8524     -3.9844       6.4142     -2.6143
       -3.3206    -17.1917       3.3914          -2.
Ca+2               Ca(+2)
Ca+2               Ca(1)+(2)
ref:2              3.Jun.87
      -132120.    -129800.     -13.500
        -.1947     -7.2520       5.2966     -2.4792
        9.0000     -2.5220       1.2366          2.
CaOH+              CaOH(+1)
CaOH+              Ca(1)O(1)H(1)+(1)
ref:21             12.Sep.97
      -171300.    -179600.       6.700
        2.7243     -1.1303       6.1958     -2.7322
       11.1286     -2.7493        .4496          1.
CaCl+              CaCl(+)
CaCl+              Ca(1)Cl(1)+(1)
ref:22             17.Sep.97
      -163100.    -168607.       4.500
        2.7148     -1.1497       6.1949     -2.7314
       20.8839      .5241        .4862          1.
CaCl2,aq           CaCl2(0)
CaCl2(aq)          Ca(1)Cl(2)+(0)
ref:22             17.Sep.97
      -194000.    -211060.       6.000
        6.2187      7.4058       2.8322     -3.0851
       23.9610      3.2720       -.0380          0.
CaF+               CaF(+)
CaF+               Ca(1)F(1)+(1)
ref:22             12.Sep.97
```

```
       -200390.     -208600.       -9.000
         .1568       -7.3958        8.6499       -2.4732
       30.1743        3.0968         .6911              1.
CaHCO3+                CaHCO3(+)
CaHCO3+                Ca(1)H(1)C(1)O(3)+(1)
ref:5                  1.Jan.91
       -273830.     -294350.       16.000
        3.1911         .0104        5.7459       -2.7794
       42.3545        8.5559         .3084              1.
CaCO3,aq               CaCO3(0)
CaCO3(aq)              Ca(1)C(1)O(3)+(0)
ref:22                 17.Sep.97
       -262850.     -287390.        2.500
         -.3907       -8.7325        9.1753       -2.4179
      -11.5309       -9.0641        -.0380              0.
CaSO4,aq               CaSO4(0)
CaSO4(aq)              Ca(1)S(1)O(4)+(0)
ref:22                 12.Sep.97
       -312930.     -345900.        5.000
        2.4079       -1.8992        6.4895       -2.7004
       -8.4942       -8.1271        -.0010              0.
Ca(HSiO3)+             Ca(HSiO3)(+1)
Ca(HSiO3)+             Ca(1)H(1)Si(1)O(3)+(1)
ref:22                 15.Sep.97
       -376299.     -403109.       -1.990
        1.0647       -5.1787        7.7785       -2.5649
       30.8048        3.6619         .5831              1.
Ca(Ae)+                CaCH3COO+
Ca(Ae)+                Ca(1)C(2)H(3)O(2)+(1)
ref:33                 5 Apr 93
       -221660.     -245620.       12.500
        5.9002        6.6232        3.1505       -3.0527
       58.1976       13.8857        0.3636              1.
Ca(Ae)2,aq             Ca(CH3COO)2
Ca(Ae)2,aq             Ca(1)C(4)H(6)O(4)
ref:33                 5 Apr 93
       -311570.     -362650.       32.300
       12.9911       23.9379       -3.6556       -3.7685
      115.9068       35.2043       -0.0300              0.
Ca(Ala)+               Ca(C3H6NO2)+
Ca(Ala)+               Ca(1)C(3)H(6)O(2)N(1)+(1)
ref:27                 14.Aug.93
       -208472.     -247083.       34.555
        8.7124       13.4888        0.4540       -3.3365
       67.7227       18.2713        0.0279              1.
Ca(Ala)2,aq            Ca(C3H6NO2)2
Ca(Ala)2,aq            Ca(1)C(6)H(12)N(2)O(4)
ref:27                 14.Aug.93
       -284046.     -364714.       78.835
       19.1765       39.0448       -9.6021       -4.3930
      146.0369       45.6768       -0.0300              0.
Ca(But)+               CaCH3(CH2)2CO2+
Ca(But)+               Ca(1)C(4)H(7)O(2)+(1)
ref:27                 14.Aug.93
       -217467.     -257034.       23.105
        9.9235       16.4497       -0.7166       -3.4589
       98.3731       28.3657        0.2025              1.
Ca(But)2,aq            Ca(CH3CH2CH2CO2)2
Ca(But)2,aq            Ca(1)C(8)H(14)O(4)
ref:27                 14.Aug.93
       -302268.     -384411.       57.401
       21.6124       44.9931      -11.9404       -4.6389
      215.3882       69.7815       -0.0300              0.
Ca(For)+               CaCHO2+
Ca(For)+               Ca(1)C(1)H(1)O(2)+(1)
ref:27                 16.Aug.93
       -217933.     -231998.       13.005
        3.9346        1.8264        5.0305       -2.8544
       27.4342        3.2242        0.3539              1.
Ca(For)2,aq            Ca(CHO2)2
Ca(For)2,aq            Ca(1)C(2)H(2)O(4)
ref:27                 16.Aug.93

       -302982.     -335050.       34.084
        8.8425       13.8094        0.3220       -3.3498
       42.6594        9.7454       -0.0300              0.
Ca(Gly)+               Ca(C2H4NO2)+
Ca(Gly)+               Ca(1)C(2)H(4)O(2)N(1)+(1)
ref:27                 16.Aug.93
       -209240.     -238629.       32.785
        6.2431        7.4595        2.8241       -3.0873
       41.4246        9.0464        0.0543              1.
Ca(Gly)2,aq            Ca(C2H4NO2)2
Ca(Gly)2,aq            Ca(1)C(4)H(8)N(2)O(4)
ref:27                 16.Aug.93
       -285555.     -347942.       74.749
       13.9371       26.2517       -4.5733       -3.8641
       82.6597       23.6485       -0.0300              0.
Ca(Glyc)+              CaCH3OCO2+
Ca(Glyc)+              Ca(1)C(2)H(3)O(3)+(1)
ref:27                 16.Aug.93
       -255541.     -285318.       17.505
        5.7854        6.3436        3.2594       -3.0411
       57.8209       13.9991        0.2873              1.
Ca(Glyc)2,aq           Ca(CH3OCO2)2
Ca(Glyc)2,aq           Ca(1)C(4)H(6)O(6)
ref:27                 16.Aug.93
       -378403.     -441481.       44.473
       12.8031       23.4820       -3.4840       -3.7496
      116.6861       35.4751       -0.0300              0.
Ca(Lac)+               CaCH3CH2OCO2+
Ca(Lac)+               Ca(1)C(3)H(5)O(3)+(1)
ref:27                 16.Aug.93
       -256587.     -294436.       23.00
        8.0009       11.7524        1.1355       -3.2647
       79.0115       21.6361        0.2025              1.
Ca(Lac)2,aq            Ca(CH3CH2OCO2)2
Ca(Lac)2,aq            Ca(1)C(6)H(10)O(6)
ref:27                 16.Aug.93
       -380563.     -459217.       57.364
       17.5477       35.0629       -8.0266       -4.2284
      169.1540       53.7117       -0.0300              0.
Ca(Pent)+              CaCH3(CH2)3CO2+
Ca(Pent)+              Ca(1)C(5)H(9)O(2)+(1)
ref:27                 16.Aug.93
       -215129.     -263187.       29.605
       12.0805       21.7185       -2.7923       -3.6767
      134.7595       41.3334        0.1023              1.
Ca(Pent)2,aq           Ca(CH3CH2CH2CH2CO2)2
Ca(Pent)2,aq           Ca(1)C(10)H(18)O(4)
ref:27                 16.Aug.93
       -297634.     -396159.       72.407
       26.2442       56.3017      -16.3832       -5.1064
      304.4798      100.7475       -0.0300              0.
Ca(Prop)+              CaCH3CH2CO2+
Ca(Prop)+              Ca(1)C(3)H(5)O(2)+(1)
ref:27                 15.Sep.93
       -219818.     -251925.       17.805
        7.8503       11.3857        1.2776       -3.2496
       84.3239       23.2239        0.2832              1.
Ca(Prop)2,aq           Ca(CH3CH2CO2)2
Ca(Prop)2,aq           Ca(1)C(6)H(10)O(4)
ref:27                 15.Sep.93
       -306942.     -374653.       45.165
       17.1716       34.1451       -7.6668       -4.1905
      180.0633       57.5034       -0.0300              0.
Cd+2                   Cd(+2)
Cd+2                   Cd(1)+(2)
ref:2                  1.Jul.87
       -18560.      -18140.       -17.400
         .0537      -10.7080       16.5176       -2.3363
       15.6573       -3.7476        1.2528              2.
CdOH+                  CdOH(+)
CdOH+                  Cd(1)O(1)H(1)+(1)
ref:21                 12.Dec.97

       -61500.      -73400.        -2.900
        0.1473       -7.4141        8.6471       -2.4724
       18.8886       -0.5290        0.5985              1.
CdO,aq                 CdO(0)
CdO(aq)                Cd(1)O(1)+(0)
ref:21                 12.Dec.97
       -47500.      -59750.        -4.200
        -0.1471      -8.1341        8.9312       -2.4426
        -0.3806      -5.2141        -0.0300              0.
CdO2-2                 CdO2(-2)
CdO2-2                 Cd(1)O(2)-(2)
ref:21                 12.Dec.97
       -67300.     -101000.       -20.300
        0.7922       -5.8401        8.0303       -2.5375
        3.4810      -15.2361        3.5190              -2.
CdCl+                  CdCl(+)
CdCl+                  Cd(1)Cl(1)+(1)
ref:22                 5.Jan.98
       -52627.      -59392.         0.750
        3.0990       -0.2116        5.8262       -2.7702
       26.6485        2.3572        0.5394              1.
CdCl2,aq               CdCl2(0)
CdCl2(aq)              Cd(1)Cl(2)+(0)
ref:22                 5.Jan.98
       -84851.     -101362.       10.310
        6.6265        8.4016        2.4408       -3.1263
       34.2501        6.8482       -0.0380              0.
CdCl3-                 CdCl3(-1)
CdCl3-                 Cd(1)Cl(3)-(1)
ref:22                 5.Jan.98
      -115971.     -144916.       10.860
       11.2826       19.7705       -2.0276       -3.5963
       56.4451        9.7459        1.4662              -1.
CdCl4-2                CdCl4(-2)
CdCl4-2                Cd(1)Cl(4)-(2)
ref:22                 5.Jan.98
      -146081.     -190793.        0.230
       16.4919       32.4903       -7.0271       -4.1221
       76.2256       11.0502        3.2060              -2.
CdF+                   CdF(+)
CdF+                   Cd(1)F(1)+(1)
ref:22                 6.Jan.98
       -87373.      -97544.       -13.110
        0.5423       -6.4544        8.2799       -2.5121
       31.0752        3.2268        0.7483              1.
CdF2,aq                CdF2(0)
CdF2(aq)               Cd(1)F(2)+(0)
ref:22                 6.Jan.98
      -155164.     -180369.       -23.720
        1.0718       -5.1614        7.7717       -2.5656
       40.2242        8.9247       -0.0380              0.
Cd(Ae)+                CdCH3COO+
Cd(Ae)+                Cd(1)C(2)H(3)O(2)+(1)
ref:33                 17 Aug 92
      -109460.     -135920.        6.600
        6.3043        7.6112        2.7593       -3.0935
       64.3035       15.7327        0.4496              1.
Cd(Ae)2,aq             Cd(CH3COO)2
Cd(Ae)2,aq             Cd(1)C(4)H(6)O(4)
ref:33                 17 Aug 92
      -199400.     -254520.       24.600
       13.4090       24.9584       -4.0570       -3.8107
      126.2752       38.8081       -0.0300              0.
Cd(Ae)3-               Cd(CH3COO)3-
Cd(Ae)3-               Cd(1)C(6)H(9)O(6)-(1)
ref:33                 10 Sep 92
      -288030.     -376010.       31.900
       21.9033       45.7036      -12.2199       -4.6683
      213.8505       65.4786        1.1469              -1.
Cd(Ala)+               Cd(C3H6NO2)+
Cd(Ala)+               Cd(1)C(3)H(6)O(2)N(1)+(1)
ref:27                 14.Aug.93
```

```
      -100082.    -141016.       29.238
       9.1151     14.4742       0.0630      -3.3773
      73.7914     20.1183       0.1098            1.
Cd(Ala)2,aq         Cd(C3H6NO2)2
Cd(Ala)2,aq         Cd(1)C(6)H(12)N(2)O(4)
ref:27              14.Aug.93
      -179940.    -263420.       71.877
      19.5944     40.0653      -10.0034      -4.4352
     156.4053     49.2806       -0.0300            0.
Cd(But)+            CdCH3(CH2)2CO2+
Cd(But)+            Cd(1)C(4)H(7)O(2)+(1)
ref:27              14.Aug.93
      -105285.    -147174.       17.788
      10.3259     17.4297       -1.0970      -3.4994
     104.4311     30.2127        0.2832            1.
Cd(But)2,aq         Cd(CH3CH2CH2CO2)2
Cd(But)2,aq         Cd(1)C(8)H(14)O(4)
ref:27              14.Aug.93
      -191463.    -276419.       50.443
      22.0303     46.0136      -12.3417      -4.6811
     225.7566     73.3853       -0.0300            0.
Cd(For)+            CdCHO2+
Cd(For)+            Cd(1)C(1)H(1)O(2)+(1)
ref:27              26.Aug.93
      -104932.    -121320.        7.688
       4.3381      2.8097        4.6479      -2.8951
      33.5224      5.0712        0.4379            1.
Cd(For)2,aq         Cd(CHO2)2
Cd(For)2,aq         Cd(1)C(2)H(2)O(4)
ref:27              26.Aug.93
      -191523.    -226403.       27.125
       9.2604     14.8299       -0.0792      -3.3920
      53.0278     13.3492       -0.0300            0.
Cd(Gly)+            Cd(C2H4NO2)+
Cd(Gly)+            Cd(1)C(2)H(4)O(2)N(1)+(1)
ref:27              27.Aug.93
      -100236.    -132088.       27.000
       6.6477      8.4525        2.4231      -3.1283
      47.5446     10.8935        0.1417            1.
Cd(Gly)2,aq         Cd(C2H4NO2)2
Cd(Gly)2,aq         Cd(1)C(4)H(8)N(2)O(4)
ref:27              27.Aug.93
      -180576.    -246607.       65.000
      14.3550     27.2722       -4.9746      -3.9063
      93.0282     27.2523       -0.0300            0.
Cd(Glyc)+           CdCH3OCO2+
Cd(Glyc)+           Cd(1)C(2)H(3)O(3)+(1)
ref:27              30.Aug.93
      -142281.    -174381.       12.188
       6.1880      7.3293        2.8656      -3.0819
      63.8836     15.8461        0.3686            1.
Cd(Glyc)2,aq        Cd(CH3OCO2)2
Cd(Glyc)2,aq        Cd(1)C(4)H(6)O(6)
ref:27              30.Aug.93
      -265388.    -331279.       37.514
      13.2210     24.5024       -3.8851      -3.7918
     127.0546     39.0789       -0.0300            0.
Cd(Lac)+            CdCH3CH2OCO2+
Cd(Lac)+            Cd(1)C(3)H(5)O(3)+(1)
ref:27              30.Aug.93
      -143409.    -183519.       17.888
       8.4019     12.7361        0.7390      -3.3054
      85.0322     23.4831        0.2792            1.
Cd(Lac)2,aq         Cd(CH3CH2OCO2)2
Cd(Lac)2,aq         Cd(1)C(6)H(10)O(6)
ref:27              30.Aug.93
      -267699.    -349085.       50.673
      17.9656     36.0834       -8.4279      -4.2706
     179.5224     57.3155       -0.0300            0.
Cd(Pent)+           CdCH3(CH2)3CO2+
Cd(Pent)+           Cd(1)C(5)H(9)O(2)+(1)
ref:carla           31.Aug.93

      -103384.    -153764.       24.288
      12.4829     22.6985       -3.1719      -3.7173
     140.8184     43.1804        0.1832            1.
Cd(Pent)2,aq        Cd(CH3CH2CH2CH2CO2)2
Cd(Pent)2,aq        Cd(1)C(10)H(18)O(4)
ref:27              31.Aug.93
      -187389.    -288726.       65.449
      26.6621     57.3222      -16.7845      -5.1486
     314.8482    104.3513       -0.0300            0.
Cd(Prop)+           CdCH3CH2CO2+
Cd(Prop)+           Cd(1)C(3)H(5)O(2)+(1)
ref:27              15.Sep.93
      -107908.    -142338.       12.488
       8.2526     12.3660        0.8957      -3.2901
      90.3786     25.0710        0.3636            1.
Cd(Prop)2,aq        Cd(CH3CH2CO2)2
Cd(Prop)2,aq        Cd(1)C(6)H(10)O(4)
ref:27              15.Sep.93
      -196520.    -267043.       38.207
      17.5895     35.1655       -8.0682      -4.2326
     190.4317     61.1072       -0.0300            0.
Ce+2                Ce(+2)
Ce+2                Ce(1)+(2)
ref:21              9.Dec.97
       -74900.     -70300.        1.400
       0.1315      -7.4538        8.6653      -2.4708
       8.5755      -5.5196        1.0376            2.
Ce+3                Ce(+3)
Ce+3                Ce(1)+(3)
ref:21              10.Dec.97
      -161600.    -167400.      -49.000
       -3.4833    -16.2789       12.1302      -2.1059
       -0.3550    -12.7510        2.3265            3.
CeOH+2              CeOH+2
CeOH+2              Ce(1)O(1)H(1)+(2)
ref:25              1.Dec.95
      -206800.    -218200.       -2.7
       2.7525      -1.0606        6.1673      -2.7351
      -3.6840      -9.9807        1.1000            2.
CeO+                CeO+
CeO+                Ce(1)O(1)+(1)
ref:25              1.Dec.95
      -195900.    -208900.       13.4
       2.8409      -0.8430        6.0772      -2.7441
     -35.2162     -18.5361        0.3491            1.
CeO2-               CeO2-
CeO2-               Ce(1)O(2)-(1)
ref:25              1.Dec.95
      -222100.    -230300.       38.6
       5.0465      4.5418        3.9626      -2.9667
     -51.0768     -26.2767        1.0449           -1.
CeCl+2              CeCl+2
CeCl+2              Ce(1)Cl(1)+(2)
ref:25              1.Dec.95
      -193400.    -203800.      -22.1
      -0.1746      -8.1993        8.9525      -2.4399
      14.4780      -4.6011        1.3914            2.
CeCl2+              CeCl2+
CeCl2+              Ce(1)Cl(2)+(1)
ref:25              1.Dec.95
      -224400.    -242300.       -5.1
       2.9511      -0.5763        5.9777      -2.7551
       2.5793      -6.3002        0.6305            1.
CeCl3,aq            CeCl3(aq)
CeCl3(aq)           Ce(1)Cl(3)
ref:25              1.Dec.95
      -255200.    -283500.        2.6
       6.4972      8.0855        2.5659      -3.1132
     -31.3975     -15.9948       -0.0300            0.
CeCl4-              CeCl4-
CeCl4-              Ce(1)Cl(4)-(1)
ref:25              1.Dec.95

      -286100.    -327600.        0.3
      11.2558     19.7046       -2.0003      -3.5935
     -67.0564     -33.6847        1.6238           -1.
CeF+2               CeF+2
CeF+2               Ce(1)F(1)+(2)
ref:25              1.Dec.95
      -234700.    -242000.      -14.3
       -2.8281    -14.6820       11.5084      -2.1719
       15.8334     -3.7656        1.2776            2.
CeF2+               CeF2+
CeF2+               Ce(1)F(2)+(1)
ref:25              1.Dec.95
      -306200.    -324100.      -10.1
       -2.5538    -14.0092       11.2373      -2.1998
        8.9628     -4.3051        0.7003            1.
CeF3,aq             CeF3(aq)
CeF3(aq)            Ce(1)F(3)
ref:25              1.Dec.95
      -376600.    -409300.      -19.7
       -2.2777    -13.3348       10.9718      -2.2276
      -21.3883    -12.5158       -0.0300            0.
CeF4-               CeF4-
CeF4-               Ce(1)F(4)-(1)
ref:25              1.Dec.95
      -446500.    -498900.      -46.1
       -0.8995     -9.9693        9.6488      -2.3668
      -45.3959    -28.3978        2.3239           -1.
CeBr+2              CeBr+2
CeBr+2              Ce(1)Br(1)+(2)
ref:25              1.Dec.95
      -186988.    -195709.      -25.01
        0.8072     -5.8045        8.0178      -2.5389
       13.8428     -4.9716        1.4382            2.
CeHCO3+2            CeHCO3+2
CeHCO3+2            Ce(1)H(1)C(1)O(3)+(2)
ref:25              1.Dec.95
      -304500.    -330200.       -9.5
        0.6941     -6.0823        8.1309      -2.5275
       35.5792      3.3307        1.2048            2.
CeCO3+              CeCO3+
CeCO3+              Ce(1)C(1)O(3)+(1)
ref:25              1.Dec.95
      -297887.    -309988.      -40.6
       -0.9160    -10.0134        9.6736      -2.3649
      -21.4145    -16.3769        1.1729            1.
CeH2PO4+2           CeH2PO4+2
CeH2PO4+2           Ce(1)H(2)P(1)O(4)+(2)
ref:25              1.Dec.95
      -435100.    -480100.      -25.9
        1.6930     -3.6450        7.1770      -2.6282
       39.4058      3.8826        1.4477            2.
CeNO3+2             CeNO3+2
CeNO3+2             Ce(1)N(1)O(3)+(2)
ref:25              1.Dec.95
      -189900.    -223200.      -32.2
        1.4120     -4.3253        7.4319      -2.6001
       30.1006      0.3288        1.5475            2.
CeIO3+2             CeIO3+2
CeIO3+2             Ce(1)I(1)O(3)+(2)
ref:25              1.Dec.95
      -194792.    -225358.      -28.97
        0.9706     -5.4027        7.8548      -2.5556
       29.8495      0.4044        1.4967            2.
CeClO4+2            CeClO4+2
CeClO4+2            Ce(1)Cl(1)O(4)+(2)
ref:25              1.Dec.95
      -166246.    -210026.      -36.06
        3.5099      0.7863        5.4456      -2.8114
       42.4445      4.4497        1.6005            2.
CeSO4+              CeSO4+
CeSO4+              Ce(1)S(1)O(4)+(1)
ref:25              1.Dec.95
```

```
      -334500.    -380200.     -12.6
       1.5220     -4.0622      7.3397     -2.6110
     -22.4285    -15.3380      0.7384           1.
Ce(Ae)+2          CeCH3COO+2
Ce(Ae)+2          Ce(1)C(2)H(3)O(2)+(2)
ref:33            10 Sep 92
      -253590.    -286390.     -25.400
       2.9487     -0.5825      5.9809     -2.7548
      53.6757      8.8731      1.4382           2.
Ce(Ae)2+          Ce(CH3COO)2+
Ce(Ae)2+          Ce(1)C(4)H(6)O(4)+(1)
ref:33            10 Sep 92
      -344550.    -405090.     -4.300
       9.5157     15.4527     -0.3219     -3.4177
      95.0022     25.8754      0.6143           1.
Ce(Ae)3,aq        Ce(CH3COO)3
Ce(Ae)3,aq        Ce(1)C(6)H(9)O(6)
ref:33            10 Sep 92
      -434760.    -524960.     10.300
      16.9252     33.5426     -7.4282     -4.1656
     130.0191     40.1094     -0.0300           0.
Ce+4              Ce(+4)
Ce+4              Ce(1)+(4)
ref:21            10.Dec.97
      -121300.    -137700.    -100.100
      -4.2792    -18.2247     12.8996     -2.0255
      40.2790     -3.0141      3.6964           4.
Cl-               Cl(-)
Cl-               Cl(1)-(1)
ref:2             11.Sep.97
       -31379.     -39933.      13.560
       4.0320      4.8010      5.5630     -2.8470
      -4.4000     -5.7140      1.4560           -1.
ClO-              ClO(-)
ClO-              Cl(1)O(1)-(1)
ref:21            11.Sep.97
        -8800.     -25600.      10.000
       2.3599     -2.0164      6.5356     -2.6955
       3.4786     -8.6974      1.4767           -1.
ClO2-             ClO2(-)
ClO2-             Cl(1)O(2)-(1)
ref:21            11.Sep.97
         4100.     -15900.      24.200
       5.2163      4.9580      3.7949     -2.9839
       6.4977     -6.9659      1.2637           -1.
ClO3-             ClO3(-)
ClO3-             Cl(1)O(3)-(1)
ref:2             12.Jul.87
        -1900.     -24850.      38.800
       7.1665      9.7172      1.9307     -3.1807
       8.5561     -5.5401      1.0418           -1.
ClO4-             ClO4(-)
ClO4-             Cl(1)O(4)-(1)
ref: 21           11.Sept.97
        -2040.     -30910.      43.500
       8.1411     15.5654     -7.8077     -3.4224
      16.4500     -6.5700       .9699           -1.
Cm+2              Cm(+2)
Cm+2              Cm(1)+(2)
ref:36            16.Jan.98
       -77100.     -74100.     -4.000
       0.0094     -7.7516      8.7810     -2.4584
       9.9946     -5.2956      1.1216           2.
Cm+3              Cm(+3)
Cm+3              Cm(1)+(3)
ref:36            16.Jan.98
      -141200.    -147000.     -49.200
      -2.9633    -15.0142     11.6438     -2.1582
       6.6776    -10.3066      2.3265           3.
Cm+4              Cm(+4)
Cm+4              Cm(1)+(4)
ref:36            16.Jan.98
```

```
       -70700.     -88200.    -104.000
      -4.3164     -18.3144     12.9330     -2.0218
      40.0550      -3.2586      3.7484           4.
Co+2              Co(+2)
Co+2              Co(1)+(2)
ref:21            15.Sep.97
       -13000.     -13900.     -27.000
      -1.2252      -8.9356      5.3191     -2.4095
      15.2013      -4.6234      1.4769           2.
CoOH+             CoOH(+)
CoOH+             Co(1)O(1)H(1)+(1)
ref:21            11.Dec.97
       -56025.     -68450.     -10.000
      -0.2561      -8.4039      9.0457     -2.4315
      26.6839       1.8542      0.7003           1.
CoO,aq            CoO(0)
CoO(aq)           Co(1)O(1)+(0)
ref:21            11.Dec.97
       -44000.     -58800.     -17.800
      -1.5566     -11.5736     10.2791     -2.3004
       8.7031      -2.0567     -0.0300           0.
CoO2-2            CoO2(-2)
CoO2-2            Co(1)O(2)-(2)
ref:21            11.Dec.97
       -63200.     -99000.     -32.700
      -0.0590      -7.9219      8.8540     -2.4514
      21.8518      -9.4714      3.7127           -2.
CoCl+             CoCl(+)
CoCl+             Co(1)Cl(1)+(1)
ref:22            5.Jan.98
       -45157.     -53965.     -11.270
       1.8028      -3.3766      7.0702     -2.6394
      22.7656       0.4323      0.7191           1.
CoF+              CoF(+)
CoF+              Co(1)F(1)+(1)
ref:22            6.Jan.98
       -81732.     -93191.     -22.600
      -0.7659      -9.6486      9.5354     -2.3801
      26.8657       1.3018      0.8926           1.
Co(Ae)+           CoCH3COO+
Co(Ae)+           Co(1)C(2)H(3)O(2)+(1)
ref:33            17 Aug 92
      -103260.    -132080.     -6.500
       5.0294      4.4992      3.9806     -2.9649
      60.4543     13.7619      0.6472           1.
Co(Ae)2,aq        Co(CH3COO)2
Co(Ae)2,aq        Co(1)C(4)H(6)O(4)
ref:33            10 Sep 92
      -192770.    -251460.      7.500
      11.9141     21.3120     -2.6321     -3.6599
     115.2121     34.9629     -0.0300           0.
Co(Ae)3-          Co(CH3COO)3-
Co(Ae)3-          Co(1)C(6)H(9)O(6)-(1)
ref:33            10 Sep 92
      -281890.    -373730.     10.400
      20.3474     41.8989    -10.7127     -4.5110
     198.1420     58.9793      1.4714           -1.
Co(Ala)+          Co(C3H6NO2)+
Co(Ala)+          Co(1)C(3)H(6)N(1)O(2)+(1)
ref:27            14.Aug.93
       -94099.    -136245.     20.000
       7.8202     11.3148      1.2990     -3.2467
      69.3955     18.1475      0.2482           1.
Co(Ala)2,aq       Co(C3H6NO2)2
Co(Ala)2,aq       Co(1)C(6)H(12)N(2)O(4)
ref:27            14.Aug.93
       -173793.    -259272.     60.000
      18.0995     36.4127     -8.5626     -4.2842
     145.3423     45.4353     -0.0300           0.
Co(But)+          CoCH3(CH2)2CO2+
Co(But)+          Co(1)C(4)H(7)O(2)+(1)
ref:27            14.Aug.93
```

```
       -99984.    -144234.      4.699
       9.0507     14.3185      0.1200     -3.3708
     100.5727     28.2419      0.4799           1.
Co(But)2,aq       Co(CH3CH2CH2CO2)2
Co(But)2,aq       Co(1)C(8)H(14)O(4)
ref:27            14.Aug.93
      -186135.    -274655.     33.314
      20.5354     42.3610    -10.9009     -4.5301
     214.6936     69.5400     -0.0300           0.
Co(For)+          CoCHO2+
Co(For)+          Co(1)C(1)H(1)O(2)+(1)
ref:27            26.Aug.93
       -99399.    -118148.     -5.401
       3.0614     -0.3037      5.8638     -2.7663
      29.6264      3.1004      0.6305           1.
Co(For)2,aq       Co(CHO2)2
Co(For)2,aq       Co(1)C(2)H(2)O(4)
ref:27            26.Aug.93
      -184926.    -223371.      9.997
       7.7655     11.1773      1.3615     -3.2410
      41.9649      9.5039     -0.0300           0.
Co(Gly)+          Co(C2H4NO2)+
Co(Gly)+          Co(1)C(2)H(4)N(1)O(2)+(1)
ref:27            27.Aug.93
       -95195.    -129082.     15.000
       5.3683      5.3273      3.6539     -2.9991
      43.5722      8.9227      0.3260           1.
Co(Gly)2,aq       Co(C2H4NO2)2
Co(Gly)2,aq       Co(1)C(4)H(8)N(2)O(4)
ref:27            27.Aug.93
      -175957.    -243427.     55.000
      12.8601     23.6197     -3.5341     -3.7553
      81.9652     23.4070     -0.0300           0.
Co(Glyc)+         CoCH3OCO2+
Co(Glyc)+         Co(1)C(2)H(3)O(3)+(1)
ref:27            30.Aug.93
      -136871.    -171331.     -0.901
       4.9137      4.2158      4.0944     -2.9532
      60.0521     13.8754      0.5681           1.
Co(Glyc)2,aq      Co(CH3OCO2)2
Co(Glyc)2,aq      Co(1)C(4)H(6)O(6)
ref:27            30.Aug.93
      -260101.    -329556.     20.386
      11.7260     20.8501     -2.4444     -3.6408
     115.9914     35.2337     -0.0300           0.
Co(Lac)+          CoCH3CH2OCO2+
Co(Lac)+          Co(1)C(3)H(5)O(3)+(1)
ref:27            30.Aug.93
      -137385.    -179856.      4.799
       7.1281      9.6212      1.9722     -3.1766
      81.2111     21.5123      0.4799           1.
Co(Lac)2,aq       Co(CH3CH2OCO2)2
Co(Lac)2,aq       Co(1)C(6)H(10)O(6)
ref:27            30.Aug.93
      -261457.    -346408.     33.545
      16.4707     32.4370     -7.0030     -4.1198
     168.4594     53.4702     -0.0300           0.
Co(Pent)+         CoCH3(CH2)3CO2+
Co(Pent)+         Co(1)C(5)H(9)O(2)+(1)
ref:27            31.Aug.93
       -97933.    -150673.     11.199
      11.2090     19.5901     -1.9551     -3.5888
     136.9956     41.2096      0.3837           1.
Co(Pent)2,aq      Co(CH3CH2CH2CH2CO2)2
Co(Pent)2,aq      Co(1)C(10)H(18)O(4)
ref:27            31.Aug.93
      -182034.    -286935.     48.320
      25.1672     53.6696    -15.3437     -4.9976
     303.7853    100.5060     -0.0300           0.
Co(Prop)+         CoCH3CH2CO2+
Co(Prop)+         Co(1)C(3)H(5)O(2)+(1)
ref:27            15.Sep.93
```

```
      -101557.    -138347.      -0.601
       6.9775      9.2545      2.1152      -3.1615
      86.5252     23.1002      0.5608           1.
Co(Prop)2,aq      Co(CH3CH2CO2)2
Co(Prop)2,aq      Co(1)C(6)H(10)O(4)
ref:27            15.Sep.93
      -189405.    -263492.     21.078
      16.0946     31.5192     -6.6433      -4.0819
     179.3685     57.2620     -0.0300           0.
Co+3              Co(+3)
Co+3              Co(1)+(3)
ref:21            5.Jan.98
       32000.      22000.     -73.000
      -2.8678    -14.7777     11.5439      -2.1680
      16.4739     -8.0659      2.6901           3.
CoOH+2            CoOH(+2)
CoOH+2            Co(1)O(1)H(1)+(2)
ref:21            11.Dec.97
      -23000.     -36100.     -27.800
      -1.0884    -10.4353      9.8425      -2.3475
      16.5492     -4.1549      1.4769           2.
Cr+2              Cr(+2)
Cr+2              Cr(1)+(2)
ref:21            15.Sep.97
      -39400.     -39000.     -24.200
       -.8036     -9.7400      9.5688      -2.3762
      15.0502     -4.5215      1.4287           2.
Cr+3              Cr(+3)
Cr+3              Cr(1)+(3)
ref:21            15.Sep.97
      -49300.     -60000.     -77.000
      -2.7824    -14.5709     11.4661      -2.1765
      17.9914     -7.6992      2.7403           3.
CrOH+2            CrOH(+2)
CrOH+2            Cr(1)O(1)H(1)+(2)
ref:21            16.Sep.97
      -100500.    -118600.     -46.100
      -2.6482    -14.2423     11.3347      -2.1901
      31.4127      .1024       1.7607           2.
CrO+              CrO(+)
CrO+              Cr(1)O(1)+(1)
ref:21            16.Sep.97
      -92800.     -105000.     -26.300
      -1.1728    -10.6385      9.9161      -2.3391
      -3.1901     -9.3085       .9437           1.
CrO2-             CrO2(-)
CrO2-             Cr(1)O(2)-(1)
ref:21            16.Sep.97
      -125300.    -148300.      -6.700
       1.2013     -4.8403      7.6350      -2.5788
      10.0021     -7.2511      1.7331          -1.
CrO4-2            CrO4(-2)
CrO4-2            Cr(1)O(4)-(2)
ref:21            11.Sep.97
      -174800.    -210930.      13.800
       5.4891      5.6223      3.5382      -3.0113
      -2.8608    -15.7861      3.0024          -2.
Cr2O7-2           Cr2O7(-2)
Cr2O7-2           Cr(2)O(7)-(2)
ref:21            11.Sep.97
      -312970.    -355370.      72.000
      12.4303     22.5680     -3.1161      -3.7119
       8.6580     -8.9622      2.1216          -2.
Cs+               Cs(+)
Cs+               Cs(1)+(1)
ref:2             1.Jul.87
      -69710.     -61670.      31.750
       6.1475      -.1309      4.2094      -2.7736
       6.2700     -5.7360       .0974           1.
CsOH,aq           CsOH
CsOH(aq)          Cs(1)O(1)H(1)+(0)
ref:21            12.Sep.97

      -105000.    -112300.      35.900
       5.6685      6.0571      3.3740      -3.0293
     -12.8052     -9.5325      -.0300           0.
CsCl,aq           CsCl(0)
CsCl(aq)          Cs(1)Cl(1)+(0)
ref:22            13.Sep.97
      -100900.    -100950.      52.580
       8.4010     12.7344       .7379      -3.3054
      -6.0563     -7.9234       .2000           0.
CsBr,aq           CsBr(0)
CsBr(aq)          Cs(1)Br(1)+(0)
ref:22            13.Sep.97
       -94610.     -88490.      57.300
       9.5646     15.5757      -.3789      -3.4228
      -9.4143     -8.4469      -.0010           0.
CsI,aq            CsI(0)
CsI(aq)           Cs(1)I(1)+(0)
ref:22            13.Sep.97
       -83460.     -77820.      60.300
      11.6513     20.6709     -2.3815      -3.6335
      -7.2120     -8.0048       .1000           0.
Cs(Ae),aq         CsCH3COO
Cs(Ae),aq         Cs(1)C(2)H(3)O(2)
ref:33            19 Aug 92
      -158010.    -176320.      57.500
      11.7865     20.9974     -2.5020      -3.6469
      29.6579      5.2264      -0.0300           0.
Cs(Ae)2-          Cs(CH3COO)2-
Cs(Ae)2-          Cs(1)C(4)H(6)O(4)-(1)
ref:33            10 Sep 92
      -245900.    -293570.      73.200
      19.8839     40.7670     -10.2671      -4.4642
      71.0739     17.8580       0.5208          -1.
Cu+               Cu(+)
Cu+               Cu(1)+(1)
ref:21            1.May.97
       11950.      17132.       9.700
        .8070     -5.8040       8.0165      -2.5390
      17.9233      -.2438        .4046           1.
CuCl,aq           CuCl(0)
CuCl(aq)          Cu(1)Cl(1)+(0)
ref:22            14.Sep.97
       -22608.     -26338.      22.060
       4.1084      2.2530       4.8575      -2.8721
      17.3292       .9670       -.0380           0.
CuCl2-            CuCl2(-1)
CuCl2-            Cu(1)Cl(2)-(1)
ref:22            14.Sep.97
       -58038.     -72903.      26.960
       8.3943     12.7182       0.7442      -3.3047
      36.7555      3.6846       1.2219          -1.
CuCl3-2           CuCl3(-2)
CuCl3-2           Cu(1)Cl(3)-(2)
ref:22            14.Sep.97
       -89963.    -118524.      23.280
      13.2482     24.5700      -3.9140      -3.7947
      63.9808      7.9089       2.8579          -2.
Cu(Ae),aq         CuCH3COO
Cu(Ae),aq         Cu(1)C(2)H(3)O(2)
ref:33            19 Aug 92
       -76770.     -99970.      28.700
       7.3009     10.0483       1.7946      -3.1943
      56.0175     14.3883       -0.0300           0.
Cu(Ae)2-          Cu(CH3COO)2-
Cu(Ae)2-          Cu(1)C(4)H(6)O(4)-(1)
ref:33            10 Sep 92
      -165000.    -219740.      37.000
      15.0715     29.0205      -5.6592      -3.9786
     127.5564     35.7339       1.0691          -1.
Cu+2              Cu(+2)
Cu+2              Cu(1)+(2)
ref:2             1.Jul.87

       15675.      15700.     -23.200
      -1.1021    -10.4726      9.8662      -2.3461
      20.3000     -4.3900      1.4769           2.
CuOH+             CuOH(+1)
CuOH+             Cu(1)O(1)H(1)+(1)
ref:21            1.May.97
       -30200.     -41700.      -6.100
       -.0277     -7.8416       8.8142      -2.4547
      21.5062      .2246        .6472           1.
CuO,aq            CuO(0)
CuO(aq)           Cu(1)O(1)+(0)
ref:21            1.May.97
       -20800.     -34200.     -12.400
       -.3937     -8.7360       9.1675      -2.4178
      12.1490     -3.3197       .7384           0.
CuO2-2            CuO2(-2)
CuO2-2            Cu(1)O(2)-(2)
ref:21            1.May.97
       -41200.     -74400.     -23.100
        .6024     -6.3038       8.2129      -2.5183
       7.6532    -13.9325      3.5647          -2.
CuCl+             CuCl(+1)
CuCl+             Cu(1)Cl(1)+(1)
ref:22            14.Sep.97
       -16250.     -23847.      -6.510
       1.7480     -3.5103       7.1228      -2.6338
      29.3560      2.9530        .6472           1.
CuCl2,aq          CuCl2(0)
CuCl2(aq)         Cu(1)Cl(2)+(0)
ref:22            14.Sep.97
       -46142.     -64160.       0.780
       5.0806      4.6270       3.9244      -2.9702
      37.5948      8.0108       -.0380           0.
CuCl3-            CuCl3(-1)
CuCl3-            Cu(1)Cl(3)-(1)
ref:22            14.Sep.97
       -75338.    -106846.      -2.210
       9.6259     15.7252       -.4377      -3.4290
      63.8881     11.7108       1.6605          -1.
CuCl4-2           CuCl4(-2)
CuCl4-2           Cu(1)Cl(4)-(2)
ref:22            14.Sep.97
      -103579.    -152534.     -18.480
      14.6696     28.0407      -5.2782      -3.9382
      87.5037     14.0532       3.4923          -2.
CuF+              CuF(+1)
CuF+              Cu(1)F(1)+(1)
ref:22            15.Sep.97
       -53739.     -64285.     -18.840
       -.8164     -9.7719       9.5838      -2.3750
      33.5733      3.8226        .8334           1.
Cu(Ae)+           CuCH3COO+
Cu(Ae)+           Cu(1)C(2)H(3)O(2)+(1)
ref:33            19 Aug 92
       -75640.    -103120.      -1.300
       4.9722      4.3620       4.0290      -2.9592
      62.4950     14.7244       0.5681           1.
Cu(Ae)2,aq        Cu(CH3COO)2
Cu(Ae)2,aq        Cu(1)C(4)H(6)O(4)
ref:33            19 Aug 92
      -165820.    -222690.      14.200
      11.8801     21.2264      -2.5925      -3.6564
     120.6150     36.8408       -0.0300           0.
Cu(Ae)3-          Cu(CH3COO)3-
Cu(Ae)3-          Cu(1)C(6)H(9)O(6)-(1)
ref:33            10 Sep 92
      -255810.    -345320.      18.990
      20.2654     41.7019      -10.6422      -4.5029
     206.0700     62.1534       1.3408          -1.
Cu(Ala)+          Cu(C3H6NO2)+
Cu(Ala)+          Cu(1)C(3)H(6)N(1)O(2)+(1)
ref:27            16.Aug.93
```

```
      -70595.    -109970.       25.000
       7.7387    11.1165      1.3762     -3.2385
      70.7759    19.1100      0.0974           1.
Cu(Ala)2,aq        Cu(C3H6NO2)2
Cu(Ala)2,aq        Cu(1)C(6)H(12)N(2)O(4)
ref:27             16.Aug.93
      -154654.   -237360.       65.000
      18.0655    36.3271      -8.5230     -4.2807
     150.7452    47.3132      -0.0300           0.
Cu(But)+           CuCH3(CH2)2CO2+
Cu(But)+           Cu(1)C(4)H(7)O(2)+(1)
ref:27             14.Aug.93
       -71854.    -114768.       9.880
       8.9947    14.1844      0.1682     -3.3653
      102.6486    29.2044      0.4046           1.
Cu(But)2,aq        Cu(CH3CH2CH2CO2)2
Cu(But)2,aq        Cu(1)C(8)H(14)O(4)
ref:27             14.Aug.93
      -158470.   -245176.       40.094
      20.5014    42.2754     -10.8613     -4.5266
     220.0963    71.4180      -0.0300           0.
Cu(For)+           CuCHO2+
Cu(For)+           Cu(1)C(1)H(1)O(2)+(1)
ref:27             16.Aug.93
       -70888.    -88300.       -0.220
       3.0050    -0.4430       5.9211     -2.7606
      31.6869     4.0629       0.5536           1.
Cu(For)2,aq        Cu(CHO2)2
Cu(For)2,aq        Cu(1)C(2)H(2)O(4)
ref:27             16.Aug.93
      -156551.   -193183.       16.777
       7.7315    11.0979      1.3851     -3.2377
      47.3676    11.3819      -0.0300           0.
Cu(Gly)+           Cu(C2H4NO2)+
Cu(Gly)+           Cu(1)C(2)H(4)N(1)O(2)+(1)
ref:27             16.Aug.93
       -71295.    -102408.       25.000
       5.2864     5.1238       3.7413     -2.9907
      44.9395     9.8852       0.1739           1.
Cu(Gly)2,aq        Cu(C2H4NO2)2
Cu(Gly)2,aq        Cu(1)C(4)H(8)N(2)O(4)
ref:27             16.Aug.93
      -156477.   -221770.       63.000
      12.8262    23.5338      -3.4944     -3.7518
      87.3679    25.2850      -0.0300           0.
Cu(Glyc)+          CuCH3OCO2+
Cu(Glyc)+          Cu(1)C(2)H(3)O(3)+(1)
ref:27             16.Aug.93
      -109438.   -142561.        4.280
       4.8555     4.0750       4.1470     -2.9474
      62.0660    14.8378       0.4862           1.
Cu(Glyc)2,aq       Cu(CH3OCO2)2
Cu(Glyc)2,aq       Cu(1)C(4)H(6)O(6)
ref:27             16.Aug.93
      -233022.   -300664.       27.166
      11.6921    20.7705      -2.4205     -3.6376
     121.3943    37.1116      -0.0300           0.
Cu(Lac)+           CuCH3CH2OCO2+
Cu(Lac)+           Cu(1)C(3)H(5)O(3)+(1)
ref:27             16.Aug.93
      -110347.   -151481.       9.980
       7.0703     9.4856       2.0147     -3.1710
      83.2379    22.4748       0.3993           1.
Cu(Lac)2,aq        Cu(CH3CH2OCO2)2
Cu(Lac)2,aq        Cu(1)C(6)H(10)O(6)
ref:27             16.Aug.93
      -235047.   -318184.       40.325
      16.4367    32.3514      -6.9634     -4.1163
     173.8623    55.3481      -0.0300           0.
Cu(Pent)+          CuCH3(CH2)3CO2+
Cu(Pent)+          Cu(1)C(5)H(9)O(2)+(1)
ref:27             16.Aug.93
```

```
      -69817.    -121221.       16.380
      11.1516    19.4472      -1.8933     -3.5828
     139.0314    42.1721       0.3041           1.
Cu(Pent)2,aq       Cu(CH3CH2CH2CH2CO2)2
Cu(Pent)2,aq       Cu(1)C(10)H(18)O(4)
ref:27             16.Aug.93
      -154382.   -257470.       55.100
      25.1332    53.5902     -15.3200     -4.9943
     309.1882   102.3839      -0.0300           0.
Cu(Prop)+          CuCH3CH2CO2+
Cu(Prop)+          Cu(1)C(3)H(5)O(2)+(1)
ref:27             16.Aug.93
       -74124.    -109577.       4.580
       6.9197     9.1126       2.1719     -3.1556
      88.5486    24.0627       0.4799           1.
Cu(Prop)2,aq       Cu(CH3CH2CO2)2
Cu(Prop)2,aq       Cu(1)C(6)H(10)O(4)
ref:27             16.Aug.93
      -162995.   -235268.       27.858
      16.0606    31.4336      -6.6036     -4.0784
     184.7714    59.1399      -0.0300           0.
Dy+2               Dy(+2)
Dy+2               Dy(1)+(2)
ref:21             10.Dec.97
      -102800.    -99900.       -3.600
       0.0206    -7.7248       8.7724     -2.4596
       9.8690    -5.3159       1.1144           2.
Dy+3               Dy(+3)
Dy+3               Dy(1)+(3)
ref:2              13.Jul.87
      -158700.   -166500.      -55.200
      -3.0003   -15.1074      11.6879     -2.1545
       9.5076    -9.4919       2.3792           3.
DyOH+2             DyOH+2
DyOH+2             Dy(1)O(1)H(1)+(2)
ref:25             1.Dec.95
      -204700.   -216500.      -10.9
       2.6154    -1.3941       6.2950     -2.7213
       2.8769    -8.0863       1.2206           2.
DyO+               DyO+
DyO+               Dy(1)O(1)+(1)
ref:25             1.Dec.95
      -193400.   -209000.        4.6
       2.6935    -1.2056       6.2255     -2.7291
     -28.1511   -16.4991       0.4799           1.
DyO2-              DyO2-
DyO2-              Dy(1)O(2)-(1)
ref:25             1.Dec.95
      -226400.   -237700.       28.6
       4.7414     3.7936       4.2636     -2.9357
     -37.5629   -22.0601       1.1949           -1.
DyCl+2             DyCl+2
DyCl+2             Dy(1)Cl(1)+(2)
ref:25             1.Dec.95
      -190400.   -203200.      -29.5
      -0.2729    -8.4410       9.0516     -2.4299
      24.6385    -1.4386       1.5067           2.
DyCl2+             DyCl2+
DyCl2+             Dy(1)Cl(2)+(1)
ref:25             1.Dec.95
      -221400.   -242200.      -14.4
       2.8449    -0.8347       6.0770     -2.7444
      21.6041    -0.1300       0.7686           1.
DyCl3,aq           DyCl3(aq)
DyCl3(aq)          Dy(1)Cl(3)
ref:25             1.Dec.95
      -252200.   -284200.       -9.6
       6.3268     7.6646       2.7424     -3.0958
      -1.3925    -5.5657      -0.0300           0.
DyCl4-             DyCl4-
DyCl4-             Dy(1)Cl(4)-(1)
ref:25             1.Dec.95
```

```
      -283000.   -329600.      -16.4
      11.1518    19.4467      -1.8909     -3.5828
     -18.8614   -17.7460       1.8776           -1.
DyF+2              DyF+2
DyF+2              Dy(1)F(1)+(2)
ref:25             1.Dec.95
      -232400.   -241100.      -18.4
      -2.9451   -14.9683      11.6229     -2.1601
      25.4842    -0.6031       1.3375           2.
DyF2+              DyF2+
DyF2+              Dy(1)F(2)+(1)
ref:25             1.Dec.95
      -304500.   -323800.      -14.1
      -2.6837   -14.3302      11.3726     -2.1865
      27.3446     1.8651       0.7686           1.
DyF3,aq            DyF3(aq)
DyF3(aq)           Dy(1)F(3)
ref:25             1.Dec.95
      -375400.   -409800.      -25.0
      -2.4481   -13.7557      11.1483     -2.2102
       8.6168    -2.0868      -0.0300           0.
DyF4-              DyF4-
DyF4-              Dy(1)F(4)-(1)
ref:25             1.Dec.95
      -445600.   -500800.      -54.9
      -1.0402   -10.3182       9.7972     -2.3523
       1.7998   -12.4591       2.4692           -1.
DyHCO3+2           DyHCO3+2
DyHCO3+2           Dy(1)H(1)C(1)O(3)+(2)
ref:25             1.Dec.95
      -301300.   -329700.      -18.2
       0.6017    -6.3082       8.2207     -2.5181
      45.9011     6.4931       1.3375           2.
DyCO3+             DyCO3+
DyCO3+             Dy(1)C(1)O(3)+(1)
ref:25             1.Dec.95
      -295800.   -310100.      -48.1
      -0.9340   -10.0536       9.6821     -2.3633
     -16.3311   -14.9713       1.2858           1.
DyH2PO4+2          DyH2PO4+2
DyH2PO4+2          Dy(1)H(2)P(1)O(4)+(2)
ref:25             1.Dec.95
      -431800.   -479700.      -34.8
       1.6038    -3.8668       7.2721     -2.6190
      49.8123     7.0451       1.5897           2.
DyNO3+2            DyNO3+2
DyNO3+2            Dy(1)N(1)O(3)+(2)
ref:25             1.Dec.95
      -185400.   -223200.      -43.8
       1.3347    -4.5159       7.5104     -2.5922
      40.8317     3.4913       1.7247           2.
DySO4+             DySO4+
DySO4+             Dy(1)S(1)O(4)+(1)
ref:25             1.Dec.95
      -341600.   -379000.      -17.9
      -1.4956    -4.1268       7.3650     -2.6083
     -17.6132   -13.9325       0.8222           1.
Dy(Ae)+2           DyCH3COO+2
Dy(Ae)+2           Dy(1)C(2)H(3)O(2)+(2)
ref:33             11.Sep.92
      -250590.   -286150.      -34.200
       2.8591    -0.7970       6.0561     -2.7460
      64.0720    12.0356       1.5790           2.
Dy(Ae)2+           Dy(CH3COO)2+
Dy(Ae)2+           Dy(1)C(4)H(6)O(4)+(1)
ref:33             11.Sep.92
      -341450.   -405710.      -16.300
       9.4257    15.2330      -0.2363     -3.4086
     114.4678    32.0457       0.8002           1.
Dy(Ae)3,aq         Dy(CH3COO)3
Dy(Ae)3,aq         Dy(1)C(6)H(9)O(6)
ref:33             11.Sep.92
```

```
      -431590.    -526620.      -5.400
     16.7548     33.1279      -7.2677      -4.1484
    160.0243     50.5384      -0.0300           0.
Dy+4                 Dy(+4)
Dy+4                 Dy(1)+(4)
ref:21               10.Dec.97
      -55700.     -73400.    -104.000
     -4.3164    -18.3144     12.9330      -2.0218
     40.0550     -3.2586      3.7484           4.
Er+2                 Er(+2)
Er+2                 Er(1)+(2)
ref:21               10.Dec.97
      -91600.     -89150.      -5.500
     -0.0104     -7.7996      8.7981      -2.4565
     10.3150     -5.2548      1.1437           2.
Er+3                 Er(+3)
Er+3                 Er(1)+(3)
ref:2                13.Jul.87
     -159900.    -168500.     -58.300
     -3.3041    -15.8492     11.9794      -2.1238
      8.2815    -10.0215      2.4115           3.
ErOH+2               ErOH+2
ErOH+2               Er(1)O(1)H(1)+(2)
ref:25               1.Dec.95
     -206000.    -219000.     -14.6
      2.5526     -1.5478      6.3556      -2.7149
      5.8637     -7.2307      1.2776           2.
ErO+                 ErO+
ErO+                 Er(1)O(1)+(1)
ref:25               1.Dec.95
     -194800.    -211600.       0.6
      2.6315     -1.3551      6.2803      -2.7229
    -24.9068    -15.5621      0.5394           1.
ErO2-                ErO2-
ErO2-                Er(1)O(2)-(1)
ref:25               1.Dec.95
     -228800.    -241500.      24.0
      4.6152      3.4877      4.3792      -2.9231
    -31.3910    -20.1453      1.2669          -1.
ErCl+2               ErCl+2
ErCl+2               Er(1)Cl(1)+(2)
ref:25               1.Dec.95
     -191700.    -205400.     -33.2
     -0.6062     -9.2588      9.3810      -2.3961
     21.6825     -2.6303      1.5579           2.
ErCl2+               ErCl2+
ErCl2+               Er(1)Cl(2)+(1)
ref:25               1.Dec.95
     -222600.    -244700.     -19.0
      2.4799     -1.7255      6.4270      -2.7076
     15.6173     -2.4550      0.8449           1.
ErCl3,aq             ErCl3(aq)
ErCl3(aq)            Er(1)Cl(3)
ref:25               1.Dec.95
     -253400.    -287100.     -15.6
      5.8915      6.6023      3.1580      -3.0518
    -12.6987     -9.4955     -0.0300           0.
ErCl4-               ErCl4-
ErCl4-               Er(1)Cl(4)-(1)
ref:25               1.Dec.95
     -284200.    -333200.     -24.7
     10.7108     18.3744     -1.4789      -3.5385
    -34.9400    -23.7519      2.0080          -1.
ErF+2                ErF+2
ErF+2                Er(1)F(1)+(2)
ref:25               1.Dec.95
     -233700.    -242900.     -20.4
     -3.2867    -15.8018     11.9486      -2.1257
     22.3012     -1.7948      1.3642           2.
ErF2+                ErF2+
ErF2+                Er(1)F(2)+(1)
ref:25               1.Dec.95
```

```
      -305900.    -325700.     -16.1
     -3.0637    -15.2566     11.7333      -2.1482
     20.9464     -0.4598      0.8002           1.
ErF3,aq              ErF3(aq)
ErF3(aq)             Er(1)F(3)
ref:25               1.Dec.95
     -376800.    -411900.     -27.7
     -2.8834    -14.8179     11.5640      -2.1663
     -2.6893     -6.0166     -0.0300           0.
ErF4-                ErF4-
ErF4-                Er(1)F(4)-(1)
ref:25               1.Dec.95
     -447100.    -503500.     -59.3
     -1.5016    -11.4431     10.2350      -2.3058
    -14.8367    -18.4650      2.5390          -1.
ErHCO3+2             ErHCO3+2
ErHCO3+2             Er(1)H(1)C(1)O(3)+(2)
ref:25               1.Dec.95
     -302600.    -332200.     -22.6
      0.2724     -7.1116      8.5345      -2.4849
     43.0537      5.3015      1.4006           2.
ErCO3+               ErCO3+
ErCO3+               Er(1)C(1)O(3)+(1)
ref:25               1.Dec.95
     -297200.    -312600.     -51.9
     -1.0539    -10.3510      9.8086      -2.3510
    -17.2819    -15.5009      1.3480           1.
ErH2PO4+2            ErH2PO4+2
ErH2PO4+2            Er(1)H(2)P(1)O(4)+(2)
ref:25               1.Dec.95
     -433100.    -482200.     -39.3
      1.2754     -4.6600      7.5655      -2.5863
     46.9907      5.8534      1.6556           2.
ErNO3+2              ErNO3+2
ErNO3+2              Er(1)N(1)O(3)+(2)
ref:25               1.Dec.95
     -186600.    -226000.     -49.7
      1.0128     -5.3011      7.8182      -2.5598
     38.1891      2.2996      1.8100           2.
ErSO4+               ErSO4+
ErSO4+               Er(1)S(1)O(4)+(1)
ref:25               1.Dec.95
     -342700.    -381048.     -21.1
      1.3743     -4.4228      7.4814      -2.5961
    -18.7119    -14.4621      0.8683           1.
Er(Ae)+2             ErCH3COO+2
Er(Ae)+2             Er(1)C(2)H(3)O(2)+(2)
ref:33               11 Sept 92
     -251770.    -288520.     -38.600
      2.5305     -1.6022      6.3787      -2.7127
     61.2455     10.8439      1.6444           2.
Er(Ae)2+             Er(CH3COO)2+
Er(Ae)2+             Er(1)C(4)H(6)O(4)+(1)
ref:33               11 Sept 92
     -342620.    -408540.     -22.300
      9.0662     14.3528      0.1146      -3.3722
    108.6293     29.7206      0.8926           1.
Er(Ae)3,aq           Er(CH3COO)3
Er(Ae)3,aq           Er(1)C(6)H(9)O(6)
ref:33               11 Sept 92
     -432750.    -529990.     -13.200
     16.3195     32.0657      -6.8520      -4.1045
    148.7181     46.6086      -0.0300           0.
Er+4                 Er(+4)
Er+4                 Er(1)+(4)
ref:21               10.Dec.97
      -28100.     -45900.    -104.700
     -4.3256    -18.3402     12.9496      -2.0207
     40.0003     -3.3197      3.7615           4.
Eu+2                 Eu(+2)
Eu+2                 Eu(1)+(2)
ref:21               10.Dec.97
```

```
      -129200.    -126150.      -2.400
      0.0407     -7.6776      8.7578      -2.4615
      9.5539     -5.3567      1.0929           2.
EuCl+                EuCl+
EuCl+                Eu(1)Cl(1)+(1)
ref:25               1.Dec.95
     -161000.    -164000.      19.5
      5.1742      4.8499      3.8487      -2.9794
     36.2777      6.6125      0.2557           1.
EuCl2,aq             EuCl2(aq)
EuCl2(aq)            Eu(1)Cl(2)
ref:25               1.Dec.95
     -193600.    -204600.      35.00
      9.1152     14.4740      0.0641      -3.3773
     58.1447     15.1277     -0.0300           0.
EuCl3-               EuCl3-
EuCl3-               Eu(1)Cl(3)-(1)
ref:25               1.Dec.95
     -226000.    -246800.      44.7
     13.9460     26.2721      -4.5790      -3.8650
     91.9571     23.7331      0.9527          -1.
EuCl4-2              EuCl4-2
EuCl4-2              Eu(1)Cl(4)-(2)
ref:25               1.Dec.95
     -258500.    -290600.      48.6
     19.4730     39.7656      -9.8784      -4.4228
    131.0045     32.4289      2.4755          -2.
EuF+                 EuF+
EuF+                 Eu(1)F(1)+(1)
ref:25               1.Dec.95
     -194600.    -202200.       1.7
      2.6504     -1.3110      6.2669      -2.7247
     41.1681      7.4480      0.5256           1.
EuF2,aq              EuF2(aq)
EuF2(aq)             Eu(1)F(1)
ref:25               1.Dec.95
     -261000.    -282200.      -4.1
      3.5866      0.9784      5.3596      -2.8193
     63.8849     17.1229     -0.0300           0.
EuF3-                EuF3-
EuF3-                Eu(1)F(3)-(1)
ref:25               1.Dec.95
     -327700.    -365700.     -20.5
      5.5026      5.6556      3.5244      -3.0127
    111.0055     27.2121      1.9339          -1.
EuF4-2               EuF4-2
EuF4-2               Eu(1)F(4)-(2)
ref:25               1.Dec.95
     -394600.    -455700.     -58.1
      7.6287     10.8431      1.4936      -3.2272
    161.1451     37.7158      4.0961          -2.
Eu(Ala)+             Eu(C3H6NO2)+
Eu(Ala)+             Eu(1)C(3)H(6)N(1)O(2)+(1)
ref:27               14.Aug.93
     -205330.    -242060.      49.7
     11.0532     19.2058      -1.7947      -3.5729
     83.4588     24.4724      -0.2006          1.
Eu(Ala)2,aq          Eu(C3H6NO2)2
Eu(Ala)2,aq          Eu(1)C(6)H(12)N(2)O(4)
ref:27               14.Aug.93
     -281120.    -358510.      98.6
     21.8707     45.6205     -12.1799      -4.6649
    180.8470     57.7759      -0.0300           0.
Eu(But)+             EuCH3(CH2)2CO2+
Eu(But)+             Eu(1)C(4)H(7)O(2)+(1)
ref:27               14.Aug.93
     -214119.    -251804.      38.239
     12.2638     22.1618      -2.9570      -3.6951
    114.0923     34.5668      -0.0278          1.
Eu(But)2,aq          Eu(CH3CH2CH2CO2)2
Eu(But)2,aq          Eu(1)C(8)H(14)O(4)
ref:27               14.Aug.93
```

```
      -298525.    -377392.      77.206
     24.3067     51.5686    -14.5188     -4.9107
    250.1983     81.8806     -0.0300           0.
Eu(For)+          EuCHO2+
Eu(For)+          Eu(1)C(1)H(1)O(2)+(1)
ref:27            26.Aug.93
      -214872.    -227054.      28.139
      6.2755      7.5431      2.7814     -3.0907
     43.1702      9.4253      0.1254           1.
Eu(For)2,aq       Eu(CHO2)2
Eu(For)2,aq       Eu(1)C(2)H(2)O(4)
ref:27            26.Aug.93
      -300521.    -329314.      53.889
     11.5367     20.3852     -2.2565     -3.6216
     77.4695     21.8445     -0.0300           0.
Eu(Gly)+          Eu(C2H4NO2)+
Eu(Gly)+          Eu(1)C(2)H(4)N(1)O(2)+(1)
ref:27            27.Aug.93
      -206629.    -234136.      47.919
      8.5841     13.1760      0.5767     -3.3236
     57.1645     15.2476     -0.1738           1.
Eu(Gly)2,aq       Eu(C2H4NO2)2
Eu(Gly)2,aq       Eu(1)C(4)H(8)N(2)O(4)
ref:27            27.Aug.93
      -283817.    -342929.      94.554
     16.6314     32.8272     -7.1514     -4.1360
    117.4699     35.7476     -0.0300           0.
Eu(Glyc)+         EuCH3OCO2+
Eu(Glyc)+         Eu(1)C(2)H(3)O(3)+(1)
ref:27            30.Aug.93
      -252044.    -279938.      32.639
      8.1255     12.0562      1.0166     -3.2773
     73.5346     20.2002      0.0564           1.
Eu(Glyc)2,aq      Eu(CH3OCO2)2
Eu(Glyc)2,aq      Eu(1)C(4)H(6)O(6)
ref:27            30.Aug.93
      -374046.    -433849.      64.278
     15.4973     30.0577     -6.0619     -4.0215
    151.4961     47.5743     -0.0300           0.
Eu(Lac)+          Eu(CH3CH2OCO2)+
Eu(Lac)+          Eu(1)C(3)H(5)O(3)+(1)
ref:27            30.Aug.93
      -252899.    -288803.      38.339
     10.3407     17.4658     -1.1113     -3.5009
     94.7163     27.8372     -0.0294           1.
Eu(Lac)2,aq       Eu(CH3CH2OCO2)2
Eu(Lac)2,aq       Eu(1)C(6)H(10)O(6)
ref:27            30.Aug.93
      -376425.    -451723.      77.437
     20.2419     41.6449    -10.6207     -4.5005
    203.9641     65.8108     -0.0300           0.
Eu(Pent)+         EuCH3(CH2)3CO2+
Eu(Pent)+         Eu(1)C(5)H(9)O(2)+(1)
ref:27            31.Aug.93
      -211714.    -257888.      44.739
     14.4215     27.4350     -5.0392     -3.9131
    150.5000     47.5345     -0.1257           1.
Eu(Prop)+         EuCH3CH2CO2+
Eu(Prop)+         Eu(1)C(3)H(5)O(2)+(1)
ref:27            15.Sep.93
      -216648.    -246872.      32.939
     10.1903     17.0986     -0.9659     -3.4858
    100.0361     29.4251      0.0521           1.
Eu(Prop)2,aq      Eu(CH3CH2CO2)2
Eu(Prop)2,aq      Eu(1)C(6)H(10)O(4)
ref:27            15.Sep.93
      -303186.    -367621.      64.970
     19.8658     40.7270    -10.2606     -4.4626
    214.8734     69.6025     -0.0300           0.
Eu+3              Eu(+3)
Eu+3              Eu(1)+(3)
ref:2             13.Jul.87

      -137300.    -144700.     -53.000
     -3.1037     -15.3599     11.7871     -2.1440
      6.0548     -10.4900      2.3161           3.
EuOH+2            EuOH+2
EuOH+2            Eu(1)O(1)H(1)+(2)
ref:25            1.Dec.95
      -183200.    -194373.      -8.0
      2.6569      -1.2969      6.2659     -2.7253
      0.5828      -8.7585      1.1815           2.
EuO+              EuO+
EuO+              Eu(1)O(1)+(1)
ref:25            1.Dec.95
      -171700.    -186500.       7.7
      2.7458      -1.0743      6.1663     -2.7345
    -30.6415     -17.2120      0.4322           1.
EuO2-             EuO2-
EuO2-             Eu(1)O(2)-(1)
ref:25            1.Dec.95
      -203600.    -214100.      32.1
      4.8468      4.0541      4.1548     -2.9465
    -42.3249     -23.5471      1.1424          -1.
EuCl+2            EuCl+2
EuCl+2            Eu(1)Cl(1)+(2)
ref:25            1.Dec.95
      -169100.    -181300.     -26.9
     -0.3777     -8.6968      9.1514     -2.4194
     17.8123     -3.6844      1.4671           2.
EuCl2+            EuCl2+
EuCl2+            Eu(1)Cl(2)+(1)
ref:25            1.Dec.95
      -200000.    -220100.     -11.1
      2.7262     -1.122       6.1870     -2.7325
      8.5409     -4.5117      0.7191           1.
EuCl3,aq          EuCl3(aq)
EuCl3(aq)         Eu(1)Cl(3)
ref:25            1.Dec.95
      -230800.    -261800.      -5.3
      6.2132      7.3881      2.8493     -3.0843
    -22.7003     -12.9719     -0.0300           0.
EuCl4-            EuCl4-
EuCl4-            Eu(1)Cl(4)-(1)
ref:25            1.Dec.95
      -261600.    -306800.     -10.5
     10.9946     19.0660     -1.7473     -3.5671
    -52.2612     -29.0648      1.7870          -1.
EuF+2             EuF+2
EuF+2             Eu(1)F(1)+(2)
ref:25            1.Dec.95
      -210700.    -219200.     -17.0
     -3.0453     -15.2112     11.7137     -2.1501
     18.7828      -2.8489      1.3115           2.
EuF2+             EuF2+
EuF2+             Eu(1)F(2)+(1)
ref:25            1.Dec.95
      -282500.    -301700.     -12.7
     -2.7958     -14.6044     11.4813     -2.1752
     14.4597      -2.5166      0.7384           1.
EuF3,aq           EuF3(aq)
EuF3(aq)          Eu(1)F(3)
ref:25            1.Dec.95
      -353200.    -387300.     -23.1
     -2.5616     -14.0324     11.2555     -2.1988
    -12.6911      -9.4929     -0.0300           0.
EuF4-             EuF4-
EuF4-             Eu(1)F(4)-(1)
ref:25            1.Dec.95
      -423200.    -477800.     -51.8
     -1.1887     -10.6780      9.9326     -2.3375
    -31.3648     -23.7779      2.4042          -1.
EuSO4+            EuSO4+
EuSO4+            Eu(1)S(1)O(4)+(1)
ref:25            1.Dec.95

      -320200.    -347200.     -15.3
     -1.4399      -4.2627      7.4184     -2.6027
    -20.8829     -14.9306      0.7790           1.
EuHCO3+2          EuHCO3+2
EuHCO3+2          Eu(1)H(1)C(1)O(3)+(2)
ref:25            1.Dec.95
      -279800.    -307500.     -15.2
      0.4928      -6.5720      8.3198     -2.5072
     38.9648      4.2473      1.2860           2.
EuCO3+            EuCO3+
EuCO3+            Eu(1)C(1)O(3)+(1)
ref:25            1.Dec.95
      -274300.    -287900.     -45.4
     -0.9842     -10.1779      9.7343     -2.3581
    -19.5642     -15.9695      1.2465           1.
EuH2PO4+2         EuH2PO4+2
EuH2PO4+2         Eu(1)H(2)P(1)O(4)+(2)
ref:25            1.Dec.95
      -410500.    -457600.     -31.7
      1.4946      -4.1236      7.3517     -2.6084
     42.8673      4.7993      1.5372           2.
EuNO3+2           EuNO3+2
EuNO3+2           Eu(1)N(1)O(3)+(2)
ref:25            1.Dec.95
      -165000.    -201800.     -39.7
      1.2198      -4.7951      7.6178     -2.5807
     33.7330      1.2455      1.6556           2.
Eu(Ae)+2          EuCH3COO+2
Eu(Ae)+2          Eu(1)C(2)H(3)O(2)+(2)
ref:33            10 Sep 92
      -229390.    -264280.     -31.100
      2.7500      -1.0666      6.1690     -2.7348
     57.1309      9.7898      1.5269           2.
Eu(Ae)2+          Eu(CH3COO)2+
Eu(Ae)2+          Eu(1)C(4)H(6)O(4)+(1)
ref:33            10 Sep 92
      -320420.    -383670.     -12.000
      9.3029      14.9307      -0.1123     -3.3961
    101.2917      27.6639      0.7384           1.
Eu(Ae)3,aq        Eu(CH3COO)3
Eu(Ae)3,aq        Eu(1)C(6)H(9)O(6)
ref:33            10 Sep 92
      -410690.    -504320.       0.200
     16.6413     32.8512      -7.1605     -4.1370
    138.7162     43.1323      -0.0300           0.
Eu(But)+2         EuCH3(CH2)2CO2+2
Eu(But)+2         Eu(1)C(4)H(7)O(2)+(2)
ref:27            14.Aug.93
      -225716.    -276036.     -19.856
      6.7698      8.7503      2.3069     -3.1406
     97.2089     24.2698      1.3552           2.
Eu(But)2+         Eu(CH3CH2CH2CO2)2+
Eu(But)2+         Eu(1)C(8)H(14)O(4)+(1)
ref:27            14.Aug.93
      -313068.    -405964.      14.439
     17.7879     35.6504      -8.2592     -4.2527
    197.0574     62.2411      0.3351           1.
Eu(For)+2         EuCHO2+2
Eu(For)+2         Eu(1)C(1)H(1)O(2)+(2)
ref:27            26.Aug.93
      -224968.    -249786.     -29.956
      0.7809      -5.8667      8.0384     -2.5364
     26.2700      -0.8716      1.5067           2.
Eu(For)2+         Eu(CHO2)2+
Eu(For)2+         Eu(1)C(2)H(2)O(4)+(1)
ref:27            26.Aug.93
      -311559.    -354544.      -9.431
      5.1383      4.7630      3.8812     -2.9758
     27.6085      2.2050      0.6911           1.
Eu(Pent)+2        EuCH3(CH2)3CO2+2
Eu(Pent)+2        Eu(1)C(5)H(9)O(2)+(2)
ref:27            1.Sep.93
```

```
      -223706.    -282516.     -13.356
       8.9288     14.0201      0.2395     -3.3585
     133.6500     37.2375      1.2610          2.
Eu(Pent)2+          Eu(CH3CH2CH2CH2CO2)2+
Eu(Pent)2+          Eu(1)C(10)H(18)O(4)+(1)
ref:27              1.Sep.93
      -309035.    -418206.     29.802
     22.3402     46.7679    -12.6335     -4.7123
     283.9817    93.2071      0.0999          1.
Eu(Prop)+2          EuCH3CH2CO2+2
Eu(Prop)+2          Eu(1)C(3)H(5)O(2)+(2)
ref:27              15.Sep.93
      -227972.    -270831.     -25.156
       4.6974     3.6905       4.2941     -2.9315
      83.1800     19.1280      1.4382          2.
Eu(Prop)2+          Eu(CH3CH2CO2)2+
Eu(Prop)2+          Eu(1)C(6)H(10)O(4)+(1)
ref:27              15.Sep.93
      -317566.    -396115.       1.913
      13.4114     24.9646     -4.0601     -3.8109
     163.4871     49.9630      0.5256          1.
Eu+4                Eu(+4)
Eu+4                Eu(1)+(4)
ref:21              10.Dec.97
        5000.       -12700.    -103.300
      -4.3071    -18.2951     12.9322     -2.0226
      40.0515     -3.2178      3.7353          4.
F-                  F(-)
F-                  F(1)-(1)
ref:2               1.Jul.87
       -67340.      -80150.     -3.150
        .6870      1.3588       7.6033     -2.8352
       4.4600     -7.4880       1.7870          -1.
Fe+2                Fe(+2)
Fe+2                Fe(1)+(2)
ref:21              11.Sep.97
       -21870.      -22050.     -25.300
       -.7867     -9.6969       9.5479     -2.3780
      14.7860     -4.6437       1.4382          2.
FeOH+               FeOH(+1)
FeOH+               Fe(1)O(1)H(1)+(1)
ref:21              12.Sep.97
       -65850.      -78080.     -10.000
       -.2561     -8.4039       9.0457     -2.4315
      21.4093       .0209        .7003          1.
FeO,aq              FeO
FeO(aq)             Fe(1)O(1)+(0)
ref:21              1.May.97
       -50720.      -62950.     -10.000
       -.5029     -9.0053       9.2791     -2.4066
       5.8901     -3.0345       -.0300          0.
FeCl+               FeCl(+)
FeCl+               Fe(1)Cl(1)+(1)
ref:22              12.Sep.97
       -53030.      -61260.     -10.060
       2.1468     -2.5367       6.7401     -2.6741
      24.6912      1.1617        .7003          1.
FeCl2,aq            FeCl2(0)
FeCl2(aq)           Fe(1)Cl(2)+(0)
ref:22              17.Sep.97
       -73480.      -78490.      43.000
       5.5057      5.6650       3.5164     -3.0131
      22.9295      2.9135       -.0380          0.
FeF+                FeF(+1)
FeF+                Fe(1)F(1)+(1)
ref:22              15.Sep.97
       -91157.     -101452.     -20.920
       -.4234     -8.8124       9.2067     -2.4146
      26.3785      1.2102        .8683          1.
Fe(Ae)+             Fe(CH3COO)(+)
Fe(Ae)+             Fe(1)C(2)H(3)O(2)+(1)
ref:22              12.Sep.97
       -111900.     -139060.     -1.500
        5.2246      4.9785       3.7863     -2.9848
       59.1160     13.5263       .5756           1.
Fe(Ae)2,aq          Fe(CH3COO)2(0)
Fe(Ae)2(aq)         Fe(1)C(4)H(6)O(4)+(0)
ref:22              12.Sep.97
       -201800.     -259100.     11.530
       12.1698     21.9370      -2.8791     -3.6858
      113.7691     34.4870       -.0380          0.
Fe(Ala)+            Fe(C3H6NO2)+
Fe(Ala)+            Fe(1)C(3)H(6)N(1)O(2)+(1)
ref:27              14.Aug.93
       -103252.     -145225.     18.058
        8.1661     12.1558       0.9760     -3.2814
       69.2856     18.0100       0.2792          1.
Fe(Ala)2,aq         Fe(C3H6NO2)2
Fe(Ala)2,aq         Fe(1)C(6)H(12)N(2)O(4)
ref:27              14.Aug.93
       -182987.     -268535.     57.246
       18.4732     37.3244      -8.9189     -4.3219
      144.5703     45.1671      -0.0300          0.
Fe(But)+            FeCH3(CH2)2CO2+
Fe(But)+            Fe(1)C(4)H(7)O(2)+(1)
ref:27              14.Aug.93
       -108714.     -151642.      6.608
        9.3758     15.1141      -0.1954     -3.4037
       99.8978     28.1044       0.4496          1.
Fe(But)2,aq         Fe(CH3CH2CH2CO2)2
Fe(But)2,aq         Fe(1)C(8)H(14)O(4)
ref:27              14.Aug.93
       -194743.     -281765.     35.812
       20.9091     43.2727     -11.2572     -4.5678
      213.9216     69.2718      -0.0300          0.
Fe(For)+            FeCHO2+
Fe(For)+            Fe(1)C(1)H(1)O(2)+(1)
ref:27              16.Aug.93
       -108225.     -125651.     -3.492
        3.3887      0.4923       5.5575     -2.7993
       29.0080      2.9629       0.6063          1.
Fe(For)2,aq         Fe(CHO2)2
Fe(For)2,aq         Fe(1)C(2)H(2)O(4)
ref:27              16.Aug.93
       -193710.     -230658.     12.495
        8.1392     12.0952       0.9892     -3.2789
       41.1929      9.2357      -0.0300          0.
Fe(Gly)+            Fe(C2H4NO2)+
Fe(Gly)+            Fe(1)C(2)H(4)N(1)O(2)+(1)
ref:27              16.Aug.93
       -103038.     -134682.     20.000
        5.6774      6.0837       3.3533     -3.0304
       42.4593      8.7852       0.2482          1.
Fe(Gly)2,aq         Fe(C2H4NO2)2
Fe(Gly)2,aq         Fe(1)C(4)H(8)N(2)O(4)
ref:27              16.Aug.93
       -182709.     -248527.     58.018
       13.2339     24.5311      -3.8903     -3.7930
       81.1932     23.1388      -0.0300          0.
Fe(Glyc)+           FeCH3OCO2+
Fe(Glyc)+           Fe(1)C(2)H(3)O(3)+(1)
ref:27              16.Aug.93
       -146010.     -179149.      1.008
        7.4836     10.4932       1.6217     -3.2127
       59.3916     13.7379       0.5394          1.
Fe(Glyc)2,aq        Fe(CH3OCO2)2
Fe(Glyc)2,aq        Fe(1)C(4)H(6)O(6)
ref:27              16.Aug.93
       -269459.     -337416.     22.883
       16.8444     33.3487      -7.3593     -4.1575
      115.2196     34.9654      -0.0300          0.
Fe(Lac)+            FeCH3CH2OCO2+
Fe(Lac)+            Fe(1)C(3)H(5)O(3)+(1)
ref:27              30.Aug.93
       -147289.     -188437.      6.708
        7.4532     10.4168       1.6567     -3.2095
       80.5362     21.3748       0.4496          1.
Fe(Lac)2,aq         Fe(CH3CH2OCO2)2
Fe(Lac)2,aq         Fe(1)C(6)H(10)O(6)
ref:27              30.Aug.93
       -272042.     -355495.     36.043
       16.8444     33.3487      -7.3593     -4.1575
      167.6874     53.2020      -0.0300          0.
Fe(Pent)+           FeCH3(CH2)3CO2+
Fe(Pent)+           Fe(1)C(5)H(9)O(2)+(1)
ref:27              1.Sep.93
       -106635.     -158054.     13.108
       11.5343     20.3852      -2.2687     -3.6216
      136.3259     41.0721       0.3539          1.
Fe(Pent)2,aq        Fe(CH3CH2CH2CH2CO2)2
Fe(Pent)2,aq        Fe(1)C(10)H(18)O(4)
ref:27              16.Aug.93
       -190586.     -293990.     50.8
       25.5409     54.5813     -15.7000     -5.0353
      303.0133    100.2378      -0.0300          0.
Fe(Prop)+           FeCH3CH2CO2+
Fe(Prop)+           Fe(1)C(3)H(5)O(2)+(1)
ref:27              16.Aug.93
       -110833.     -146301.      1.308
        7.3034     10.0542       1.7914     -3.1945
       85.8682     22.9627       0.5324          1.
Fe(Prop)2,aq        Fe(CH3CH2CO2)2
Fe(Prop)2,aq        Fe(1)C(6)H(10)O(4)
ref:27              16.Aug.93
       -199008.     -271598.     23.576
       16.4683     32.4309      -6.9996     -4.1196
      178.5967     56.9937      -0.0300          0.
Fe+3                Fe(+3)
Fe+3                Fe(1)+(3)
ref:21              11.Sep.97
        -4120.      -11850.     -66.300
       -2.4256    -13.6961      11.1141     -2.2127
       19.0459     -6.8233       2.5812          3.
FeOH+2              FeOH(+2)
FeOH+2              Fe(1)O(1)H(1)+(2)
ref:21              1.May.97
       -57800.      -70000.     -25.400
       -1.1562    -10.6009       9.9077     -2.3407
       14.6102     -4.7048       1.4382          2.
FeO+                FeO(+1)
FeO+                Fe(1)O(1)+(1)
ref:21              1.May.97
       -53100.      -61000.     -11.100
       -3.7118    -16.8408      12.3595     -2.0827
      -15.3982    -12.8325        .7191          1.
FeO2-               FeO2(-1)
FeO2-               Fe(1)O(2)-(1)
ref:21              1.May.97
       -88000.     -110700.      10.600
        2.3837     -1.9602       6.5182     -2.6979
      -13.3207    -14.5028       1.4662          -1.
FeCl+2              FeCl(+2)
FeCl+2              Fe(1)Cl(1)+(2)
ref:22              14.Sep.97
       -37518.      -50820.     -42.740
        -.7164     -9.5277       9.4878     -2.3851
       23.8149     -2.3482       1.7013          2.
FeF+2               FeF(+2)
FeF+2               Fe(1)F(1)+(2)
ref:22              15.Sep.97
       -79645.      -87141.     -25.700
       -3.4294    -16.1520      12.0915     -2.1112
       23.9805     -1.4787       1.4477          2.
Fr+                 Fr(+)
Fr+                 Fr(1)+(1)
ref:21              12.Dec.97
```

```
       -70500.      -62500.       35.100
       4.7139       3.7284       4.2849      -2.9330
       2.5442      -4.3586       0.0203           1.
Ga+3                 Ga(+3)
Ga+3                 Ga(1)+(3)
ref:21               15.Sep.97
       -38000.      -50600.      -79.000
      -2.8378     -14.7065      11.5197      -2.1709
      16.2356      -8.4326       2.7787           3.
GaOH+                GaOH(+)
GaOH+                Ga(1)O(1)H(1)+(1)
ref:21               10.Dec.97
       -91100.      -116700.     -67.300
       1.6572       -3.7321      7.2107      -2.6246
      48.3870        5.0115      2.0700           1.
GaO+                 GaO(+)
GaO+                 Ga(1)O(1)+(1)
ref:21               10.Dec.97
       -86600.      -100900.     -29.200
       2.1299       -2.5806      6.7629      -2.6722
      -0.7503       -8.6363      0.9986           1.
GaO2-                GaO2(-)
GaO2-                Ga(1)O(2)-(1)
ref:21               10.Dec.97
      -128700.      -153900.     -10.000
       3.6247        1.0721      5.3221      -2.8232
      14.3978       -5.8659      1.7777          -1.
Gd+2                 Gd(+2)
Gd+2                 Gd(1)+(2)
ref:21               10.Dec.97
       -70600.       -67400.      -4.300
       0.0094       -7.7516      8.7810      -2.4584
       9.9946       -5.2956      1.1216           2.
Gd+3                 Gd(+3)
Gd+3                 Gd(1)+(3)
ref:2                13.Jul.87
      -158600.      -164200.     -49.200
      -2.9771      -15.0506     11.6656      -2.1568
       6.5606      -10.3474      2.3265           3.
GdOH+2               GdOH+2
GdOH+2               Gd(1)O(1)H(1)+(2)
ref:25               1.Dec.95
      -204500.      -213400.      -2.9
       2.7389       -1.0936      6.1786      -2.7237
      -3.5082       -9.9196      1.1000           2.
GdO+                 GdO+
GdO+                 Gd(1)O(1)+(1)
ref:25               1.Dec.95
      -193000.      -205500.      13.1
       2.8425       -0.8409      6.0801      -2.7441
     -34.9963      -18.4750       0.3539          1.
GdO2-                GdO2-
GdO2-                Gd(1)O(2)-(1)
ref:25               1.Dec.95
      -225000.      -233000.      38.3
       5.0344        4.5111      3.9769      -2.9654
     -50.6235      -26.1341       1.0495          -1.
GdCl+2               GdCl+2
GdCl+2               Gd(1)Cl(1)+(2)
ref:25               1.Dec.95
      -190400.      -200600.     -22.3
      -0.2630       -8.4170      9.0425      -2.4309
      18.1232       -3.3636      1.4006           2.
GdCl2+               GdCl2+
GdCl2+               Gd(1)Cl(2)+(1)
ref:25               1.Dec.95
      -221300.      -239000.      -5.4
       2.8492       -0.8272      6.0803      -2.7447
       9.5260       -3.8858      0.6305           1.
GdCl3,aq             GdCl3(aq)
GdCl3(aq)            Gd(1)Cl(3)
ref:25               1.Dec.95
      -252100.      -280200.       2.2
       6.3836        7.8028      2.6888      -3.1015
     -19.6565      -11.9138      -0.0300           0.
GdCl4-               GdCl4-
GdCl4-               Gd(1)Cl(4)-(1)
ref:25               1.Dec.95
      -282900.      -324300.      -0.2
      11.1317       19.3995      -1.8761     -3.5809
     -49.0467      -27.4478       1.6310          -1.
GdF+2                GdF+2
GdF+2                Gd(1)F(1)+(2)
ref:25               1.Dec.95
      -232200.      -239300.      -14.4
       -2.9196      -14.9041      11.5935     -2.1628
       19.3937       -2.5281      1.2776           2.
GdF2+                GdF2+
GdF2+                Gd(1)F(2)+(1)
ref:25               1.Dec.95
      -304100.      -321800.      -10.2
       -2.6526      -14.2557      11.3457     -2.1896
       15.9952       -1.8906      0.7096           1.
GdF3,aq              GdF3(aq)
GdF3(aq)             Gd(1)F(3)
ref:25               1.Dec.95
      -374900.      -407400.      -19.9
       -2.3913      -13.6174      11.0949     -2.2160
       -9.6471       -8.4349      -0.0300          0.
GdF4-                GdF4-
GdF4-                Gd(1)F(4)-(1)
ref:25               1.Dec.95
      -445000.      -497300.      -46.4
       -1.0260      -10.2805       9.7756     -2.3539
      -27.4519      -22.1609       2.3239          -1.
GdHCO3+2             GdHCO3+2
GdHCO3+2             Gd(1)H(1)C(1)O(3)+(2)
ref:25               1.Dec.95
      -301200.      -326700.      -9.7
       0.6026       -6.3043       8.2153     -2.5183
      39.1396        4.5681       1.2048           2.
GdCO3+               GdCO3+
GdCO3+               Gd(1)C(1)O(3)+(1)
ref:25               1.Dec.95
      -295500.      -307600.      -40.8
       -0.9530      -10.1036       9.7095     -2.3612
      -19.8322      -15.8269       1.1729           1.
GdH2PO4+2            GdH2PO4+2
GdH2PO4+2            Gd(1)H(2)P(1)O(4)+(2)
ref:25               1.Dec.95
      -431800.      -476600.      -26.1
       1.6048       -3.8632       7.2686     -2.6192
      43.0549        5.1201       1.4574           2.
GdNO3+2              GdNO3+2
GdNO3+2              Gd(1)N(1)O(3)+(2)
ref:25               1.Dec.95
      -185700.      -219800.      -32.5
       1.3205       -4.5535       7.5323     -2.5907
      33.6609        1.5663       1.5475           2.
GdSO4+               GdSO4+
GdSO4+               Gd(1)S(1)O(4)+(1)
ref:25               1.Dec.95
      -331500.      -376800.      -12.0
       -1.4776       -4.1705      7.3822     -2.6065
      -20.9360      -14.7880      0.7287           1.
Gd(Ae)+2             GdCH3COO+2
Gd(Ae)+2             Gd(1)C(2)H(3)O(2)+(2)
ref:33               10 Sep 92
      -250490.      -283100.      -25.700
       2.8605       -0.7945       6.0567     -2.7461
      57.3241       10.1106       1.4477           2.
Gd(Ae)2+             Gd(CH3COO)2+
Gd(Ae)2+             Gd(1)C(4)H(6)O(4)+(1)
ref:33               10 Sep 92
      -341350.      -401740.      -4.700
       9.4165       15.2134       -0.2342     -3.4078
     102.0230       28.2899        0.6223          1.
Gd(Ae)3,aq           Gd(CH3COO)3
Gd(Ae)3,aq           Gd(1)C(6)H(9)O(6)
ref:33               10 Sep 92
      -431490.      -521580.       9.800
      16.8116       33.2662       -7.3215     -4.1541
     141.7603       44.1903       -0.0300          0.
Gd(But)+2            GdCH3(CH2)2CO2+2
Gd(But)+2            Gd(1)C(4)H(7)O(2)+(2)
ref:27               16.Aug.93
      -246839.      -294884.      -14.467
       6.8808        9.0211        2.2007     -3.1518
      97.4167       24.5906        1.2776           2.
Gd(But)2+            Gd(CH3CH2CH2CO2)2+
Gd(But)2+            Gd(1)C(8)H(14)O(4)+(1)
ref:27               16.Aug.93
      -334041.      -424078.       21.787
      17.9029       35.9294       -8.3657     -4.2642
     197.8246       62.8670        0.2229          1.
Gd(For)+2            GdCHO2+2
Gd(For)+2            Gd(1)C(1)H(1)O(2)+(2)
ref:27               16.Aug.93
      -246091.      -268634.      -24.567
       0.8917       -5.5954       7.9307     -2.5476
      26.4744       -0.5508       1.4287           2.
Gd(For)2+            Gd(CHO2)2+
Gd(For)2+            Gd(1)C(2)H(2)O(4)+(1)
ref:27               16.Aug.93
      -332531.      -372659.      -2.084
       5.2546        5.0511       3.7601     -2.9877
      28.4144        2.8309       0.5831           1.
Gd(Pent)+2           GdCH3(CH2)3CO2+2
Gd(Pent)+2           Gd(1)C(5)H(9)O(2)+(2)
ref:27               16.Aug.93
      -244829.      -301364.      -7.967
       9.0391       14.2927       0.1259     -3.3698
     133.8403       37.5583       1.1815           2.
Gd(Pent)2+           Gd(CH3CH2CH2CH2CO2)2+
Gd(Pent)2+           Gd(1)C(10)H(18)O(4)+(1)
ref:27               16.Aug.93
      -330007.      -436320.       37.150
      22.4554       47.0464      -12.7369     -4.7238
     284.7556       93.8330       -0.0116          1.
Gd(Prop)+2           GdCH3CH2CO2+2
Gd(Prop)+2           Gd(1)C(3)H(5)O(2)+(2)
ref:27               16.Aug.93
      -249081.      -289666.      -19.767
       4.8065        3.9537       4.1983     -2.9423
      83.3388       19.4489       1.3552           2.
Gd(Prop)2+           Gd(CH3CH2CO2)2+
Gd(Prop)2+           Gd(1)C(6)H(10)O(4)+(1)
ref:27               16.Aug.93
      -338525.      -414216.       9.261
      13.5253       25.2465      -4.1796     -3.8226
     164.2235       50.5890       0.4100          1.
Gd+4                 Gd(+4)
Gd+4                 Gd(1)+(4)
ref:21               10.Dec.97
       12600.        -5700.      -107.600
      -4.3532      -18.4052      12.9700     -2.0180
      38.8394       -3.5030       3.8013          4.
H+                   H(+)
H+                   H(1)+(1)
ref:2                17.Jul.89
          0.              0.          .000
       .0000         .0000         .0000        .0000
       .0000         .0000         .0000           1.
H2,aq                H2(0)
H2(aq)               H(2)+(0)
ref:3                13.Jul.87
```

```
        4236.       -1000.        13.800
      5.1427       4.7758       3.8729      -2.9764
     27.6251       5.0930       -.2090           0.
H2O2,aq              H2O2
H2O2(aq)             H(2)O(2)+(0)
ref:21               11.Sep.97
      -32030.       -45690.       34.400
      6.1922       7.3370       2.8686      -3.0822
     10.3600       -.9975       -.1809           0.
HO2-                 HO2(-)
HO2-                 H(1)O(2)-(1)
ref:21               11.Sep.97
      -16090.       -38320.        5.700
      2.6566      -1.2961       6.2619      -2.7253
     -1.5190     -10.6529       1.5449           -1.
HAlO2,aq             HAlO2(0)
HAlO2(aq)            H(1)Al(1)O(2)+(0)
ref:20               29.Apr.97
      -207500.      -230730.       -6.500
      3.6808       1.2058       5.2761      -2.8288
     39.0000       2.5000        .3000           0.
H2AsO3-              H2AsO3(-)
H2AsO3-              H(2)As(1)O(3)-(1)
ref:2                3.Jul.87
      -140330.      -170840.       26.400
      5.7934       6.3646       3.2485      -3.0421
     15.8032      -3.6253       1.2305           -1.
HAsO2,aq             HAsO2(0)
HAsO2(aq)            H(1)As(1)O(2)+(0)
ref:21               12.Dec.97
      -96240.       -109110.       30.100
      5.5984       5.8913       3.4280      -3.0224
      6.7990      -2.4438       -0.1158          0.
H3AsO4,aq            H3AsO4(0)
H3AsO4(aq)           H(3)As(1)O(4)+(0)
ref:21               12.Dec.97
      -183100.      -215700.       44.000
      7.9357       11.5925       1.1990      -3.2581
     18.2805       2.2209       -0.3263          0.
H2AsO4-              H2AsO4(-)
H2AsO4-              H(2)As(1)O(4)-(1)
ref:21               12.Dec.97
      -180010.      -217390.       28.000
      6.7429       8.6835       2.3351      -3.1379
     16.9206      -3.1567       1.2055           -1.
HAsO4-2              HAsO4(-2)
HAsO4-2              H(1)As(1)O(4)-(2)
ref:21               12.Dec.97
      -170790.      -216620.        -.400
      4.3994       2.9611       4.5853      -2.9013
      7.9908      -12.7102       3.2197           -2.
HBeO2-               HBeO2(-1)
HBeO2-               H(1)Be(1)O(2)-(1)
ref:21               16.Sep.97
      -172200.      -206700.      -33.300
      2.9518       -.5719       5.9708      -2.7553
     56.2537       7.5374       2.1351           -1.
HBiO2,aq             HBiO2(0)
HBiO2(aq)            H(1)Bi(1)O(2)+(0)
ref:21               16.Sep.97
      -79300.       -86300.       54.600
      5.2306       4.9892       3.7912      -2.9852
     -81.1398     -33.2840       -.0300           0.
HBrO,aq              HBrO
HBrO(aq)             H(1)Br(1)O(1)+(0)
ref:21               11.Sep.97
      -19700.       -27000.       33.800
      5.5795       5.8410       3.4565      -3.0204
      9.8576       -1.2012       -.1719           0.
HCO3-                HCO3(-)
HCO3-                H(1)C(1)O(3)-(1)
ref:2                1.Jul.87
      -140282.      -164898.       23.530
      7.5621       1.1505       1.2346      -2.8266
     12.9395       -4.7579       1.2733           -1.
HCdO2-               HCdO2(-)
HCdO2-               H(1)Cd(1)O(2)-(1)
ref:21               12.Dec.97
       -86500.       -117400.      -10.900
      0.9080       -5.5570       7.9176      -2.5492
     23.2446       -2.8512       1.7965           -1.
HCeO2,aq             HCeO2(aq)
HCeO2(aq)            H(1)Ce(1)O(2)
ref:25               1.Dec.95
      -239300.      -249500.       48.5
      5.0117       4.4582       3.9917      -2.9632
     -72.9937      -30.4525       -0.0300          0.
HCl,aq               HCl(0)
HCl(aq)              H(1)Cl(1)+(0)
ref:40               20.Jan.98
      -30411.       -30285.        0.421
     16.1573      -11.4311      -46.1866      -2.3036
     46.4716       -5.2811       0.0000           0.
HClO,aq              HClO
HClO(aq)             H(1)Cl(1)O(1)+(0)
ref:21               11.Sep.97
      -19100.       -28900.       33.900
      5.5927       5.8751       3.4387      -3.0218
      9.9023       -1.1808       -.1734           0.
HClO2,aq             HClO2
HClO2(aq)            H(1)Cl(1)O(2)+(0)
ref:21               11.Sep.97
        1400.       -12400.       45.000
      7.6706      10.9455       1.4527      -3.2314
     19.1373       2.5672       -.3415           0.
HCoO2-               HCoO2(-1)
HCoO2-               H(1)Co(1)O(2)-(1)
ref:21               11.Dec.97
       -83400.       -117100.      -25.500
      -0.0971       -8.0155       8.8926      -2.4475
     44.7712       3.9116       2.0211           -1.
HCrO2,aq             HCrO2(0)
HCrO2(aq)            H(1)Cr(1)O(2)+(0)
ref:21               16.Sep.97
      -138100.      -157300.        6.000
      1.5359       -4.0259       7.3211      -2.6125
     -16.2043      -10.7140       -.0300           0.
HCrO4-               HCrO4(-)
HCrO4-               H(1)Cr(1)O(4)-(1)
ref:21               11.Sep.97
      -183700.      -210000.       46.600
      8.2211       12.2925       0.9174      -3.2871
     15.5492       -2.7290        .9230           -1.
HCuO2-               HCuO2(-1)
HCuO2-               H(1)Cu(1)O(2)-(1)
ref:21               1.May.97
       -60100.       -86300.        .300
      1.3202       -4.5527       7.5282      -2.5907
      -3.2749       -8.0659        .5464           -1.
HDyO2,aq             HDyO2(aq)
HDyO2(aq)            H(1)Dy(1)O(2)
ref:25               1.Dec.95
      -238200.      -251100.       39.1
      4.6969       3.6855       4.3051      -2.9313
     -60.3933      -26.0730       -0.0300          0.
HEuO2,aq             HEuO2(aq)
HEuO2(aq)            HEu(1)O(2)(1)
ref:25               1.Dec.95
      -216000.      -228200.       42.4
      4.8064       3.9540       4.1968      -2.9424
     -64.9060      -27.6415       -0.3000          0.
HErO2,aq             HErO2(aq)
HErO2(aq)            H(1)Er(1)O(2)
ref:25               1.Dec.95
      -240100.      -254300.       34.8
      4.5464       3.3186       4.4476      -2.9161
     -54.7085      -24.0971       -0.0300          0.
HF2-                 HF2(-)
HF2-                 H(1)F(2)-(1)
ref:2                12.Jul.87
      -138160.      -155340.       22.100
      5.2263       4.9797       3.7928      -2.9849
     -1.3751       -9.7974       1.2934           -1.
HF,aq                HF(0)
HF(aq)               H(1)F(1)+(0)
ref:3                7.Feb.89
       -71662.       -76835.       22.500
      3.4753        .7042       5.4732      -2.8081
     14.3647       -.1828        -.0007           0.
HFeO2-               HFeO2(-1)
HFeO2-               H(1)Fe(1)O(2)-(1)
ref:21               1.May.97
       -95400.       -125700.      -15.000
       .6272       -6.2440       8.1905      -2.5208
     36.1624       1.4468       1.8564           -1.
HFeO2,aq             HFeO2
HFeO2(aq)            H(1)Fe(1)O(2)+(0)
ref:21               1.May.97
      -101100.      -120300.       22.200
      2.7401       -1.0905       6.1776      -2.7338
     -37.8300      -18.2305       -.0300           0.
HGaO2,aq             HGaO2
HGaO2(aq)            H(1)Ga(1)O(2)+(0)
ref:21               10.Dec.97
      -137300.      -158600.        2.900
      3.4470       0.6328       5.5060      -2.8051
     -12.1716       -9.2677       -0.0439          0.
HGdO2,aq             HGdO2(aq)
HGdO2(aq)            H(1)Gd(1)O(2)
ref:25               1.Dec.95
      -237500.      -247200.       48.2
      5.0117       4.4582       3.9917      -2.9632
     -72.5835      -30.3099       -0.0300          0.
HHfO2+               HHfO2(+)
HHfO2+               H(1)Hf(1)O(2)+(1)
ref:21               12.Dec.97
      -237800.      -264200.       -51.000
      2.0629       -2.7421       6.8221      -2.6655
     72.4834       15.7669       1.3268           1.
HHfO3-               HHfO3(-)
HHfO3-               H(1)Hf(1)O(3)-(1)
ref:21               12.Dec.97
      -279200.      -331800.       -34.300
      3.4908       0.7427       5.4561      -2.8096
     57.7445       8.0059       2.1506           -1.
HHgO2-               HHgO2(-1)
HHgO2-               H(1)Hg(1)O(2)-(1)
ref:21               12.Dec.97
       -45200.       -73800.        2.300
      1.8118       -3.3572       7.0689      -2.6401
      3.7588       -8.9825       1.5962           -1.
HHoO2,aq             HHoO2(aq)
HHoO2(aq)            H(1)Ho(1)O(2)
ref:25               1.Dec.95
      -241300.      -253800.       40.5
      4.7380       3.7900       4.2544      -2.9356
     -62.2688      -26.7248       -0.0300          0.
HIO,aq               HIO
HIO(aq)              H(1)I(1)O(1)+(0)
ref:21               11.Sep.97
       -23700.       -33000.       22.800
      3.8979       1.7354       5.0694      -2.8506
       .7260       -4.9085        -.0053           0.
HIO3,aq              HIO3
HIO3(aq)             H(1)I(1)O(3)+(0)
ref:21               11.Sep.97
```

```
       -31700.      -50500.       39.900
       6.8346       8.9050       2.2530      -3.1470
      14.8674        .8357       -.2642            0.
HInO2,aq            HInO2
HInO2(aq)           H(1)In(1)O(2)+(0)
ref:21              11.Dec.97
      -119800.     -135100.       27.200
       4.2864       2.6831       4.6987      -2.8898
     -44.5111     -20.5527      -0.0300            0.
HLuO2,aq            HLuO2(aq)
HLuO2(aq)           H(1)Lu(1)O(2)
ref:25              1.Dec.95
      -240200.     -255100.       27.1
       4.2864       2.6831       4.6987      -2.8898
     -44.3938     -20.5120      -0.0300            0.
HMnO2-              HMnO2(-1)
HMnO2-              H(1)Mn(1)O(2)-(1)
ref:21              12.Sep.97
      -121000.     -149900.       -9.100
       1.0354      -5.2480        7.8003      -2.5619
      20.5255      -3.7067        1.7685          -1.
HMoO4-              HMoO4(-1)
HMoO4-              H(1)Mo(1)O(4)-(1)
ref:21              5.Jan.98
      -206400.     -238500.       32.500
       7.7320      11.0966        1.3908      -3.2376
      33.3930       2.7912        1.1359          -1.
HNO2,aq             HNO2
HNO2(aq)            H(1)N(1)O(2)+(0)
ref:21              11.Sep.97
       -12100.      -28500.       32.400
       5.9151       6.6590        3.1378      -3.0542
       8.7050      -1.6697        -.1507            0.
HNO3,aq             HNO3(0)
HNO3(aq)            H(1)N(1)O(3)+(0)
ref:21              11.Sep.97
       -24730.      -45410.       42.700
       7.1623       9.7063        1.9367      -3.1802
      13.8907        .6320        -.3066            0.
HN2O2-              HN2O2(-1)
HN2O2-              H(1)N(2)O(2)-(1)
ref:21              15.Sep.97
        18200.       -9400.       34.000
       6.5748       8.2753        2.4914      -3.1210
      21.8724      -1.1401        1.1132          -1.
H2N2O2,aq           H2N2O2(0)
H2N2O2(aq)          H(2)N(2)O(2)+(0)
ref:21              15.Sep.97
         8600.      -13700.       52.000
       8.6337      13.3019         .5163      -3.3288
      24.9004       4.9097        -.4475            0.
HNbO3,aq            HNbO3(0)
HNbO3(aq)           H(1)Nb(1)O(3)+(0)
ref:21              5.Jan.98
      -236800.     -257950.       31.100
       5.7110       6.1642        3.3252      -3.0337
      20.2299       3.3616        -0.4710            0.
HNdO2,aq            HNdO2(aq)
HNdO2(aq)           H(1)Nd(1)O(2)
ref:25              1.Dec.95
      -238000.     -248000.       47.8
       4.9843       4.3865        4.0304      -2.9602
     -71.9974     -30.1062       -0.0300            0.
HNiO2-              HNiO2(-1)
HNiO2-              H(1)Ni(1)O(2)-(1)
ref:21              16.Sep.97
       -81980.      -118760.      -36.000
       -.8143       -9.7619       9.5688      -2.3753
      54.2564       6.7430        2.1664          -1.
H3PO2,aq            H3PO2(0)
H3PO2(aq)           H(3)P(1)O(2)+(0)
ref:21              15.Sep.97
      -125100.     -145600.       36.900
       6.5352       8.1731        2.5430      -3.1168
      12.4140        -.1623       -.2188            0.
H2PO2-              H2PO2(-)
H2PO2-              H(2)P(1)O(2)-(1)
ref:21              15.Sep.97
      -122400.     -146700.       24.100
       5.2026       4.9190        3.8223      -2.9823
      13.7063      -4.4604        1.2637          -1.
H3PO3,aq            H3PO3(0)
H3PO3(aq)           H(3)P(1)O(3)+(0)
ref:21              15.Sep.97
      -204800.     -230600.       43.600
       4.2704       2.6439        4.7145      -2.8882
      17.9261       2.0783        -.3203            0.
H2PO3-              H2PO3(-)
H2PO3-              H(2)P(1)O(3)-(1)
ref:21              15.Sep.97
      -202350.     -231700.       31.700
       4.1649       2.3899        4.8065      -2.8777
      19.9762      -1.9142        1.1491          -1.
HPO3-2              HPO3(-2)
HPO3-2              H(1)P(1)O(3)-(2)
ref:21              15.Sep.97
      -194000.     -231600.        4.000
       3.4463        .6347        5.4974      -2.8051
      11.6523     -11.2232        3.1527          -2.
H4P2O7,aq           H4P2O7(0)
H4P2O7(aq)          H(4)P(2)O(7)+(0)
ref:21              15.Sep.97
      -485700.     -542200.       64.000
       9.2975      14.9199        -.1130      -3.3957
      34.8301       8.9430        -.6292            0.
H3P2O7-             H3P2O7(-)
H3P2O7-             H(3)P(2)O(7)-(1)
ref:21              15.Sep.97
      -483600.     -544100.       51.000
       9.1292      14.5122         .0398      -3.3788
      35.9785       4.5838         .8568          -1.
H2P2O7-2            H2P2O7(-2)
H2P2O7-2            H(2)P(2)O(7)-(2)
ref:21              15.Sep.97
      -480400.     -544600.       39.000
       9.0963      14.4299         .0760      -3.3754
      40.6359        .5505        2.6218          -2.
HP2O7-3             HP2O7(-3)
HP2O7-3             H(1)P(2)O(7)-(3)
ref:21              15.Sep.97
      -471400.     -543700.      -11.000
       8.3302      12.5558        0.8208      -3.2980
      32.1587      -8.8807        4.6470          -3.
H3PO4,aq            H3PO4(0)
H3PO4(aq)           H(3)P(1)O(4)+(0)
ref:3               11.Jul.87
      -273100.     -307920.       38.000
       8.2727      12.4182         .8691      -3.2924
      17.9708       1.7727        -.2200            0.
H2PO4-              H2PO4(-)
H2PO4-              H(2)P(1)O(4)-(1)
ref:2               3.Jul.87
      -270140.     -309820.       21.600
       6.4875       8.0594        2.5823      -3.1122
      14.0435      -4.4605        1.3003          -1.
HPO4-2              HPO4(-2)
HPO4-2              H(1)P(1)O(4)-(2)
ref:2               3.Jul.87
      -260310.     -308815.       -8.000
       3.6315       1.0857        5.3233      -2.8239
       2.7357     -14.9103        3.3363          -2.
HPbO2-              HPbO2(-1)
HPbO2-              H(1)Pb(1)O(2)-(1)
ref:21              16.Sep.97
       -81000.     -104200.       18.000
       4.4403       3.0599        4.5482      -2.9054
     -22.3600     -17.2935        1.3566          -1.
HPrO2,aq            HPrO2(aq)
HPrO2(aq)           H(1)Pr(1)O(2)
ref:25              1.Dec.95
      -239700.     -250100.       47.0
       4.9706       4.3537        4.0423      -2.9589
     -74.0012     -29.7599       -0.0300            0.
H2S,aq              H2S(0)
H2S(aq)             H(2)S(1)+(0)
ref:3               26.Jun.87
        -6673.       -9001.       30.000
       6.5097       6.7724        5.9646      -3.0590
      32.3000       4.7300        -.1000            0.
HS-                 HS(-)
HS-                 H(1)S(1)-(1)
ref:2               1.Jul.87
         2860.       -3850.       16.300
       5.0119       4.9799        3.4765      -2.9849
       3.4200      -6.2700        1.4410          -1.
H2S2O3,aq           H2S2O3
H2S2O3(aq)          H(2)S(2)O(3)+(0)
ref:21              11.Sep.97
      -128000.     -150400.       45.000
       7.4242      10.3493        1.6762      -3.2067
      19.1373       2.5672        -.3415            0.
HS2O3-              HS2O3(-1)
HS2O3-              H(1)S(2)O(3)-(1)
ref:21              11.Sep.97
      -127200.     -153900.       30.500
       6.1964       7.3510        2.8549      -3.0828
      18.9745      -2.3216        1.1676          -1.
H2S2O4,aq           H2S2O4
H2S2O4(aq)          H(2)S(2)O(4)+(0)
ref:21              11.Sep.97
      -147400.     -175300.       51.000
       8.6525      13.3462         .5023      -3.3306
      24.1023       4.5838        -.4323            0.
HS2O4-              HS2O4(-1)
HS2O4-              H(1)S(2)O(4)-(1)
ref:21              11.Sep.97
      -146900.     -179100.       36.500
       7.6159      10.8142        1.5005      -3.2260
      23.9326        -.3049        1.0760          -1.
HSO3-               HSO3(-)
HSO3-               H(1)S(1)O(3)-(1)
ref:2               3.Jul.87
      -126130.     -149670.       33.400
       6.7014       8.5816        2.3771      -3.1338
      15.6949      -3.3198        1.1233          -1.
HSO4-               HSO4(-)
HSO4-               H(1)S(1)O(4)-(1)
ref:2               3.Jul.87
      -180630.     -212500.       30.000
       6.9788       9.2590        2.1108      -3.1618
      20.0961      -1.9550        1.1748          -1.
HSO5-               HSO5(-)
HSO5-               H(1)S(1)O(5)-(1)
ref:21              11.Sep.97
      -152370.     -185380.       50.700
       8.9391      14.0430         .2349      -3.3594
      35.7254       4.4819         .8611          -1.
HSbO2,aq            HSbO2(0)
HSbO2(aq)           H(1)Sb(1)O(2)+(0)
ref:21              11.Sep.97
       -97400.     -116600.       11.100
       2.9726       -.5203        5.9475      -2.7574
      -8.9525      -8.8400        0.1719            0.
HScO2,aq            HScO2
HScO2(aq)           H(1)Sc(1)O(2)+(0)
ref:21              11.Dec.97
```

```
      -231600.    -244300.      30.300
       3.3422      0.3770      5.6066     -2.7945
     -47.9689    -21.7545     -0.0300           0.
HSe-                 HSe(-)
HSe-                 H(1)Se(1)-(1)
ref:21               11.Sep.97
        10500.       3800.      19.000
       4.9823      4.3855      4.0227     -2.9602
       6.9147     -7.0678      1.3400          -1.
H2SeO3,aq            H2SeO3
H2SeO3(aq)           H(2)Se(1)O(3)+(0)
ref:21               11.Sep.97
      -101850.    -121290.      49.700
       7.9475     11.6240      1.1819     -3.2594
      22.9944      4.1356      -.4127           0.
HSeO3-               HSeO3(-)
HSeO3-               H(1)Se(1)O(3)-(1)
ref:21               11.Sep.97
       -98340.    -122980.      32.300
       6.4061      7.8624      2.6551     -3.1039
      20.4808     -1.7105      1.1402          -1.
HSeO4-               HSeO4(-)
HSeO4-               H(1)Se(1)O(4)-(1)
ref:21               11.Sep.97
      -108100.    -139000.      35.700
       7.5244     10.5922      1.5837     -3.2168
      23.2855      -.5697      1.0885          -1.
HSiO3-               HSiO3(-)
HSiO3-               H(1)Si(1)O(3)-(1)
ref:22               13.Sep.97
      -242801.    -273872.       5.000
       2.9735     -0.5181      5.9467     -2.7575
       8.1489     -7.3123      1.5511          -1.
HSmO2,aq             HSmO2(aq)
HSmO2(aq)            H(1)Sm(1)O(2)
ref:25               1.Dec.95
      -237100.    -247700.       45.9
       4.9296      4.2552      4.0768     -2.9548
     -69.5359    -29.2507     -0.3000           0.
HSnO2-               HSnO2(-1)
HSnO2-               H(1)Sn(1)O(2)-(1)
ref:21               12.Sep.97
       -97300.    -122100.       9.400
       4.1971      2.4678      4.7779     -2.8809
      -6.7372    -12.2825      1.4874          -1.
HTbO2,aq             HTbO2(aq)
HTbO2(aq)            H(1)Tb(1)O(2)
ref:25               1.Dec.95
      -238700.    -251000.       40.9
       4.7517      3.8228      4.2425     -2.9369
     -62.8548    -26.9285     -0.0300           0.
HTlO2,aq             HTlO2
HTlO2(aq)            H(1)Tl(1)O(2)+(0)
ref:21               11.Dec.97
       -57600.     -65600.      53.100
       5.1759      4.8579      3.8372     -2.9797
     -79.1473    -32.5914     -0.0300           0.
HTmO2,aq             HTmO2(aq)
HTmO2(aq)            H(1)Tm(1)O(2)
ref:25               1.Dec.95
      -240300.    -254500.       34.7
       4.5464      3.3186      4.4476     -2.9161
     -55.5327    -24.0360     -0.0300           0.
HUO2,aq              HUO2(0)
HUO2(aq)             U(1)U(1)O(2)+(0)
ref:37               20.Jan.98
      -198000.    -205100.      52.900
       5.1622      4.8252      3.8489     -2.9784
     -78.8543    -32.4895     -0.0300           0.
HUO2+                HUO2(+)
HUO2+                H(1)U(1)O(2)+(1)
ref:37               20.Jan.98
      -233200.    -254800.     -11.400
       3.2291      0.1055      5.7039     -2.7833
      14.0517     -2.6271      0.7287          1.
HUO3-                HUO3(-)
HUO3-                H(1)U(1)O(3)-(1)
ref:37               20.Jan.98
      -274100.    -321200.     -41.300
       3.1824     -0.0092      5.7491     -2.7785
      68.0400     11.2651      2.2503          -1.
HUO4-                HUO4(-)
HUO4-                H(1)U(1)O(4)-(1)
ref:37               20.Jan.98
      -314800.    -362900.     -20.100
       4.9364      4.2748      4.0637     -2.9556
      36.9351      1.4672      1.9339          -1.
H3VO4,aq             H3VO4(0)
H3VO4(aq)            H(3)V(1)O(4)+(0)
ref:21               5.Jan.98
      -249200.    -284600.      37.100
       6.9310      9.1392      2.1640     -3.1567
      15.3166      0.8561     -0.2218          0.
H2VO4-               H2VO4(-)
H2VO4-               H(2)V(1)O(4)-(1)
ref:21               5.Jan.98
      -243990.    -280620.      29.000
       6.4502      7.9653      2.6252     -3.1082
      38.1088      4.2579      1.1898          -1.
HVO4-2               HVO4(-2)
HVO4-2               H(1)V(1)O(4)-(2)
ref:21               5.Jan.98
      -233000.    -277000.       4.000
       4.5410      3.3077      4.4469     -2.9156
      86.3755     14.7484      3.1527          -2.
HWO4-                HWO4(-1)
HWO4-                H(1)W(1)O(4)-(1)
ref:21               15.Sep.97
      -223400.    -255000.      31.200
       7.7661     11.1820      1.3532     -3.2412
      34.7493      3.1986      1.1559          -1.
HYO2,aq              HYO2
HYO2(aq)             H(1)Y(1)O(2)+(0)
ref:21               12.Dec.97
      -241700.    -254600.      31.800
       4.4506      3.0828      4.5443     -2.9063
     -50.6646    -22.6916     -0.0300           0.
HYbO2,aq             HYbO2(aq)
HYbO2(aq)            H(1)Yb(1)O(2)
ref:25               1.Dec.95
      -233800.    -246500.       36.5
       4.6011      3.4560      4.3859     -2.9218
     -58.9357    -24.8711     -0.0300           0.
HZnO2-               HZnO2(-1)
HZnO2-               H(1)Zn(1)O(2)-(1)
ref:21               17.Sep.97
      -110720.    -142370.     -16.000
        .5623      -6.4047      8.2588     -2.5141
      35.0874      1.0394      1.8669          -1.
HZrO2+               HZrO2(+1)
HZrO2+               H(1)Zr(1)O(2)+(1)
ref:21               1.May.97
      -239700.    -265300.     -49.700
       2.1106     -2.6299      6.7878     -2.6702
      70.5343     15.1558      1.3060          1.
HZrO3-               HZrO3(-1)
HZrO3-               H(1)Zr(1)O(3)-(1)
ref:21               1.May.97
      -281500.    -333300.     -32.700
       3.5625       .9168      5.3901     -2.8168
      55.3517      7.2726      2.1199          -1.
He,aq                He(0)
He(aq)               He(1)+(0)
ref:3                13.Jul.87
        4658.       -150.       14.020
       3.4722       .6967      5.4762     -2.8078
      26.0707     4.5634       -.2123           0.
Hf+4                 Hf(+4)
Hf+4                 Hf(1)+(4)
ref:21               12.Dec.97
      -132600.    -150250.     -111.200
      -4.3761    -18.4638      12.9996     -2.0156
      39.6914     -3.7271       3.8552          4.
HfOH+3               HfOH(+3)
HfOH+3               Hf(1)O(1)H(1)+(3)
ref:21               12.Dec.97
      -189000.    -211800.      -72.800
       0.9047     -5.5670       7.9267     -2.5488
      57.6774      6.2949       2.6777          3.
HfO+2                HfO(+2)
HfO+2                Hf(1)O(1)+(2)
ref:21               12.Dec.97
      -186000.    -200900.      -46.200
       2.0179     -2.8551       6.8743     -2.6609
      17.6401     -4.6845       1.7607          2.
HfO2,aq              HfO2
HfO2(aq)             Hf(1)O(2)+(0)
ref:21               12.Dec.97
      -231400.    -262600.      -45.100
       1.8096     -3.3639       7.0739     -2.6398
      40.1163      8.8615      -0.0300          0.
Hg2+2                Hg2(+2)
Hg2+2                Hg(2)+(2)
ref:21               10.Dec.97
        36710.      39880.       15.710
       4.0263      2.0479       4.9491     -2.8636
      21.8090     -0.2234        .8201          2.
Hg+2                 Hg(+2)
Hg+2                 Hg(1)+(2)
ref:2                1.Jul.87
        39360.      40670.       -8.680
       -.5280     -9.0707       9.3152     -2.4040
      18.0613     -2.5865       1.1512          2.
HgOH+                HgOH(+)
HgOH+                Hg(1)O(1)H(1)+(1)
ref:21               12.Dec.97
       -12700.     -20400.       16.700
       1.2505     -4.7196       7.5872     -2.5838
      36.1808      6.4374       0.2998          1.
HgO,aq               HgO
HgO(aq)              Hg(1)O(1)+(0)
ref:21               12.Dec.97
        -8900.     -19200.        8.200
       0.6191     -6.2664       8.2051     -2.5198
      -8.6440     -8.0863      -0.0300          0.
HgCl+                HgCl(+)
HgCl+                Hg(1)Cl(1)+(1)
ref:22               6.Jan.98
        -2155.      -7374.       11.670
       2.4941     -1.6886       6.4067     -2.7091
      32.5048      4.9328       0.3735          1.
HgCl2,aq             HgCl2(0)
HgCl2(aq)            Hg(1)Cl(2)+(0)
ref:22               6.Jan.98
       -42838.     -56787.       24.640
       6.0150      6.9084       3.0277     -3.0645
      48.6578     11.8560      -0.0380          0.
HgCl3-               HgCl3(-)
HgCl3-               Hg(1)Cl(3)-(1)
ref:22               6.Jan.98
       -74504.     -99299.       30.510
      10.5003     17.8603       -1.2769     -3.5173
      78.0458     18.2101        1.1676          -1.
HgCl4-2              HgCl4(-2)
HgCl4-2              Hg(1)Cl(4)-(2)
ref:22               6.Jan.98
```

	-106988.	-145023.	28.360	
	15.5903	30.2888	-6.1618	-4.0311
	109.5610	23.9860	2.7846	-2.
HgF+		HgF(+)		
HgF+		Hg(1)F(1)+(1)		
ref:22		6.Jan.98		
	-30204.	-39512.	-4.480	
	-0.0492	-7.8986	8.8475	-2.4524
	37.2987	5.7934	0.6223	1.
Hg(Ae)+		HgCH3COO+		
Hg(Ae)+		Hg(1)C(2)H(3)O(2)+(1)		
ref:33		17 Aug 92		
	-54760.	-79390.	18.500	
	5.6341	5.9787	3.3935	-3.0261
	70.1764	18.3452	0.2712	1.
Hg(Ae)2,aq		Hg(CH3COO)2		
Hg(Ae)2,aq		Hg(1)C(4)H(6)O(4)		
ref:33		17 Aug 92		
	-146580.	-198780.	40.100	
	12.7295	23.3004	-3.4080	-3.7421
	140.9402	43.9053	-0.0300	0.
Hg(Ae)3-		Hg(CH3COO)3-		
Hg(Ae)3-		Hg(1)C(6)H(9)O(6)-(1)		
ref:33		10 Sep 92		
	-239020.	-321900.	51.400	
	21.0462	43.6061	-11.3861	-4.5816
	235.9096	74.0939	0.8508	-1.
Ho+2		Ho(+2)		
Ho+2		Ho(1)+(2)		
ref:21		10.Dec.97		
	-96900.	-94200.	-4.300	
	0.0094	-7.7516	8.7810	-2.4584
	9.9946	-5.2956	1.1216	2.
Ho+3		Ho(+3)		
Ho+3		Ho(1)+(3)		
ref:2		13.Jul.87		
	-161400.	-169000.	-54.300	
	-3.1198	-15.3992	11.8026	-2.1424
	8.6686	-9.8178	2.3899	3.
HoOH+2		HoOH+2		
HoOH+2		Ho(1)O(1)H(1)+(2)		
ref:25		1.Dec.95		
	-207500.	-219000.	-9.7	
	2.6374	-1.3394	6.2715	-2.7235
	1.9108	-8.3714	1.2048	2.
HoO+		HoO+		
HoO+		Ho(1)O(1)+(1)		
ref:25		1.Dec.95		
	-196200.	-211400.	5.9	
	2.7146	-1.1548	6.2077	-2.7312
	-29.1412	-16.7843	0.4615	1.
HoO2-		HoO2-		
HoO2-		Ho(1)O(2)-(1)		
ref:25		1.Dec.95		
	-229100.	-240000.	30.0	
	4.7894	3.9112	4.2160	-2.9406
	-39.5064	-22.6712	1.1748	-1.
HoCl+2		HoCl+2		
HoCl+2		Ho(1)Cl(1)+(2)		
ref:25		1.Dec.95		
	-193100.	-205600.	-28.4	
	-0.4168	-8.7940	9.1934	-2.4154
	22.3450	-2.1720	1.4867	2.
HoCl2+		HoCl2+		
HoCl2+		Ho(1)Cl(2)+(1)		
ref:25		1.Dec.95		
	-224100.	-244600.	-13.1	
	2.6851	-1.2272	6.2371	-2.7282
	17.3007	-1.5607	0.7483	1.
HoCl3,aq		HoCl3(aq)		
HoCl3(aq)		Ho(1)Cl(3)		
ref:25		1.Dec.95		
	-254900.	-286400.	-7.8	
	6.1565	7.2496	2.9030	-3.0786
	-8.3500	-7.9841	-0.0300	0.
HoCl4-		HoCl4-		
HoCl4-		Ho(1)Cl(4)-(1)		
ref:25		1.Dec.95		
	-285700.	-331700.	-14.0	
	10.9513	18.9611	-1.7081	-3.5628
	-29.7863	-21.4419	1.8460	-1.
HoF+2		HoF+2		
HoF+2		Ho(1)F(1)+(2)		
ref:25		1.Dec.95		
	-235200.	-243800.	-17.8	
	-3.0852	-15.3064	11.7462	-2.1461
	23.2937	-1.3364	1.3288	2.
HoF2+		HoF2+		
HoF2+		Ho(1)F(2)+(1)		
ref:25		1.Dec.95		
	-307400.	-326500.	-13.5	
	-2.8400	-14.7070	11.5098	-2.1709
	23.1340	0.4343	0.7584	1.
HoF3,aq		HoF3(aq)		
HoF3(aq)		Ho(1)F(3)		
ref:25		1.Dec.95		
	-378300.	-412500.	-24.2	
	-2.6184	-14.1706	11.3090	-2.1931
	1.6591	-4.5051	-0.0300	0.
HoF4-		HoF4-		
HoF4-		Ho(1)F(4)-(1)		
ref:25		1.Dec.95		
	-448500.	-503400.	-53.7	
	-1.2375	-10.7997	9.9860	-2.3324
	-9.0382	-16.1550	2.4471	-1.
HoHCO3+2		HoHCO3+2		
HoHCO3+2		Ho(1)H(1)C(1)O(3)+(2)		
ref:25		1.Dec.95		
	-304000.	-332100.	-17.0	
	0.4557	-6.6620	8.3538	-2.5035
	43.5512	5.7598	1.3115	2.
HoCO3+		HoCO3+		
HoCO3+		Ho(1)C(1)O(3)+(1)		
ref:25		1.Dec.95		
	-298600.	-312600.	-47.0	
	-0.9954	-10.2047	9.7433	-2.3570
	-17.4516	-15.2972	1.2659	1.
HoH2PO4+2		HoH2PO4+2		
HoH2PO4+2		Ho(1)H(2)P(1)O(4)+(2)		
ref:25		1.Dec.95		
	-434600.	-482100.	-33.5	
	1.4594	-4.2123	7.3930	-2.6048
	47.5067	6.3118	1.5684	2.
HoNO3+2		HoNO3+2		
HoNO3+2		Ho(1)N(1)O(3)+(2)		
ref:25		1.Dec.95		
	-188200.	-225600.	-42.1	
	1.1895	-4.8717	7.6537	-2.5775
	38.5060	2.7579	1.7013	2.
HoSO4+		HoSO4+		
HoSO4+		Ho(1)S(1)O(4)+(1)		
ref:25		1.Dec.95		
	-344200.	-381500.	-17.0	
	-1.4371	-4.2696	7.4212	-2.6024
	-18.6528	-14.2584	0.8111	1.
Ho(Ae)+2		HoCH3COO+2		
Ho(Ae)+2		Ho(1)C(2)H(3)O(2)+(2)		
ref:33		11.Sep.92		
	-253270.	-288520.	-32.900	
	2.7148	-1.1553	6.2089	-2.7311
	61.7679	11.3023	1.5579	2.
Ho(Ae)2+		Ho(CH3COO)2+		
Ho(Ae)2+		Ho(1)C(4)H(6)O(4)+(1)		
ref:33		11 Sept 92		
	-344120.	-407930.	-14.600	
	9.2621	14.8317	-0.0744	-3.3920
	110.0599	30.6149	0.7686	1.
Ho(Ae)3,aq		Ho(CH3COO)3		
Ho(Ae)3,aq		Ho(1)C(6)H(9)O(6)		
ref:33		11 Sept 92		
	-434250.	-528670.	-3.100	
	16.5845	32.7130	-7.1070	-4.1313
	153.0665	48.1201	-0.0300	0.
Ho+4		Ho(+4)		
Ho+4		Ho(1)+(4)		
ref:21		10.Dec.97		
	-30500.	-48300.	-104.200	
	-4.3164	-18.3144	12.9330	-2.0218
	39.9963	-3.2789	3.7484	4.
I-		I(-)		
I-		I(1)-(1)		
ref:2		1.Jul.87		
	-12410.	-13600.	25.500	
	7.7623	8.2762	1.4609	-3.1211
	-6.2700	-4.9440	1.2934	-1.
I3-		I3(-)		
I3-		I(3)-(1)		
ref:2		12.Jul.87		
	-12300.	-12300.	57.200	
	9.8500	16.2697	-.6447	-3.4516
	20.8712	-.3661	.7628	-1.
IO-		IO(-)		
IO-		I(1)O(1)-(1)		
ref:21		11.Sep.97		
	-9200.	-25700.	-1.400	
	.6131	-6.2757	8.1983	-2.5195
	1.1172	-10.0825	1.6530	-1.
IO3-		IO3(-)		
IO3-		I(1)O(3)-(1)		
ref:2		12.Jul.87		
	-30600.	-52900.	28.300	
	5.7148	6.1725	3.3240	-3.0342
	7.7293	-6.3345	1.2002	-1.
IO4-		IO4(-)		
IO4-		I(1)O(4)-(1)		
ref:21		30.Apr.97		
	-14000.	-36200.	53.000	
	9.2831	14.8827	-.0933	-3.3942
	12.6081	-3.4419	.8264	-1.
In+3		In(+3)		
In+3		In(1)+(3)		
ref:21		12.Dec.97		
	-23400.	-25000.	-63.000	
	-2.2361	-13.2378	10.9433	-2.2316
	20.3744	-6.2122	2.5346	3.
InOH+2		InOH(+2)		
InOH+2		In(1)O(1)H(1)+(2)		
ref:21		11.Dec.97		
	-74600.	-94700.	-44.700	
	2.0372	-2.8058	6.8493	-2.6629
	30.2531	-0.2234	1.7366	2.
InO+		InO(+)		
InO+		In(1)O(1)+(1)		
ref:21		11.Dec.97		
	-69400.	-76900.	-2.600	
	2.5804	-1.4833	6.3385	-2.7176
	-22.2654	-14.8084	0.5907	1.
InO2-		InO2(-)		
InO2-		In(1)O(2)-(1)		
ref:21		11.Dec.97		
	-106700.	-125300.	15.900	
	4.3832	2.9224	4.5983	-2.8997
	-20.4685	-16.7435	1.3901	-1.
InCl+2		InCl(+2)		
InCl+2		In(1)Cl(1)+(2)		
ref:22		6.Jan.98		

```
       -59226.      -66209.      -38.800
      -0.6441      -9.3513       9.4185      -2.3924
      22.2354      -2.7149       1.6444           2.
InF+2                InF(+2)
InF+2                In(1)F(1)+(2)
ref:22               6.Jan.98
       -97016.      -98718.      -23.530
      -3.3507     -15.9600      12.0160      -2.1192
      22.5771      -1.8453       1.4099           2.
K+                   K(+)
K+                   K(1)+(1)
ref:2                3.Jun.87
       -67510.      -60270.       24.150
       3.5590      -1.4730       5.4350      -2.7120
       7.4000      -1.7910        .1927           1.
KOH,aq               KOH
KOH(aq)              K(1)O(1)H(1)+(0)
ref:24               17.Sep.97
      -103877.     -112104.       28.000
       3.6808       1.2058       5.2761      -2.8288
       -.4880        .6520       -.0500           0.
KCl,aq               KCl(0)
KCl(aq)              K(1)Cl(1)+(0)
ref:23               15.Sep.97
       -96500.      -97400.       39.100
       7.2386       9.8928       1.8616      -3.1880
      -1.434        6.0310       -.0300           0.
KBr,aq               KBr(0)
KBr(aq)              K(1)Br(1)+(0)
ref:22               13.Sep.97
       -90010.      -86320.       47.500
       8.0580      11.8970       1.0670      -3.2708
       1.4496      -4.6580       -.0050           0.
KI,aq                KI(0)
KI(aq)               K(1)I(1)+(0)
ref:22               13.Sep.97
       -77740.      -71829.       49.200
       9.8369      16.2406       -.6402      -3.4503
       2.7214      -4.2160       -.0050           0.
KAlO2,aq             KAlO2(0)
KAlO2(aq)            K(1)Al(1)O(2)+(0)
ref:24               17.Sep.97
      -264381.     -274982.       35.700
       6.0070       6.8858       3.0436      -3.0637
       1.3940       1.2120       -.0500           0.
KHSO4,aq             KHSO4(0)
KHSO4(aq)            K(1)H(1)S(1)O(4)+(0)
ref:22               17.Sep.97
      -243400.     -267400.       55.000
       9.1226      14.4964        .0453      -3.3782
      39.9849       8.7230       -.0010           0.
KSO4-                KSO4(-)
KSO4-                K(1)S(1)O(4)-(1)
ref:22               12.Sep.97
      -246640.     -276980.       35.000
       5.9408       6.7274       3.0989      -3.0571
       9.9089      -5.2549       1.0996          -1.
K(Ae),aq             KCH3COO
K(Ae),aq             K(1)C(2)H(3)O(2)
ref:33               17 Aug 92
      -155420.     -175220.       47.600
       9.9020      16.3937       -0.6874     -3.4566
      40.5631       9.0167       -0.0300          0.
K(Ae)2-              K(CH3COO)2-
K(Ae)2-              K(1)C(4)H(6)O(4)-(1)
ref:33               10 Sep 92
      -242990.     -292900.       60.700
      17.8481      35.7984       -8.3193     -4.2588
      94.0916      25.2533        0.7097          -1.
K(But),aq            KCH3(CH2)2CO2
K(But),aq            K(1)C(4)H(7)O(2)
ref:27               26.Aug.93
       -152161.     -187401.       58.768
       13.9798      26.3520       -4.6040     -3.8683
       82.2231      23.4967       -0.0300           0.
K(But)2-             K(CH3CH2CH2CO2)2-
K(But)2-             K(1)C(8)H(14)O(4)-(1)
ref:27               26.Aug.93
       -236375.     -316310.       85.956
       26.3402      56.5369      -16.4778     -5.1161
      190.0492      59.8305        0.3272          -1.
K(For),aq            KCHO2
K(For),aq            K(1)C(1)H(1)O(2)
ref:27               26.Aug.93
       -151413.     -161151.       48.668
        7.9397      11.6070        1.1839     -3.2587
        9.8889      -1.6447       -0.0300           0.
K(For)2-             K(CHO2)2-
K(For)2-             K(1)C(2)H(2)O(4)-(1)
ref:27               26.Aug.93
       -234866.     -264561.       63.193
       13.6868      25.6408       -4.3345     -3.8389
       20.4973      -0.2055        0.6721          -1.
K(Glyc),aq           KCH3OCO2
K(Glyc),aq           K(1)C(2)H(3)O(3)
ref:27               30.Aug.93
       -188721.     -214171.       53.168
        9.8131      16.1774       -0.6044     -3.4477
       40.8892       9.1302       -0.0300           0.
K(Glyc)2-            K(CH3OCO2)2-
K(Glyc)2-            K(1)C(4)H(6)O(6)-(1)
ref:27               30.Aug.93
       -309741.     -370519.       73.335
       17.5955      35.1810       -8.0761     -4.2333
       93.1092      25.5242        0.5185          -1.
K(Lac),aq            KCH3CH2OCO2
K(Lac),aq            K(1)C(3)H(5)O(3)
ref:27               30.Aug.93
       -190081.     -223541.       58.868
       12.0572      21.6610       -2.7676     -3.6744
       62.8615      16.7671       -0.0300           0.
K(Lac)2-             K(CH3CH2OCO2)2-
K(Lac)2-             K(1)C(6)H(10)O(6)-(1)
ref:27               30.Aug.93
       -312475.     -388842.       86.182
       22.2742      46.6039      -12.5625     -4.7055
      143.7822      43.7607        0.3236          -1.
K(Pent),aq           KCH3(CH2)3CO2
K(Pent),aq           K(1)C(5)H(9)O(2)
ref:27               1.Sep.93
       -150151.     -193881.       65.268
       16.1707      31.7005       -6.7050     -4.0894
      119.5323      36.4644       -0.0300           0.
K(Pent)2-            K(CH3CH2CH2CH2CO2)2-
K(Pent)2-            K(1)C(10)H(18)O(4)-(1)
ref:27               1.Sep.93
       -232342.     -328765.      100.606
       30.8965      67.6627      -20.8507     -5.5761
      277.0852      90.7965        0.1041          -1.
K(Prop),aq           KCH3CH2CO2
K(Prop),aq           K(1)C(3)H(5)O(2)
ref:27               15.Sep.93
       -154321.     -182101.       53.468
       11.8793      21.2223       -2.5860     -3.6562
       67.4299      18.3550       -0.0300           0.
K(Prop)2-            K(CH3CH2CO2)2-
K(Prop)2-            K(1)C(6)H(10)O(4)-(1)
ref:27               15.Sep.93
       -240709.     -306125.       74.011
       21.9605      45.8408      -12.2686     -4.6740
      156.3920      47.5525        0.5082          -1.
Kr,aq                Kr(0)
Kr(aq)               Kr(1)+(0)
ref:3                13.Jul.87
         3554.       -3650.       15.060
       6.2721       7.5333       2.7891      -3.0904
      37.8226       8.6985       -.2281           0.
La+2                 La(+2)
La+2                 La(1)+(2)
ref:21               9.Dec.97
       -77700.      -72200.        0.700
       0.1064      -7.5128       8.6825      -2.4683
       8.7551      -5.4789       1.0444           2.
La+3                 La(+3)
La+3                 La(1)+(3)
ref:2                13.Jul.87
      -164000.     -169600.      -52.000
      -2.7880     -14.3824      10.9602      -2.1844
       4.2394     -10.6122       2.1572           3.
LaOH+2               LaOH+2
LaOH+2               La(1)O(1)H(1)+(2)
ref:25               1.Dec.95
      -208900.     -218200.       -6.6
       2.6766      -1.2486       6.2460      -2.7273
      -0.5065      -9.0640       1.1586           2.
LaO+                 
LaO+                 La(1)O(1)+(1)
ref:25               1.Dec.95
      -195900.     -208900.        9.2
       2.7794      -0.9938       6.1373      -2.7378
      -31.7836     -17.5379       0.4100           1.
LaO2H,aq             LaO2H(aq)
LaO2H(aq)            La(1)O(2)H(1)
ref:25               1.Dec.95
      -239300.     -249500.       44.0
       4.8611       4.0853       4.1503      -2.9478
      -66.8987     -28.3340      -0.0300           0.
LaO2-                LaO2-
LaO2-                La(1)O(2)-(1)
ref:25               1.Dec.95
      -221700.     -230200.       33.8
       4.8931       4.1637       4.1178      -2.9510
      -44.4914     -24.2193       1.1172          -1.
LaCl+2               LaCl+2
LaCl+2               La(1)Cl(1)+(2)
ref:25               1.Dec.95
      -195800.     -206100.       -25.7
       0.0273      -7.7112       8.7724      -2.4601
      16.8429      -3.9594       1.4477           2.
LaCl2+               LaCl2+
LaCl2+               La(1)Cl(2)+(1)
ref:25               1.Dec.95
      -226700.     -244900.       -9.6
       3.1785      -0.0177       5.7515      -2.7782
       6.8244      -5.0483       0.7003           1.
LaCl3,aq             LaCl3(aq)
LaCl3(aq)            La(1)Cl(3)
ref:25               1.Dec.95
      -257600.     -286400.       -3.3
       6.7243       8.6386       2.3517      -3.1360
      -25.3096     -13.8787      -0.0300           0.
LaCl4-               LaCl4-
LaCl4-               La(1)Cl(4)-(1)
ref:25               1.Dec.95
      -288400.     -331200.       -7.8
      11.5517      20.4270       -2.2839     -3.6234
      -56.5845     -30.4508       1.7506          -1.
LaF+2                LaF+2
LaF+2                La(1)F(1)+(2)
ref:25               1.Dec.95
      -236600.     -243400.      -16.3
       -2.6366     -14.2103      11.3144      -2.1914
       17.9127      -3.1239       1.3029           2.
LaF2+                LaF2+
LaF2+                La(1)F(2)+(1)
ref:25               1.Dec.95
```

```
      -307800.    -325200.      -12.0
      -2.3404    -13.4887     11.0343      -2.2213
      12.8261     -3.0531      0.7287            1.
LaF3,aq             LaF3(aq)
LaF3(aq)            La(1)F(3)
ref:25              1.Dec.95
      -377900.    -410200.      -22.3
      -2.0506    -12.7816     10.7577      -2.2505
     -15.3002    -10.3998     -0.0300            0.
LaF4-               LaF4-
LaF4-               La(1)F(4)-(1)
ref:25              1.Dec.95
      -447500.    -500100.      -50.4
      -0.6263     -9.3060      9.3958      -2.3942
     -35.5432    -25.1639      2.3834           -1.
LaHCO3+2            LaHCO3+2
LaHCO3+2            La(1)H(1)C(1)O(3)+(2)
ref:25              1.Dec.95
      -307000.    -332900.      -13.7
       0.8988     -5.5828      7.9358      -2.5481
      38.0197      3.9723      1.2693            2.
LaCO3+              LaCO3+
LaCO3+              La(1)C(1)O(3)+(1)
ref:25              1.Dec.95
      -299900.    -313100.      -44.2
      -0.8237     -9.7872      9.5838      -2.3743
     -20.0908    -16.0917      1.2275            1.
LaNO3+2             LaNO3+2
LaNO3+2             La(1)N(1)O(3)+(2)
ref:25              1.Dec.95
      -191300.    -226000.      -37.8
       1.6239     -3.8134      7.2430      -2.6213
      32.7363      0.9705      1.6332            2.
LaH2PO4+2           LaH2PO4+2
LaH2PO4+2           La(1)H(2)P(1)O(4)+(2)
ref:25              1.Dec.95
      -437600.    -482800.      -30.2
       1.8993     -3.1434      6.9845      -2.6490
      41.8879      4.5243      1.5168            2.
LaSO4+              LaSO4+
LaSO4+              La(1)S(1)O(4)+(1)
ref:25              1.Dec.95
      -346900.    -382600.      -16.0
       1.6077     -3.8530      7.2584      -2.6197
     -27.1374    -15.0529      0.7895            1.
La(Ae)+2            LaCH3COO+2
La(Ae)+2            La(1)C(2)H(3)O(2)+(2)
ref:33              17 Aug 92
      -255750.    -288710.      -29.600
       3.1548     -0.0804      5.7863      -2.7756
      56.1530      9.5148      1.5067            2.
La(Ae)2+            La(CH3COO)2+
La(Ae)2+            La(1)C(4)H(6)O(4)+(1)
ref:33              17 Aug 92
      -346160.    -407330.      -10.100
       9.7487     16.0216      -0.5464      -3.4412
      99.3969     27.1273       0.7003            1.
La(Ae)3,aq          La(CH3COO)3
La(Ae)3,aq          La(1)C(6)H(9)O(6)
ref:33              10 Sep 92
      -436550.    -527920.       2.800
      17.1523     34.1020      -7.6583      -4.1887
     136.1072     42.2254      -0.0300            0.
La(But)+2           LaCH3(CH2)2CO2+2
La(But)+2           La(1)C(4)H(7)O(2)+(2)
ref:27              26.Aug.93
      -252198.    -300593.      -18.438
       7.1755      9.7404       1.9188      -3.1816
      96.2547     23.9948       1.3375            2.
La(But)2+           La(CH3CH2CH2CO2)2+
La(But)2+           La(1)C(8)H(14)O(4)+(1)
ref:27              26.Aug.93
      -339359.    -430176.      16.373
      18.2361     36.7475      -8.6968      -4.2980
     195.2278     61.7045       0.3041            1.
La(For)+2           LaCHO2+2
La(For)+2           La(1)C(1)H(1)O(2)+(2)
ref:27              26.Aug.93
      -251450.    -274343.      -28.538
       1.1858     -4.8808       7.6567      -2.5771
      25.2949     -1.1466       1.4867            2.
La(For)2+           La(CHO2)2+
La(For)2+           La(1)C(2)H(2)O(4)+(1)
ref:27              26.Aug.93
      -337849.    -378757.      -7.498
       5.5879      5.8627       3.4454      -3.0213
      25.8186      1.6684       0.6644            1.
La(Pent)+2          LaCH3(CH2)3CO2+2
La(Pent)+2          La(1)C(5)H(9)O(2)+(2)
ref:27              1.Sep.93
      -250188.    -307073.      -11.938
       9.3322     15.0037      -0.1439      -3.3992
     132.6336     36.9625       1.2366            2.
La(Pent)2+          La(CH3CH2CH2CH2CO2)2+
La(Pent)2+          La(1)C(10)H(18)O(4)+(1)
ref:27              1.Sep.93
      -335325.    -442418.      31.735
      22.7893     47.8627     -13.0596      -4.7575
     282.1786     92.6705       0.0717            1.
La(Prop)+2          LaCH3CH2CO2+2
La(Prop)+2          La(1)C(3)H(5)O(2)+(2)
ref:27              15.Sep.93
      -254208.    -295142.      -23.738
       5.1026      4.6756       3.9168      -2.9722
      82.2145     18.8530       1.4192            2.
La(Prop)2+          La(CH3CH2CO2)2+
La(Prop)2+          La(1)C(6)H(10)O(4)+(1)
ref:27              15.Sep.93
      -343420.    -419891.       3.847
      13.8589     26.0573      -4.4896      -3.8561
     161.6388     49.4265       0.4925            1.
Li+                 Li(+)
Li+                 Li(1)+(1)
ref:2               2.Jun.87
       -69933.     -66552.       2.700
       -.0237      -.0690      11.5800      -2.7761
      19.2000      -.2400       .4862            1.
LiOH,aq             LiOH
LiOH(aq)            Li(1)O(1)H(1)+(0)
ref:21              12.Sep.97
      -108000.    -121500.       1.900
       2.2749     -2.2242       6.6181      -2.6870
       9.8752     -1.6493       -.0300            0.
LiCl,aq             LiCl(0)
LiCl(aq)            Li(1)Cl(1)+(0)
ref:22              13.Sep.97
       -99250.    -105680.      13.140
       5.5837      5.8554       3.4416      -3.0210
      17.7136      1.1006       -.0380            0.
Li(Ae),aq           LiCH3COO
Li(Ae),aq           Li(1)C(2)H(3)O(2)
ref:33              17 Aug 92
      -158610.    -184240.      19.500
       8.3880     12.6976       0.7639      -3.3038
      56.6767     14.6175      -0.0300            0.
Li(Ae)2-            Li(CH3COO)2-
Li(Ae)2-            Li(1)C(4)H(6)O(4)-(1)
ref:33              10 Sept 92
      -246810.    -304670.      25.500
      16.3412     32.1211      -6.8785      -4.1068
     130.4373     36.1810       1.2422           -1.
Lu+3                Lu(+3)
Lu+3                Lu(1)+(3)
ref:2               13.Jul.87
      -159400.    -167900.      -63.100
      -3.5630    -16.4812      12.2279      -2.0977
       9.5650     -9.7160       2.4554            3.
LuOH+2              LuOH+2
LuOH+2              Lu(1)O(1)H(1)+(2)
ref:25              1.Dec.95
      -205700.    -219000.      -21.3
       2.4374     -1.8325       6.4754      -2.7031
      11.3407     -5.6622       1.3823            2.
LuO+                LuO+
LuO+                Lu(1)O(1)+(1)
ref:25              1.Dec.95
      -195200.    -212400.       -6.6
       2.5066     -1.6582       6.3958      -2.7104
     -19.0294    -13.8917       0.6557            1.
LuO2-               LuO2-
LuO2-               Lu(1)O(2)-(1)
ref:25              1.Dec.95
      -229200.    -242700.       15.8
       4.3695      2.8897       4.6099      -2.8984
     -20.2927    -16.6824       1.3901           -1.
LuHCO3+2            LuHCO3+2
LuHCO3+2            Lu(1)H(1)C(1)O(3)+(2)
ref:25              1.Dec.95
      -302300.    -332400.      -29.5
       0.0033     -7.7669       8.7884      -2.4578
      47.0638      6.3556       1.5067            2.
LuCO3+              LuCO3+
LuCO3+              Lu(1)C(1)O(3)+(1)
ref:25              1.Dec.95
      -296900.    -314100.      -57.7
      -1.1546    -10.5926       9.8949      -2.3410
     -15.3205    -15.0324       1.4146            1.
LuCl+2              LuCl+2
LuCl+2              Lu(1)Cl(1)+(2)
ref:25              1.Dec.95
      -190700.    -204600.      -38.9
      -0.8820     -9.9277       9.6353      -2.3685
      25.5113     -1.5761       1.6444            2.
LuCl2+              LuCl2+
LuCl2+              Lu(1)Cl(2)+(1)
ref:25              1.Dec.95
      -221300.    -244000.      -26.2
       2.1736     -2.4767       6.7285      -2.6765
      22.4451     -0.3982       0.9437            1.
LuCl3,aq            LuCl3(aq)
LuCl3(aq)           Lu(1)Cl(3)
ref:25              1.Dec.95
      -251900.    -286846.      -25.1
       5.5129      5.6785       3.5203      -3.0136
      -2.6969     -6.0192      -0.0300            0.
LuCl4-              LuCl4-
LuCl4-              Lu(1)Cl(4)-(1)
ref:25              1.Dec.95
      -282500.    -333800.      -37.7
      10.3535     17.5009       -1.1323      -3.5024
     -17.8947    -18.4390       2.1990           -1.
LuF+2               LuF+2
LuF+2               Lu(1)F(1)+(2)
ref:25              1.Dec.95
      -233300.    -241900.      -23.6
      -3.5730    -16.4994      12.2192      -2.0968
      25.8414     -0.7406       1.4192            2.
LuF2+               LuF2+
LuF2+               Lu(1)F(2)+(1)
ref:25              1.Dec.95
      -305600.    -324800.      -19.2
      -3.3883    -16.0473      12.0392      -2.1155
      27.2751      1.5969       0.8449            1.
LuF3,aq             LuF3(aq)
LuF3(aq)            Lu(1)F(3)
ref:25              1.Dec.95
```

```
      -376563.    -411300.      -31.8
      -3.2619    -15.7420     11.9264     -2.1281
       7.3122     -2.5402     -0.0300           0.
LuF4-              LuF4-
LuF4-              Lu(1)F(4)-(1)
ref:25             1.Dec.95
      -446900.    -503800.      -66.1
      -1.8892    -12.3870     10.6014     -2.2668
       1.3820    -13.1521      2.6403          -1.
LuH2PO4+2          LuH2PO4+2
LuH2PO4+2          Lu(1)H(1)P(1)O(4)+(2)
ref:25             1.Dec.95
      -432800.    -482400.      -46.3
       1.0060     -5.3207      7.8310     -2.5589
      50.9918      6.9076      1.7607           2.
LuNO3+2            LuNO3+2
LuNO3+2            Lu(1)N(1)O(3)+(2)
ref:25             1.Dec.95
      -186700.    -227300.      -58.7
       0.7523     -5.9353      8.0622     -2.5335
      42.4310      3.3538      1.9413           2.
LuSO4+             LuSO4+
LuSO4+             Lu(1)S(1)O(4)+(1)
ref:25             1.Dec.95
      -342200.    -380630.      -26.6
       1.2811     -4.6503      7.5708     -2.5867
     -16.5465    -13.9936      0.9570           1.
Lu(Ae)+2           LuCH3COO+2
Lu(Ae)+2           Lu(1)C(2)H(3)O(2)+(2)
ref:33             10 Sep 92
      -251290.    -288534.      -45.400
       2.2608     -2.2622      6.6412     -2.6854
      65.2386     11.8981      1.7486           2.
Lu(Ae)2+           Lu(CH3COO)2+
Lu(Ae)2+           Lu(1)C(4)H(6)O(4)+(1)
ref:33             10 Sep 92
      -342150.    -409310.      -31.600
       8.7721     13.6382      0.3879     -3.3427
     115.7906     31.7774      1.0276           1.
Lu(Ae)3,aq         Lu(CH3COO)3
Lu(Ae)3,aq         Lu(1)C(6)H(9)O(6)
ref:33             10 Sep 92
      -432290.    -531620.      -25.300
      15.9409     31.1419      -6.4897     -4.0663
     158.7197     50.0850      -0.0300           0.
Lu+4               Lu(+4)
Lu+4               Lu(1)+(4)
ref:21             10.Dec.97
       27000.       9800.     -108.000
      -4.3487    -18.3921     12.9608     -2.0186
      39.9042     -3.5234      3.8147           4.
Mg+2               Mg(+2)
Mg+2               Mg(1)+(2)
ref:2              1.Jul.87
      -108505.    -111367.      -33.000
       -.8217     -8.5990      8.3900     -2.3900
      20.8000     -5.8920      1.5372           2.
MgOH+              MgOH(+1)
MgOH+              Mg(1)O(1)H(1)+(1)
ref:21             12.Sep.97
      -149255.    -152955.      -19.100
       2.3105     -2.1365      6.5827     -2.6906
      32.0008      3.2394       .8449           1.
MgCl+              MgCl(+)
MgCl+              Mg(1)Cl(1)+(1)
ref:22             12.Sep.97
      -139700.    -150933.      -19.000
       2.2230     -2.3505      6.6669     -2.6818
      28.6016      2.058        .8449           1.
MgF+               MgF(+)
MgF+               Mg(1)F(1)+(1)
ref:22             12.Sep.97

      -177690.    -190950.      -28.070
       -.2975     -8.5049      9.0858     -2.4274
      38.0239      4.9301       .9706           1.
MgHCO3+            MgHCO3(+)
MgHCO3+            Mg(1)H(1)C(1)O(3)+(1)
ref:5              JAN.91
      -250200.    -275750.      -3.000
       2.7171     -1.1469      6.2008     -2.7316
      49.0065      9.9391       .5985           1.
MgCO3,aq           MgCO3(0)
MgCO3(aq)          Mg(1)C(1)O(3)+(0)
ref:22             17.Sep.97
      -238760.    -270570.      -24.000
       -.7355     -9.5745      9.5062     -2.3831
     -10.2416     -8.6159      -.0380           0.
Mg(HSiO3)+         Mg(HSiO3)(+1)
Mg(HSiO3)+         Mg(1)H(1)Si(1)O(3)+(1)
ref:22             15.Sep.97
      -353025.    -385700.      -23.780
        .6289     -6.2428      8.1967     -2.5209
      36.7882      4.6702       .9177           1.
Mg(Ae)+            MgCH3COO+
Mg(Ae)+            Mg(1)C(2)H(3)O(2)+(1)
ref:33             17 Mar 93
      -198520.    -229480.      -13.100
       5.4981      5.6424      3.5341     -3.0122
      64.6297     14.8894      0.7483           1.
Mg(Ae)2,aq         Mg(CH3COO)2
Mg(Ae)2,aq         Mg(1)C(4)H(6)O(4)
ref:33             17 Mar 93
      -287830.    -349260.      -1.200
      12.3982     22.4898      -3.0853     -3.7086
     121.5413     37.1627      -0.0300           0.
Mg(Ala)+           Mg(C3H6NO2)+
Mg(Ala)+           Mg(1)C(3)H(6)N(1)O(2)+(1)
ref:27             14.Aug.93
      -185839.    -231745.       7.968
       8.3169     12.5282      0.8210     -3.2968
      74.3351     19.2750      0.4322           1.
Mg(Ala)2,aq        Mg(C3H6NO2)2
Mg(Ala)2,aq        Mg(1)C(6)H(12)N(2)O(4)
ref:27             14.Aug.93
      -262231.    -352641.      44.042
      18.5836     37.5967      -9.0318     -4.3331
     151.6713     47.6352      -0.0300           0.
Mg(But)+           MgCH3(CH2)2CO2+
Mg(But)+           Mg(1)C(4)H(7)O(2)+(1)
ref:27             26.Aug.93
      -193879.    -240741.      -3.482
       9.5279     15.4831      -0.3354     -3.4190
     104.9814     29.3694       0.6063           1.
Mg(But)2,aq        Mg(CH3CH2CH2CO2)2
Mg(But)2,aq        Mg(1)C(8)H(14)O(4)
ref:27             26.Aug.93
      -278694.    -370578.      22.608
      21.0196     43.5448     -11.3703     -4.5790
     221.0226     71.7399      -0.0300           0.
Mg(For)+           MgCHO2+
Mg(For)+           Mg(1)C(1)H(1)O(2)+(1)
ref:27             26.Aug.93
      -194318.    -215678.     -13.582
       3.5392      0.8593       5.4140     -2.8144
      34.0484      4.2279       0.7584           1.
Mg(For)2,aq        Mg(CHO2)2
Mg(For)2,aq        Mg(1)C(2)H(2)O(4)
ref:27             26.Aug.93
      -279367.    -321177.      -0.709
       8.2496     12.3613       0.8923     -3.2899
      48.2938     11.7038      -0.0300           0.
Mg(Gly)+           Mg(C2H4NO2)+
Mg(Gly)+           Mg(1)C(2)H(4)N(1)O(2)+(1)
ref:27             30.Aug.93

      -188490.    -225174.       6.198
       5.8466      6.4953       3.1944     -3.0474
      48.0086     10.0502       0.4555           1.
Mg(Gly)2,aq        Mg(C2H4NO2)2
Mg(Gly)2,aq        Mg(1)C(4)H(8)N(2)O(4)
ref:27             30.Aug.93
      -267874.    -340003.      39.956
      13.3443     24.8034      -4.0028     -3.8043
      88.2942     25.6069      -0.0300           0.
Mg(Glyc)+          MgCH3OCO2+
Mg(Glyc)+          Mg(1)C(2)H(3)O(3)+(1)
ref:27             30.Aug.93
      -231489.    -266450.      -2.000
       5.3533      5.2917       3.6660     -2.9977
      63.4339     15.0028       0.5831           1.
Mg(Glyc)2,aq       Mg(CH3OCO2)2
Mg(Glyc)2,aq       Mg(1)C(4)H(6)O(6)
ref:27             30.Aug.93
      -353983.    -424040.      18.948
      12.2102     22.0339      -2.9133     -3.6898
     122.3206     37.4335      -0.0300           0.
Mg(Lac)+           MgCH3CH2OCO2+
Mg(Lac)+           Mg(1)C(3)H(5)O(3)+(1)
ref:27             30.Aug.93
      -232904.    -274593.       8.000
       7.5465     10.6466       1.5614     -3.2190
      84.0159     22.6398       0.4322           1.
Mg(Lac)2,aq        Mg(CH3CH2OCO2)2
Mg(Lac)2,aq        Mg(1)C(6)H(10)O(6)
ref:27             30.Aug.93
      -356826.    -440700.      37.734
      16.9548     33.6148      -7.4563     -4.1685
     174.7884     55.6701      -0.0300           0.
Mg(Pent)+          MgCH3(CH2)3CO2+1
Mg(Pent)+          Mg(1)C(5)H(9)O(2)+(1)
ref:27             7.Sep.93
      -191528.    -246880.       3.018
      11.6846     20.7465      -2.3979     -3.6366
     141.3617     42.3371       0.5055           1.
Mg(Pent)2,aq       Mg(CH3CH2CH2CH2CO2)2
Mg(Pent)2,aq       Mg(1)C(10)H(18)O(4)
ref:27             7.Sep.93
      -274046.    -382313.      37.615
      25.6513     54.8536     -15.8129     -5.0465
     310.1143    102.7059      -0.0300           0.
Mg(Prop)+          MgCH3CH2CO2+
Mg(Prop)+          Mg(1)C(3)H(5)O(2)+(1)
ref:27             15.Sep.93
      -196257.    -235660.      -8.782
       7.4530     10.4173       1.6547     -3.2096
      90.8863     24.2277       0.6821           1.
Mg(Prop)2,aq       Mg(CH3CH2CO2)2
Mg(Prop)2,aq       Mg(1)C(6)H(10)O(4)
ref:27             15.Sep.93
      -283437.    -360889.      10.373
      16.5787     32.6970      -7.0965     -4.1306
     185.6977     59.4618      -0.0300           0.
Mn+2               Mn(+2)
Mn+2               Mn(1)+(2)
ref:21             30.Apr.97
       -55100.     -52900.     -16.200
       -.1015     -8.0040       8.8400     -2.4480
      16.6672     -3.8697       1.4006           2.
MnOH+              MnOH(+)
MnOH+              Mn(1)O(1)H(1)+(1)
ref:21             12.Sep.97
       -97300.    -106800.        .300
        .3213     -6.9901       8.4821     -2.4899
      16.2994     -1.2623        .5464           1.
MnO,aq             MnO
MnO(aq)            Mn(1)O(1)+(0)
ref:21             12.Sep.97
```

```
      -81500.     -99100.      -2.500
       -.0376     -7.8656      8.8229     -2.4537
     -1.5528      -5.6215      -.0300           0.
MnO2-2                MnO2(-2)
MnO2-2                Mn(1)O(2)-(2)
ref:21                12.Sep.97
     -102600.    -133300.     -15.200
      1.1489     -4.9713      7.6937     -2.5734
     -4.0375    -17.5991      3.4408          -2.
MnCl+                 MnCl(+)
MnCl+                 Mn(1)Cl(1)+(1)
ref:22                17.Sep.97
      -86290.     -88280.      12.000
      2.8119      -.9126      6.1017     -2.7412
     24.2838      2.0824       .3686           1.
MnF+                  MnF(+)
MnF+                  Mn(1)F(1)+(1)
ref:22                15.Sep.97
     -123641.    -132454.     -13.300
       .3136     -7.0128      8.4994     -2.4890
     30.2840      2.9518       .7483           1.
MnSO4,aq              MnSO4(0)
MnSO4(aq)             Mn(1)S(1)O(4)+(0)
ref:22                17.Sep.97
     -235640.    -266750.      5.000
      2.1354     -2.5645      6.7510     -2.6729
     -6.2564     -7.2308      -.0380          0.
Mn(Ae)+               MnCH3COO+
Mn(Ae)+               Mn(1)C(2)H(3)O(2)+(1)
ref:33                17 Aug 92
     -144430.    -169560.      6.300
      6.0776      7.0570      2.9786     -3.0706
     63.5668     15.4577      0.4555           1.
Mn(Ae)2,aq            Mn(CH3COO)2
Mn(Ae)2,aq            Mn(1)C(4)H(6)O(4)
ref:33                10 Sept 92
     -233850.    -287670.     24.200
     13.1542     24.3405     -3.8236     -3.7851
    124.7315     38.2716     -0.0300           0.
Mn(Ae)3-              Mn(CH3COO)3-
Mn(Ae)3-              Mn(1)C(6)H(9)O(6)-(1)
ref:33                10 Sep 92
     -322580.    -408280.     31.500
     21.6217     45.0124     -11.9409     -4.6397
    211.3036     64.5717       1.1536          -1.
Mn(Ala)+              Mn(C3H6NO2)+
Mn(Ala)+              Mn(1)C(3)H(6)N(1)O(2)+(1)
ref:27                14.Aug.93
     -133580.    -173180.     28.965
      8.8873     13.9167      0.2842     -3.3542
     73.0237     19.8433      0.1124           1.
Mn(Ala)2,aq           Mn(C3H6NO2)2
Mn(Ala)2,aq           Mn(1)C(6)H(12)N(2)O(4)
ref:27                14.Aug.93
     -212074.    -294245.     71.520
     19.3395     39.4414     -9.7539     -4.4094
    154.8617     48.7440     -0.0300           0.
Mn(But)+              MnCH3(CH2)2CO2+
Mn(But)+              Mn(1)C(4)H(7)O(2)+(1)
ref:27                26.Aug.93
     -140788.    -181344.     17.515
     10.0986     16.8770      -0.8847     -3.4766
    103.6776     29.9377       0.2873           1.
Mn(But)2,aq           Mn(CH3CH2CH2CO2)2
Mn(But)2,aq           Mn(1)C(8)H(14)O(4)
ref:27                26.Aug.93
     -226367.    -310012.     50.086
     21.7755     45.3895     -12.0924     -4.6553
    224.2130     72.8487      -0.0300           0.
Mn(For)+              MnCHO2+
Mn(For)+              Mn(1)C(1)H(1)O(2)+(1)
ref:27                26.Aug.93
     -140681.    -155735.      7.415
      4.1094      2.2545      4.8590     -2.8721
     32.7312      4.7962      0.4379           1.
Mn(For)2,aq           Mn(CHO2)2
Mn(For)2,aq           Mn(1)C(2)H(2)O(4)
ref;27                26.Aug.93
     -226030.    -259601.     26.769
      9.0055     14.2060      0.1701     -3.3662
     51.4842     12.8126      -0.0300           0.
Mn(Gly)+              Mn(C2H4NO2)+
Mn(Gly)+              Mn(1)C(2)H(4)N(1)O(2)+(1)
ref:27                27.Aug.93
     -134771.    -165803.     25.000
      6.4299      7.9186      2.6372     -3.1063
     47.0493     10.6185      0.1739           1.
Mn(Gly)2,aq           Mn(C2H4NO2)2
Mn(Gly)2,aq           Mn(1)C(4)H(8)N(2)O(4)
ref:27                27.Aug.93
     -214101.    -278847.     64.561
     14.1002     26.6481      -4.7253     -3.8805
     91.4846     26.7157      -0.0300           0.
Mn(Glyc)+             MnCH3OCO2+
Mn(Glyc)+             Mn(1)C(2)H(3)O(3)+(1)
ref:27                30.Aug.93
     -177828.    -208594.     11.915
      5.9609      6.7761      3.0811     -3.0590
     63.1381     15.5712      0.3735           1.
Mn(Glyc)2,aq          Mn(CH3OCO2)2
Mn(Glyc)2,aq          Mn(1)C(4)H(6)O(6)
ref:27                30.Aug.93
     -300155.    -364736.     37.157
     12.9661     23.8786      -3.6359     -3.7660
    125.5108     38.5424      -0.0300           0.
Mn(Lac)+              MnCH3CH2OCO2+
Mn(Lac)+              Mn(1)C(3)H(5)O(3)+(1)
ref:27                30.Aug.93
     -178981.    -217756.     17.615
      8.1746     12.1772      0.9667     -3.2823
     84.2783     23.2081      0.2832           1.
Mn(Lac)2,aq           Mn(CH3CH2OCO2)2
Mn(Lac)2,aq           Mn(1)C(6)H(10)O(6)
ref:27                30.Aug.93
     -302971.    -383047.     50.317
     17.7108     35.4655      -8.1945     -4.2450
    177.9788     56.7789      -0.0300           0.
Mn(Pent)+             MnCH3(CH2)3CO2+
Mn(Pent)+             Mn(1)C(5)H(9)O(2)+(1)
ref:27                9.Sep.93
     -138601.    -187646.     24.015
     12.2563     22.1440      -2.9511     -3.6943
    140.0855     42.9054       0.1895           1.
Mn(Pent)2,aq          Mn(CH3CH2CH2CH2CO2)2
Mn(Pent)2,aq          Mn(1)C(10)H(18)O(4)
ref:27                9.Sep.93
     -222006.    -322033.     65.092
     26.4073     56.6981     -16.5352     -5.1228
    313.3047    103.8147      -0.0300           0.
Mn(Prop)+             MnCH3CH2CO2+
Mn(Prop)+             Mn(1)C(3)H(5)O(2)+(1)
ref:27                15.Sep.93
     -143016.    -176112.     12.215
      8.0255     11.8128       1.1111     -3.2672
     89.6329     24.7960       0.3686           1.
Mn(Prop)2,aq          Mn(CH3CH2CO2)2
Mn(Prop)2,aq          Mn(1)C(6)H(10)O(4)
ref:27                15.Sep.93
     -230823.    -300037.     37.850
     17.3347     34.5476      -7.8345     -4.2071
    188.8879     60.5707      -0.0300           0.
Mn+3                  Mn(+3)
Mn+3                  Mn(1)+(3)
ref:21                11.Sep.97
      -20300.     -30700.     -74.000
      -2.9320    -14.9340     11.6041     -2.1615
     16.0611      -8.2492      2.7025           3.
MnO4-2                MnO4(-2)
MnO4-2                Mn(1)O(4)-(2)
ref:21                11.Sep.97
     -120400.    -156600.     15.500
      5.6596      6.0368      3.3786     -3.0285
     -5.2910    -16.5602      2.9803          -2.
MnO4-                 MnO4(-)
MnO4-                 Mn(1)O(4)-(1)
ref:21                30.Apr.97
     -107600.    -129900.     46.500
      7.8248     11.3277      1.2912     -3.2472
     13.6317      -3.4012      .9248          -1.
MoO4-2                MoO4(-2)
MoO4-2                Mo(1)O(4)-(2)
ref:21                11.Sep.97
     -200400.    -238300.      9.000
      6.9651      2.7095     18.6617     -2.8909
      6.6829    -12.7102      3.0777          -2.
N2,aq                 N2(0)
N2(aq)                N(2)+(0)
ref:3                 7.Feb.89
        4347.       -2495.     22.900
      6.2046      7.3685      2.8539     -3.0836
     35.7911      8.3726      -.3468           0.
N2H5+                 N2H5(+)
N2H5+                 N(2)H(5)+(1)
ref:21                15.Sep.97
       19700.       -1800.     36.100
      5.5711      5.8193      3.4672     -3.0195
     16.0644       .3876       .0057           1.
N2H6+2                N2H6(+2)
N2H6+2                N(2)H(6)+(2)
ref:21                15.Sep.97
       21100.       -4000.     24.000
      4.4762      3.1468      4.5160     -2.9090
     21.7574       .1635       .6936           2.
NH3,aq                NH3(0)
NH3(aq)               N(1)H(3)+(0)
ref:3                 13.Jul.87
       -6383.      -19440.     25.770
      5.0911      2.7970      8.6248     -2.8946
     20.3000     -1.1700      -.0500           0.
NH4+                  NH4(+)
NH4+                  N(1)H(4)+(1)
ref:2                 1.Jul.87
      -18990.      -31850.     26.570
      3.8763      2.3448      8.5605     -2.8759
     17.4500      -.0210       .1502           1.
NH4(Ae),aq            NH4CH3COO
NH4(Ae),aq            N(1)C(2)H(7)O(2)
ref:33                10 Sep 92
     -107550.    -147230.     50.700
     11.2849     19.7719      -2.0187     -3.5963
     58.7075     15.3233      -0.0300           0.
NH4(Ae)2-             NH4(CH3COO)2-
NH4(Ae)2-             N(1)C(4)H(10)O(4)-(1)
ref:33                10 Sep 92
     -195640.    -265200.     64.700
     19.3685     39.5090      -9.7736     -4.4122
    128.9386     37.5581       0.6495          -1.
N2O2-2                N2O2(-2)
N2O2-2                N(2)O(2)-(2)
ref:21                15.Sep.97
       33200.       -2590.      6.600
      3.3102       .2986      5.6380     -2.7912
       .1067     -15.1139      3.1145          -2.
NO2-                  NO2(-)
NO2-                  N(1)O(2)-(1)
ref:2                 3.Jul.87
```

```
       -7700.      -25000.       29.400
      5.5864      5.8590       3.4472      -3.0212
      3.4260     -7.7808       1.1847           -1.
NO3-                NO3(-)
NO3-                N(1)O(3)-(1)
ref:2               1.Jul.87
      -26507.      -49429.       35.120
      7.3161      6.7824       -4.6838      -3.0594
      7.7000     -6.7250       1.0977           -1.
Na+                 Na(+)
Na+                 Na(1)+(1)
ref:20              12.Sep.97
      -62591.      -57433.       13.960
      1.8390     -2.2850       3.2560       -2.7260
     18.1800     -2.9810        .3306            1.
NaOH,aq             NaOH
NaOH(aq)            Na(1)O(1)H(1)+(0)
ref:20              12.Sep.97
      -99095.     -112927.        6.000
      1.4675     -4.1982       7.4001       -2.6054
     22.0000      3.0000       -.7200            0.
NaCl,aq             NaCl(0)
NaCl(aq)            Na(1)Cl(1)+(0)
ref:20              29.Apr.97
      -92910.      -96160.       28.000
      5.0363      4.7365       3.4154       -2.9748
     10.8000     -1.3000       -.0380            0.
NaF,aq              NaF(0)
NaF(aq)             Na(1)F(1)+(0)
ref:22              13.Sep.97
     -128570.     -135860.       12.000
      2.5336     -1.5922       6.3689       -2.7131
     12.3804      -.7531       -.0380            0.
NaBr,aq             NaBr(0)
NaBr(aq)            Na(1)Br(1)+(0)
ref:22              13.Sep.97
      -85610.      -84830.       34.100
      6.1257      7.1789       2.9214       -3.0757
     10.1926     -1.4111       -.0700            0.
NaI,aq              NaI(0)
NaI(aq)             Na(1)I(1)+(0)
ref:22              13.Sep.97
      -72900.      -69101.       37.700
      7.6488     10.8979       1.4597       -3.2295
     12.1001      -.9690       -.0010            0.
NaAlO2,aq           NaAlO2
NaAlO2(aq)          Na(1)Al(1)O(2)+(0)
ref:20              29.Apr.97
     -260277.     -277259.       11.100
      4.7640       .4850      12.6690       -4.8975
     32.4300      3.8000       -.1000            0.
NaB(OH)4,aq         NaBOH4(0)
NaB(OH)4            Na(1)B(1)O(4)H(4)+(0)
ref:39              20.Jan.98
     -338580.     -378810.       39.200
      6.2600      7.5100       2.8000       -3.0900
     73.5000    -18.9000       0.0000            0.
NaSO4-              NaSO4(-)
NaSO4-              Na(1)S(1)O(4)-(1)
ref:39              20.Jan.98
     -241780.     -275480.       20.440
      4.7500      3.8300       4.2500       -2.7300
     21.0500     -2.0200       1.3100           -1.
NaHSiO3,aq          NaHSiO3(0)
NaHSiO3(aq)         Na(1)H(1)Si(1)O(3)+(0)
ref:22              17.Sep.97
     -307890.     -333894.       10.000
      3.4928       .7500       5.4483       -2.8100
     20.2395      1.9785       -.0380            0.
Na(Ae),aq           NaCH3COO
Na(Ae),aq           Na(1)C(2)H(3)O(2)
ref:33              17 Aug 92
     -150720.     -173540.       34.200
      8.3514     12.6125       0.7884       -3.3003
     49.8989     12.2617      -0.0300            0.
Na(Ae)2-            Na(CH3COO)2-
Na(Ae)2-            Na(1)C(4)H(6)O(4)-(1)
ref:33              10 Sept 92
     -238470.     -292400.       44.000
     16.2062     31.7884       -6.7416       -4.0930
    114.6437     31.5846        0.9633           -1.
Na(But),aq          NaCH3(CH2)2CO2
Na(But),aq          Na(1)C(4)H(7)O(2)
ref:27              26.Aug.93
     -147269.     -185529.       45.433
     12.4293     22.5644       -3.1127       -3.7117
     91.5590     26.7417       -0.0300            0.
Na(But)2-           Na(CH3CH2CH2CO2)2-
Na(But)2-           Na(1)C(8)H(14)O(4)-(1)
ref:27              26.Aug.93
     -231511.     -315475.       69.236
     24.6982     52.5272      -14.9010       -4.9504
    210.5987     66.1618        0.5806           -1.
Na(For),aq          NaCHO2
Na(For),aq          Na(1)C(1)H(1)O(2)
ref:27              16.Aug.93
     -146521.     -159279.       35.333
      6.3891      7.8196        2.6757       -3.1022
     19.2249      1.6002       -0.0300            0.
Na(For)2-           Na(CH02)2-
Na(For)2-           Na(1)C(2)H(2)O(4)-(1)
ref:27              16.Aug.93
     -230001.     -263725.       45.473
     12.0449     21.6308       -2.7566       -3.6731
     41.0498      6.1257        0.9257           -1.
Na(Glyc),aq         Na(CH3OCO2)
Na(Glyc),aq         Na(1)C(2)H(3)O(3)
ref:27              16.Aug.93
     -183829.     -212299.       39.833
      8.2625     12.3962        0.8714       -3.2914
     50.2253     12.3751       -0.0300            0.
Na(Glyc)2-          Na(CH3OCO2)2-
Na(Glyc)2-          Na(1)C(4)H(6)O(6)-(1)
ref:27              16.Aug.93
     -304876.     -369684.       56.615
     15.9533     31.1718       -6.5007       -4.0675
    113.6563     31.8554        0.7716           -1.
Na(Lac),aq          NaCH3CH2OCO2
Na(Lac),aq          Na(1)C(3)H(5)O(3)
ref:27              16.Aug.93
     -185189.     -221669.       45.533
     10.5067     17.8733       -1.2760       -3.5178
     72.1974     20.0121       -0.0300            0.
Na(Lac)2-           Na(CH3CH2OCO2)2-
Na(Lac)2-           Na(1)C(6)H(10)O(6)-(1)
ref:27              16.Aug.93
     -307610.     -388006.       69.462
     20.6323     42.5939      -10.9852       -4.5397
    164.3333     50.0919        0.5771           -1.
Na(Pent),aq         NaCH3(CH2)3CO2
Na(Pent),aq         Na(1)C(5)H(9)O(2)
ref:27              16.Aug.93
     -145259.     -192009.       51.933
     14.6201     27.9193       -5.2291       -3.9331
    128.8681     39.7094       -0.0300            0.
Na(Pent)2-          Na(CH3CH2CH2CH2CO2)2-
Na(Pent)2-          Na(1)C(10)H(18)O(4)-(1)
ref:27              16.Aug.93
     -227477.     -327929.       83.886
     29.2549     63.6519      -19.2699       -5.4103
    297.6442     97.1277        0.3584           -1.
Na(Prop),aq         NaCH3CH2CO2
Na(Prop),aq         Na(1)C(3)H(5)O(2)
ref:27              16.Aug.93
     -149429.     -180229.       40.133
     10.3288     17.4408       -1.1100       -3.4999
     76.7660     21.5999       -0.0300            0.
Na(Prop)2-          Na(CH3CH2CO2)2-
Na(Prop)2-          Na(1)C(6)H(10)O(4)-(1)
ref:27              16.Aug.93
     -235845.     -305289.       57.291
     20.3185     41.8311      -10.6923       -4.5082
    176.9413     53.8837        0.7616           -1.
NbO3-               NbO3(-1)
NbO3-               Nb(1)O(3)-(1)
ref:21              5.Jan.98
     -227100.     -255300.        3.200
      5.0915      4.6485        3.9273       -2.9711
     -3.3376    -11.4066        1.5829           -1.
Nd+2                Nd(+2)
Nd+2                Nd(1)+(2)
ref:21              10.Dec.97
     -100200.     -96100.        -0.500
      0.0860     -7.5654        8.7097       -2.4661
      9.0616     -5.4382        1.0649            2.
Nd+3                Nd(+3)
Nd+3                Nd(1)+(3)
ref:2               13.Jul.87
     -160600.     -166500.       -49.500
     -3.3707    -14.5452        8.3211       -2.1777
      1.6236    -11.8344        2.2550            3.
NdOH+2              NdOH+2
NdOH+2              Nd(1)O(1)H(1)+(2)
ref:25              1.Dec.95
     -206200.     -215500.       -3.3
      2.7413     -1.0874        6.1755       -2.7339
     -3.2077     -9.8381        1.1072            2.
NdO+                NdO+
NdO+                Nd(1)O(1)+(1)
ref:25              1.Dec.95
     -194000.     -207000.       12.7
      2.8304     -0.8716        6.0955       -2.7429
    -34.6589    -18.3731        0.3587            1.
NdO2-               NdO2-
NdO2-               Nd(1)O(2)-(1)
ref:25              1.Dec.95
     -223400.     -231700.       37.8
      5.0229      4.4850        3.9825       -2.9643
    -49.9788    -25.9304        1.0559           -1.
NdCl+2              NdCl+2
NdCl+2              Nd(1)Cl(1)+(2)
ref:25              1.Dec.95
     -192400.     -203000.       -22.7
     -0.6746     -9.4228        9.439        -2.3894
      8.4972     -6.7094        1.4006            2.
NdCl2+              NdCl2+
NdCl2+              Nd(1)Cl(2)+(1)
ref:25              1.Dec.95
     -223400.     -241500.       -5.9
      2.3933     -1.9354        6.5057       -2.6989
     -9.1790    -10.4138        0.6388            1.
NdCl3,aq            NdCl3(aq)
NdCl3(aq)           Nd(1)Cl(3)
ref:25              1.Dec.95
     -254300.     -282700.        1.6
      5.8726      6.5582        3.1706       -3.0500
    -51.4009    -22.9475       -0.0300            0.
NdCl4-              NdCl4-
NdCl4-              Nd(1)Cl(4)-(1)
ref:25              1.Dec.95
     -285100.     -327000.       -1.1
     10.5672     18.0205       -1.3324       -3.5239
    -97.4278    -44.3105        1.6455           -1.
NdF+2               NdF+2
NdF+2               Nd(1)F(1)+(2)
ref:25              1.Dec.95
```

```
      -233900.    -241200.     -14.6
     -3.3312    -15.9098     11.9894    -2.1212
      9.7675     -5.8738      1.2776          2.
NdF2+                NdF2+
NdF2+                Nd(1)F(2)+(1)
ref:25               1.Dec.95
     -305600.    -323500.     -10.4
     -3.1113    -15.3752     11.7849    -2.1433
     -2.7862     -8.4186      0.7096          1.
NdF3,aq              NdF3(aq)
NdF3(aq)             Nd(1)F(3)
ref:25               1.Dec.95
     -376100.    -408900.     -20.1
     -2.9023    -14.8620     11.5767    -2.1645
    -41.3917    -19.4685     -0.0300          0.
NdF4-                NdF4-
NdF4-                Nd(1)F(4)-(1)
ref:25               1.Dec.95
     -446100.    -498700.     -46.8
     -1.5889    -11.6574     10.3228    -2.2970
    -75.7884    -39.0236      2.3433          -1.
NdHCO3+2             NdHCO3+2
NdHCO3+2             Nd(1)H(1)C(1)O(3)+(2)
ref:25               1.Dec.95
     -303400.    -329200.     -10.2
      0.1936     -7.3045      8.6115    -2.4769
     29.5859      1.2224      1.2126          2.
NdCO3+               NdCO3+
NdCO3+               Nd(1)C(1)O(3)+(1)
ref:25               1.Dec.95
     -297300.    -309500.     -41.2
     -1.1199    -10.5088      9.8634    -2.3445
    -24.1105    -17.3139      1.1729          1.
NdH2PO4+2            NdH2PO4+2
NdH2PO4+2            Nd(1)H(2)P(1)O(4)+(2)
ref:25               1.Dec.95
     -433891.    -479076.     -26.57
      1.1931     -4.8625      7.6492    -2.5779
     33.4289      1.7743      1.4574          2.
NdNO3+2              NdNO3+2
NdNO3+2              Nd(1)N(1)O(3)+(2)
ref:25               1.Dec.95
     -188185.    -222586.     -33.09
      0.9124     -5.5498      7.9230    -2.5495
     24.1306     -1.7794      1.5579          2.
NdSO4+               NdSO4+
NdSO4+               Nd(1)S(1)O(4)+(1)
ref:25               1.Dec.95
     -343500.    -379100.     -12.3
      1.3167     -4.5634      7.5367    -2.5903
    -25.1244    -16.2751      0.7484          1.
Nd(Ae)+2             NdCH3COO+2
Nd(Ae)+2             Nd(1)C(2)H(3)O(2)+(2)
ref:33               17 Aug 92
     -252510.    -285470.     -26.100
      2.4521     -1.7961      6.4594    -2.7046
     47.7869      6.7648      1.4574          2.
Nd(Ae)2+             Nd(CH3COO)2+
Nd(Ae)2+             Nd(1)C(4)H(6)O(4)+(1)
ref:33               17 Aug 92
     -343330.    -404110.     -5.300
      8.9606     14.0990      0.2066    -3.3618
     83.3168     21.7619      0.6305          1.
Nd(Ae)3,aq           Nd(CH3COO)3
Nd(Ae)3,aq           Nd(1)C(6)H(9)O(6)
ref:33               10 Sep 92
     -433560.    -524090.      9.100
     16.3006     32.0216     -6.8393    -4.1027
    110.0156     33.1567     -0.0300          0.
Nd+4                 Nd(+4)
Nd+4                 Nd(1)+(4)
ref:21               10.Dec.97

      -47000.    -62900.     -98.700
     -4.2742    -18.2128     12.8958    -2.0260
     40.2772     -2.9327      3.6707          4.
Ne,aq                Ne(0)
Ne(aq)               Ne(1)+(0)
ref:3                13.Jul.87
        4565.       -870.      16.740
      4.4709      3.1352      4.5177    -2.9086
     27.0977      5.0523      -.2535          0.
Ni+2                 Ni(+2)
Ni+2                 Ni(1)+(2)
ref:2                1.Jul.87
      -10900.    -12900.     -30.800
     -1.6942    -11.9181     10.4344    -2.2863
     13.1905     -5.4179      1.5067          2.
NiOH+                NiOH(+)
NiOH+                Ni(1)O(1)H(1)+(1)
ref:21               16.Sep.97
      -52850.    -67650.     -18.000
      -.7075     -9.5051      9.4760    -2.3860
     31.9091      3.2801       .8222          1.
NiO,aq               NiO(0)
NiO(aq)              Ni(1)O(1)+(0)
ref:21               16.Sep.97
      -39340.    -56230.      25.000
     -1.4334    -11.2786     10.1751    -2.3126
     11.7507      -.9975      -.0300          0.
NiO2-2               NiO2(-2)
NiO2-2               Ni(1)O(2)-(2)
ref:21               16.Sep.97
      -64200.    -101800.     -38.900
      -.4814     -8.9493      9.2495    -2.4089
     30.9114     -6.5993      3.7992          -2.
NiCl+                NiCl(+)
NiCl+                Ni(1)Cl(1)+(1)
ref:22               12.Sep.97
      -40920.    -51400.     -17.000
      1.1319     -5.0147      7.7140    -2.5716
     18.3863     -1.3846       .8111          1.
NiF+                 NiF(+)
NiF+                 Ni(1)F(1)+(1)
ref:22               15.Sep.97
      -79768.    -92315.     -26.360
     -1.4455    -11.3080     10.1875    -2.3115
     22.3170      -.4857       .9570          1.
Ni(Ae)+              NiCH3COO+
Ni(Ae)+              Ni(1)C(2)H(3)O(2)
ref:33               17 Aug 92
      -101120.   -131450.     -11.700
      4.3556      2.8512      4.6343    -2.8968
     56.0621     11.9745      0.7287          1.
Ni(Ae)2,aq           Ni(CH3COO)2
Ni(Ae)2,aq           Ni(1)C(4)H(6)O(4)
ref:33               10 Sep 92
      -190610.   -251280.      0.700
     11.1327     19.4031     -1.8801    -3.5810
    105.1782     31.4753     -0.0300          0.
Ni(Ae)3-             Ni(CH3COO)3-
Ni(Ae)3-             Ni(1)C(6)H(9)O(6)-(1)
ref:33               10 Sep 92
      -279690.   -374030.      1.900
     19.5212     39.8827     -9.9226    -4.4277
    182.3942     53.0847      1.6030          -1.
Ni(Ala)+             Ni(C3H6NO2)+
Ni(Ala)+             Ni(1)C(3)H(6)N(1)O(2)+(1)
ref:27               14.Aug.93
      -93527.    -137131.     15.000
      7.1451      9.6640      1.9536    -3.1784
     64.9703     16.3600      0.3260          1.
Ni(Ala)2,aq          Ni(C3H6NO2)2
Ni(Ala)2,aq          Ni(1)C(6)H(12)N(2)O(4)
ref:27               14.Aug.93

      -174545.   -262972.      50.000
     17.3180     34.5040      -7.8105    -4.2053
    135.3083     41.9478      -0.0300          0.
Ni(But)+             NiCH3(CH2)2CO2+
Ni(But)+             Ni(1)C(4)H(7)O(2)+(1)
ref:27               26.Aug.93
      -97925.    -143687.     -0.482
      8.3767     12.6711      0.7713    -3.3027
     96.1758     26.4544      0.5608          1.
Ni(But)2,aq          Ni(CH3CH2CH2CO2)2
Ni(But)2,aq          Ni(1)C(8)H(14)O(4)
ref:27               26.Aug.93
      -184117.   -274625.      26.534
     19.7540     40.4521     -10.1489    -4.4512
    204.6596     66.0525      -0.0300          0.
Ni(For)+             NiCHO2+
Ni(For)+             Ni(1)C(1)H(1)O(2)+(1)
ref:27               26.Aug.93
      -97313.    -117573.     -10.582
      2.3868     -1.9558      6.5236    -2.6980
     25.2125      1.3130      0.7096          1.
Ni(For)2,aq          Ni(CHO2)2
Ni(For)2,aq          Ni(1)C(2)H(2)O(4)
ref:27               26.Aug.93
      -182853.   -223287.      3.217
      6.9840      9.2687      2.1133    -3.1621
     31.9308      6.0164      -0.0300          0.
Ni(Gly)+             Ni(C2H4NO2)+
Ni(Gly)+             Ni(1)C(2)H(4)N(1)O(2)+(1)
ref:27               27.Aug.93
       -94541.    -129289.     12.000
      4.6813      3.6515      4.3097    -2.9299
     38.8214      7.1352      0.3686          1.
Ni(Gly)2,aq          Ni(C2H4NO2)2
Ni(Gly)2,aq          Ni(1)C(4)H(8)N(2)O(4)
ref:27               27.Aug.93
      -176531.   -246055.      48.000
     12.0787     21.7107      -2.7819    -3.6764
     71.9311     19.9195      -0.0300          0.
Ni(Glyc)+            NiCH3OCO2+
Ni(Glyc)+            Ni(1)C(2)H(3)O(3)+(1)
ref:27               30.Aug.93
      -135153.   -171125.      -6.082
      4.2391      2.5699      4.7380    -2.8851
     55.6378     12.0879      0.6472          1.
Ni(Glyc)2,aq         Ni(CH3OCO2)2
Ni(Glyc)2,aq         Ni(1)C(4)H(6)O(6)
ref:27               30.Aug.93
      -258711.   -330154.      13.605
     10.9446     18.9412      -1.6924    -3.5619
    105.9573     31.7462      -0.0300          0.
Ni(Lac)+             NiCH3CH2OCO2+
Ni(Lac)+             Ni(1)C(3)H(5)O(3)+(1)
ref:27               30.Aug.93
      -135599.   -179581.      -0.382
      6.4541      7.9800      2.6079    -3.1088
     76.8142     19.7248      0.5608          1.
Ni(Lac)2,aq          Ni(CH3CH2OCO2)2
Ni(Lac)2,aq          Ni(1)C(6)H(10)O(6)
ref:27               30.Aug.93
      -259957.   -346896.      26.765
     15.6892     30.5284      -6.2512    -4.0409
    158.4254     49.9827      -0.0300          0.
Ni(Pent)+            NiCH3(CH2)3CO2+
Ni(Pent)+            Ni(1)C(5)H(9)O(2)+(1)
ref:27               7.Sep.93
       -95874.    -150126.      6.018
     10.5339     17.9393      -1.3007    -3.5205
    132.5696     39.4221      0.4615          1.
Ni(Pent)2,aq         Ni(CH3CH2CH2CH2CO2)2
Ni(Pent)2,aq         Ni(1)C(10)H(18)O(4)
ref:27               7.Sep.93
```

```
      -180002.     -286892.       41.540
      24.3858      51.7607     -14.5917      -4.9187
      293.7512     97.0185      -0.0300            0.
Ni(Prop)+          NiCH3CH2CO2+
Ni(Prop)+          Ni(1)C(3)H(5)O(2)+(1)
ref:27             15.Sep.93
       -99635.     -137936.       -5.782
       6.3025       7.6097       2.7546      -3.0935
      82.1010      21.3127       0.6388            1.
Ni(Prop)2,aq       Ni(CH3CH2CO2)2
Ni(Prop)2,aq       Ni(1)C(6)H(10)O(4)
ref:27             15.Sep.93
      -187632.     -263708.       14.298
      15.3131      29.6105       -5.8911     -4.0030
     169.3347      53.7744       -0.0300            0.
Np+2               Np(+2)
Np+2               Np(1)+(2)
ref:36             16.Jan.98
       -57700.      -52100.       -0.400
       0.0860       -7.5654       8.7097      -2.4661
       9.0615       -5.4382       1.0649            2.
Np+3               Np(+3)
Np+3               Np(1)+(3)
ref:36             16.Jan.98
      -122500.     -126000.      -46.400
      -2.8540     -14.7452      11.5327      -2.1693
       5.9466     -10.4288       2.2853            3.
Np+4               Np(+4)
Np+4               Np(1)+(4)
ref:36             16.Jan.98
      -117800.     -133000.     -101.400
      -4.2886     -18.2500      12.9154      -2.0244
      40.1636      -3.0956       3.7093            4.
NpO2+              NpO2(+)
NpO2+              Np(1)O(2)+(1)
ref:36             18.Jan.98
      -218700.     -233800.       -5.200
       3.4012       0.5220       5.5478      -2.8005
      -1.9730      -7.8826       0.6305            1.
NpO2+2             NpO2(+2)
NpO2+2             Np(1)O(2)+(2)
ref:36             18.Jan.98
      -190200.     -205700.      -22.100
       3.0837      -0.2498       5.8429      -2.7686
      25.4318      -0.7938       1.3914            2.
O2,aq              O2(0)
O2(aq)             O(2)+(0)
ref:3              26.Jun.87
         3954.       -2900.       26.040
       5.7889       6.3536       3.2528      -3.0417
      35.3530       8.3726       -.3943            0.
OCN-               OCN(-1)
OCN-               O(1)C(1)N(1)-(1)
ref:21             11.Sep.97
       -23280.      -34900.       25.500
       5.7591       6.2815       3.2790      -3.0386
       8.3509      -6.2530       1.2422            -1.
OH-                OH(-)
OH-                O(1)H(1)-(1)
ref:2              29.Apr.97
       -37595.      -54977.       -2.560
       1.2527        .0738       1.8423      -2.7821
       4.1500     -10.3460       1.7246            -1.
PO4-3              PO4(-3)
PO4-3              P(1)O(4)-(3)
ref:21             11.Sep.97
      -243500.     -305300.      -53.000
       -.5258       -9.0576       9.2927      -2.4045
     -15.1599      -28.4155       5.6114            -3.
P2O7-4             P2O7(-4)
P2O7-4             P(2)O(7)-(4)
ref:21             15.Sep.97

      -458700.     -542800.      -28.000
       7.0687       9.4773       2.0273      -3.1707
     -11.7223      -31.3692       6.9069            -4.
Pa+2               Pa(+2)
Pa+2               Pa(1)+(2)
ref:36             16.Jan.98
       -46700.      -40600.       1.600
       0.1292       -7.4602       8.6697      -2.4705
       8.5137       -5.5196       1.0309            2.
Pa+3               Pa(+3)
Pa+3               Pa(1)+(3)
ref:36             16.Jan.98
      -104600.     -107700.      -44.300
      -2.7822     -14.5714      11.4684      -2.1765
       5.4329      -10.5103       2.2550            3.
Pa+4               Pa(+4)
Pa+4               Pa(1)+(4)
ref:36             16.Jan.98
      -144300.     -158800.      -98.800
      -4.2742     -18.2128      12.8958      -2.0260
      40.2772       -2.9327       3.6707            4.
Pb+2               Pb(+2)
Pb+2               Pb(1)+(2)
ref:2              1.Jul.87
         -5710.        220.       4.200
         -.0051       -7.7939       8.8134      -2.4568
       8.6624       -5.6216       1.0788            2.
PbOH+              PbOH(+)
PbOH+              Pb(1)O(1)H(1)+(1)
ref:21             16.Sep.97
       -53950.      -68900.      -10.000
       2.4669       -1.7600       6.4461      -2.7061
         .8970       -7.1085        .7003            1.
PbO,aq             PbO(0)
PbO(aq)            Pb(1)O(1)+(0)
ref:21             16.Sep.97
       -39350.      -44700.       22.000
       2.8906        -.7236       6.0351      -2.7490
     -18.7244      -11.5899        -.0300            0.
PbCl+              PbCl(+)
PbCl+              Pb(1)Cl(1)+(1)
ref:22             17.Sep.97
       -39050.      -38630.       28.000
       2.9756        -.5130       5.9446      -2.7577
      10.2182       -2.0364        .1281            1.
PbCl2,aq           PbCl2(0)
PbCl2(aq)          Pb(1)Cl(2)+(0)
ref:22             17.Sep.97
       -71200.      -77700.       47.000
       6.6429       8.4416       2.4251      -3.1279
       6.9886       -2.6272       -.0380            0.
PbCl3-             PbCl3(-)
PbCl3-             Pb(1)Cl(3)-(1)
ref:22             17.Sep.97
      -102150.     -117700.       59.000
      11.0547      19.2141      -1.8089      -3.5733
       5.9698       -5.4586        .7356            -1.
PbCl4-2            PbCl4(-2)
PbCl4-2            Pb(1)Cl(4)-(2)
ref:22             17.Sep.97
      -133177.     -159209.       66.000
      16.1777      31.7230      -6.7255      -4.0904
       5.9335     -10.2007       2.2126            -2.
PbF+               PbF(+)
PbF+               Pb(1)F(1)+(1)
ref:22             6.Jan.98
       -75860.      -80591.        8.260
       0.4488       -6.6827       8.3696      -2.5027
      15.9794       -0.9898       0.4266            1.
PbF2,aq            PbF2(0)
PbF2(aq)           Pb(1)F(2)+(0)
ref:22             6.Jan.98

      -145056.     -162783.       4.480
       1.0888       -5.1199       7.7554      -2.5673
      16.5543        0.6976      -0.0380            0.
Pb(HS)2,aq         Pb(HS)2(0)
Pb(HS)2(aq)        Pb(1)H(2)S(2)+(0)
ref:22             6.Jan.98
       -20058.      -22851.       52.560
       7.4825      10.4917       1.6193      -3.2127
      28.5025       4.8505      -0.0380            0.
Pb(HS)3-           Pb(HS)3(-)
Pb(HS)3-           Pb(1)H(3)S(3)-(1)
ref:22             6.Jan.98
       -18971.      -28704.       68.080
      12.3397      22.3518       -3.0422     -3.7030
      39.6902       6.7025        0.5980           -1.
Pb(Ae)+            PbCH3COO+
Pb(Ae)+            Pb(1)C(2)H(3)O(2)+(1)
ref:33             16 Feb 91
       -97250.      -115880.       36.000
       6.1543       7.2429       2.9082      -3.0783
      48.0824      11.5161       0.0057            1.
Pb(Ae)2,aq         Pb(CH3COO)2
Pb(Ae)2,aq         Pb(1)C(4)H(6)O(4)
ref:33             16 Feb 91
      -186890.     -229460.       69.800
      13.4090      24.9584       -4.0570     -3.8107
     102.6053      30.5811       -0.0300            0.
Pb(Ae)3-           Pb(CH3COO)3-
Pb(Ae)3-           Pb(1)C(6)H(9)O(6)-(1)
ref:33             08 Apr 93
      -277750.     -348760.       88.600
      21.6128      44.9921      -11.9361     -4.6389
     165.9232      51.5732        0.2871           -1.
Pb(Ala)+           Pb(C3H6NO2)+
Pb(Ala)+           Pb(1)C(3)H(6)O(2)N(1)+(1)
ref:27             14.Aug.93
       -87191.      -120275.       58.688
       8.9640       14.1088        0.1992     -3.3622
      57.5413       15.9017       -0.3372           1.
Pb(Ala)2,aq        Pb(C3H6NO2)2
Pb(Ala)2,aq        Pb(1)C(6)H(12)N(2)O(4)
ref:27             14.Aug.93
      -166271.     -239191.      110.416
      19.5944      40.0653      -10.0034     -4.4352
     132.7356      41.0535       -0.0300           0.
Pb(But)+           PbCH3(CH2)2CO2+
Pb(But)+           Pb(1)C(4)H(7)O(2)+(1)
ref:27             16.Aug.93
       -92817.      -126856.       47.238
      10.1748      17.0643       -0.9612     -3.4843
      88.1802      25.9961       -0.1639           1.
Pb(But)2,aq        Pb(CH3CH2CH2CO2)2
Pb(But)2,aq        Pb(1)C(8)H(14)O(4)
ref:27             16.Aug.93
      -179077.     -253472.       88.982
      22.0303      46.0136      -12.3417     -4.6811
     202.0867      65.1583       -0.0300           0.
Pb(For)+           PbCHO2+
Pb(For)+           Pb(1)C(1)H(1)O(2)+(1)
ref:27             16.Aug.93
       -92150.      -100688.       37.138
       4.1867       2.4389        4.7962     -2.8797
      17.2647       0.8546       -0.0100           1.
Pb(For)2,aq        Pb(CHO2)2
Pb(For)2,aq        Pb(1)C(2)H(2)O(4)
ref:27             16.Aug.93
      -177718.     -202038.       65.665
       9.2604      14.8299       -0.0792     -3.3920
      29.3579       5.1222       -0.0300           0.
Pb(Gly)+           Pb(C2H4NO2)+
Pb(Gly)+           Pb(1)C(2)H(4)O(2)N(1)+(1)
ref:27             16.Aug.93
```

```
      -88450.    -112312.      56.918
      6.4949      8.0790      2.5712     -3.1129
     31.2483      6.6769     -0.3103           1.
Pb(Gly)2,aq       Pb(C2H4NO2)2
Pb(Gly)2,aq       Pb(1)C(4)H(8)N(2)O(4)
ref:27            16.Aug.93
     -168353.    -222992.     106.330
     14.3550     27.2722     -4.9746     -3.9063
     69.3582     19.0253     -0.0300           0.
Pb(Glyc)+         PbCH3OCO2+
Pb(Glyc)+         Pb(1)C(2)H(3)O(3)+(1)
ref:27            16.Aug.93
     -130018.    -154267.      41.638
      8.2809     12.4416      0.8529     -3.2932
     47.6306     11.6296     -0.0788           1.
Pb(Glyc)2,aq      Pb(CH3OCO2)2
Pb(Glyc)2,aq      Pb(1)C(4)H(6)O(6)
ref:27            16.Aug.93
     -253616.    -308946.      76.1054
     17.9656     36.0834     -8.4279     -4.2706
    103.3846     30.8519     -0.0300           0.
Pb(Lac)+          PbCH3CH2OCO2+
Pb(Lac)+          Pb(1)C(3)H(5)O(3)+(1)
ref:27            16.Aug.93
     -131350.    -163610.      47.338
      8.2516     12.3686      0.8843     -3.2902
     68.8031     19.2665     -0.1656           1.
Pb(Lac)2,aq       Pb(CH3CH2OCO2)2
Pb(Lac)2,aq       Pb(1)C(6)H(10)O(6)
ref:27            16.Aug.93
     -256295.    -327120.      89.213
     17.9656     36.0834     -8.4279     -4.2706
    155.8527     49.0884     -0.0300           0.
Pb(Pent)+         PbCH3(CH2)3CO2+
Pb(Pent)+         Pb(1)C(5)H(9)O(2)+(1)
ref:27            7.Sep.93
     -90793.     -133322.      53.738
     12.3324     22.3315     -3.0281     -3.7021
    124.5859     38.9638     -0.2620           1.
Pb(Pent)2,aq      Pb(CH3CH2CH2CH2CO2)2
Pb(Pent)2,aq      Pb(1)C(10)H(18)O(4)
ref:27            7.Sep.93
     -175016.    -265793.     103.988
     26.6621     57.3222    -16.7845     -5.1486
    291.1785     96.1242     -0.0300           0.
Pb(Prop)+         PbCH3CH2CO2+
Pb(Prop)+         Pb(1)C(3)H(5)O(2)+(1)
ref:27            16.Aug.93
      -95672.     -122252.      41.938
      8.1013     12.0011      1.0303     -3.2750
     74.1249     20.8544     -0.0838           1.
Pb(Prop)2,aq      Pb(CH3CH2CO2)2
Pb(Prop)2,aq      Pb(1)C(6)H(10)O(4)
ref:27            16.Aug.93
     -184202.    -244164.      76.746
     17.5895     35.1655     -8.0682     -4.2326
    166.7618     52.8802     -0.0300           0.
Pd+2              Pd(+2)
Pd+2              Pd(1)+(2)
ref:2             1.Jul.87
       42200.      42080.     -22.600
      -.6079     -9.2658      9.3919     -2.3960
     15.3780     -4.3179      1.4006           2.
PdOH+             PdOH(+)
PdOH+             Pd(1)O(1)H(1)+(1)
ref:38            20.Jan.98
      -13000.     -27000.     -13.100
      0.8484     -5.7100      7.9943     -2.5429
     26.0312      1.4735      0.7483           1.
PdO,aq            PdO(0)
PdO(aq)           Pd(1)O(1)+(0)
ref:38            20.Jan.98
      -11500.     -24700.      -9.900
     -0.2867     -8.4815      9.0836     -2.4284
      1.8779     -3.7056     -0.2560           0.
PdCl+             PdCl(+)
PdCl+             Pd(1)Cl(1)+(1)
ref:38            20.Jan.98
        2500.       -5500.      -6.800
      2.1187     -2.6082      6.7752     -2.6712
     28.4586      2.6138      0.6557           1.
PdCl2,aq          PdCl2(0)
PdCl2(aq)         Pd(1)Cl(2)+(0)
ref:38            20.Jan.98
      -35200.     -53600.       0.400
      4.8050      3.9511      4.1971     -2.9423
     39.4445      9.1990     -0.2083           0.
PdCl3-            PdCl3(-)
PdCl3-            Pd(1)Cl(3)-(1)
ref:38            20.Jan.98
      -69800.    -102000.      -3.300
      8.4201     12.7782      0.7276     -3.3073
     67.2220     12.8203      1.6759           -1.
PdCl4-2           PdCl4(-2)
PdCl4-2           Pd(1)Cl(4)-(2)
ref:38            20.Jan.98
     -104000.    -154000.     -21.200
     12.0275     21.5864     -2.7344     -3.6714
     84.6986     12.9349      3.5371           -2.
Pm+2              Pm(+2)
Pm+2              Pm(1)+(2)
ref:21            10.Dec.97
      -92700.     -88400.      -1.900
      0.0520     -7.6511      8.7496     -2.4626
      9.4303     -5.3771      1.0858           2.
Pm+3              Pm(+3)
Pm+3              Pm(1)+(3)
ref:21            10.Dec.97
     -158000.    -164000.     -50.000
     -3.2471    -15.7059     11.9125     -2.1296
      1.5577    -12.1195      2.3369           3.
Pm+4              Pm(+4)
Pm+4              Pm(1)+(4)
ref:21            10.Dec.97
      -34200.     -50400.     -99.700
     -4.2836    -18.2319     12.8955     -2.0252
     40.2193     -2.9938      3.6835           4.
Pr+2              Pr(+2)
Pr+2              Pr(1)+(2)
ref:21            10.Dec.97
      -92700.     -88400.       0.700
      0.1064     -7.5128      8.6835     -2.4683
      8.7551     -5.4789      1.0444           2.
Pr+3              Pr(+3)
Pr+3              Pr(1)+(3)
ref:21            15.Sep.97
     -162600.    -168800.     -50.000
     -3.2061    -14.2894      8.5328     -2.1882
      3.9607    -11.2844      2.3369           3.
PrOH+2            PrOH+2
PrOH+2            Pr(1)O(1)H(1)+(2)
ref:25            1.Dec.95
     -208000.    -217700.      -4.0
      2.7325     -1.1081      6.1822     -2.7331
     -2.6058     -9.6751      1.1216           2.
PrO+              PrO+
PrO+              Pr(1)O(1)+(1)
ref:25            1.Dec.95
     -195700.    -209000.      12.0
      2.8201     -0.8945      6.0986     -2.7419
    -34.0998    -18.2101      0.3685           1.
PrO2-             PrO2-
PrO2-             Pr(1)O(2)-(1)
ref:25            1.Dec.95
     -224700.    -233400.      37.0
      5.0000      4.4265      4.0111     -2.9619
    -48.8607    -25.5841      1.0691           -1.
PrHCO3+2          PrHCO3+2
PrHCO3+2          Pr(1)H(1)C(1)O(3)+(2)
ref:25            1.Dec.95
     -305500.    -336800.     -28.3
      0.4387     -6.7049      8.3735     -2.5017
     35.6716      2.4598      1.4867           2.
PrCO3+            PrCO3+
PrCO3+            Pr(1)C(1)O(3)+(1)
ref:25            1.Dec.95
     -299100.    -311600.     -41.8
     -1.0523    -10.3427      9.7957     -2.3513
    -22.3638    -16.7639      1.1907           1.
PrCl+2            PrCl+2
PrCl+2            Pr(1)Cl(1)+(2)
ref:25            1.Dec.95
     -194400.    -205300.     -23.3
     -0.5190     -9.0442      9.2930     -2.4050
     12.1429     -5.4719      1.4099           2.
PrCl2+            PrCl2+
PrCl2+            Pr(1)Cl(2)+(1)
ref:25            1.Dec.95
     -225400.    -243800.      -6.6
      2.5689     -1.5094      6.3442     -2.7165
     -2.0764     -7.9993      0.6557           1.
PrCl3,aq          PrCl3(aq)
PrCl3(aq)         Pr(1)Cl(3)
ref:25            1.Dec.95
     -256300.    -285200.       0.6
      6.0618      7.0173      2.9974     -3.0690
    -39.6599    -18.8665     -0.0300           0.
PrCl4-            PrCl4-
PrCl4-            Pr(1)Cl(4)-(1)
ref:25            1.Dec.95
     -287100.    -329500.      -2.4
     10.7857     18.5526     -1.5382     -3.5459
    -79.2757    -38.0736      1.6681           -1.
PrF+2             PrF+2
PrF+2             Pr(1)F(1)+(2)
ref:25            1.Dec.95
     -235700.    -243400.     -15.0
     -3.1759    -15.5305     11.8402     -2.1369
     13.4052     -4.6364      1.2860           2.
PrF2+             PrF2+
PrF2+             Pr(1)F(2)+(1)
ref:25            1.Dec.95
     -307300.    -325600.     -10.7
     -2.9414    -14.9592     11.6187     -2.1605
      4.1602     -6.0041      0.7096           1.
PrF3,aq           PrF3(aq)
PrF3(aq)          Pr(1)F(3)
ref:25            1.Dec.95
     -377800.    -410800.     -20.5
     -2.7130    -14.4032     11.4035     -2.1835
    -29.6505    -15.3876     -0.0300           0.
PrF4-             PrF4-
PrF4-             Pr(1)F(4)-(1)
ref:25            1.Dec.95
     -447700.    -500700.     -47.6
     -1.3780    -11.1430     10.1215     -2.3182
    -57.8444    -32.7867      2.3433           -1.
PrH2PO4+2         PrH2PO4+2
PrH2PO4+2         Pr(1)H(2)P(1)O(4)+(2)
ref:25            1.Dec.95
     -436000.    -481500.     -27.3
      1.3489     -4.4844      7.5048     -2.5935
     37.0786      3.0118      1.4671           2.
PrNO3+2           PrNO3+2
PrNO3+2           Pr(1)N(1)O(3)+(2)
ref:25            1.Dec.95
```

```
      -190000.     -224900.      -34.0
       1.0684      -5.1660       7.7658      -2.5653
      27.7877      -0.5419       1.5684           2.
PrSO4+             PrSO4+
PrSO4+             Pr(1)S(1)O(4)+(1)
ref:25             1.Dec.95
      -335500.     -381500.      -13.1
      -1.3885      -4.3882       7.4678      -2.5975
     -23.4508     -15.7251       0.7483           1.
Pr(Ae)+2           PrCH3COO+2
Pr(Ae)+2           Pr(1)C(2)H(3)O(2)+(2)
ref:33             10 Sep 92
      -254570.     -287880.      -26.800
       2.6078      -1.4116       6.2996      -2.7205
      41.9424       4.7024       1.4671           2.
Pr(Ae)2+           Pr(CH3COO)2+
Pr(Ae)2+           Pr(1)C(4)H(6)O(4)+(1)
ref:33             10 Sep 92
      -345500.     -406710.      -6.200
       9.1362      14.5250       0.0441      -3.3794
      71.8931      17.7378       0.6472           1.
Pr(Ae)3,aq         Pr(CH3COO)3
Pr(Ae)3,aq         Pr(1)C(6)H(9)O(6)
ref:33             10 Sep 92
      -435690.     -526750.       7.800
      16.4898      32.4806      -7.0127      -4.1216
      90.4470      26.3552      -0.0300           0.
Pr+4               Pr(+4)
Pr+4               Pr(1)+(4)
ref:21             10.Dec.97
       -72700.      -88700.      -98.500
      -4.2742     -18.2128      12.8958      -2.0260
      40.3357      -2.9123       3.6707           4.
Pu+2               Pu(+2)
Pu+2               Pu(1)+(2)
ref:36             16.Jan.98
       -73500.      -68800.       -2.000
       0.0520      -7.6511       8.7496      -2.4626
       9.4303      -5.3771       1.0858           2.
Pu+3               Pu(+3)
Pu+3               Pu(1)+(3)
ref:36             16.Jan.98
      -137400.     -141500.      -47.100
      -2.8780     -14.8009      11.5494      -2.1670
       6.0992     -10.4084       2.2955           3.
Pu+4               Pu(+4)
Pu+4               Pu(1)+(4)
ref:36             16.Jan.98
      -114200.     -128200.     -100.300
      -4.2792     -18.2247      12.8996      -2.0255
      40.2204      -3.0345       3.6964           4.
PuO2+              PuO2(+)
PuO2+              Pu(1)O(2)+(1)
ref:36             18.Jan.98
      -203100.     -218600.       -5.200
       3.4012       0.5220       5.5478      -2.8005
      -1.9730      -7.8826       0.6305           1.
PuO2+2             PuO2(+2)
PuO2+2             Pu(1)O(2)+(2)
ref:36             18.Jan.98
      -180900.     -196500.      -21.100
       3.1049      -0.1993       5.8259      -2.7707
      24.0918      -1.2012       1.3732           2.
Ra+2               Ra(+2)
Ra+2               Ra(1)+(2)
ref:21             11.Sep.97
      -134200.     -126100.       12.900
        .3740      -6.8598       8.4279      -2.4953
       5.7496      -5.9474        .8644           2.
Ra(Ae)+            RaCH3COO+
Ra(Ae)+            Ra(1)C(2)H(3)O(2)+(1)
ref:33             11 Mar 93
      -223900.     -239380.       48.000
       6.8554       8.9566       2.2315      -3.1492
      44.1726      10.7370      -0.1754           1.
Ra(Ae)2,aq         Ra(CH3COO)2
Ra(Ae)2,aq         Ra(1)C(4)H(6)O(4)
ref:33             11 Mar 93
      -312940.     -353260.       78.800
      14.2584      27.0324      -4.8725      -3.8964
      98.2315      29.0609      -0.0300           0.
Rb+                Rb(+)
Rb+                Rb(1)+(1)
ref:2              29.Jun.87
       -67800.      -60020.       28.800
       4.2913       -.9041       7.4070      -2.7416
       5.7923      -3.6457        .1502           1.
RbOH,aq            RbOH(0)
RbOH(aq)           Rb(1)O(1)H(1)+(0)
ref:21             12.Sep.97
      -105100.     -113000.       32.000
       4.5875       3.4168       4.4132      -2.9202
     -10.2264      -8.6363       -.0300           0.
RbCl,aq            RbCl(0)
RbCl(aq)           Rb(1)Cl(1)+(0)
ref:22             13.Sep.97
       -97870.      -96800.       48.560
       7.4542      10.4227       1.6465      -3.2098
      -5.6468      -7.1086       -.0100           0.
RbF,aq             RbF(0)
RbF(aq)            Rb(1)F(1)+(0)
ref:22             13.Sep.97
      -136450.     -139710.       31.600
       4.3647       2.8788       4.6115      -2.8980
      -3.2196      -6.2938       -.0010           0.
RbBr,aq            RbBr(0)
RbBr(aq)           Rb(1)Br(1)+(0)
ref:22             13.Sep.97
       -91010.      -85730.       54.200
       8.4668      12.8952        .6747      -3.3120
      -5.1720      -6.9436       -.0100           0.
RbI,aq             RbI(0)
RbI(aq)            Rb(1)I(1)+(0)
ref:22             13.Sep.97
       -78900.      -71720.       56.300
      10.5225      17.9145      -1.2982      -3.5195
      -3.8174      -6.5015       -.0010           0.
Rb(Ae),aq          RbCH3COO
Rb(Ae),aq          Rb(1)C(2)H(3)O(2)
ref:33             19 Aug 92
      -156110.     -174950.       53.700
      10.6948      18.3352      -1.4623      -3.5369
      33.9961       6.7343      -0.0300           0.
Rb(Ae)2-           Rb(CH3COO)2-
Rb(Ae)2-           Rb(1)C(4)H(6)O(4)-(1)
ref:33             10 Sep 92
      -244000.     -292490.       68.300
      18.6924      37.8608      -9.1318      -4.3441
      80.2139      20.8000       0.5941           -1.
ReO4-              ReO4(-)
ReO4-              Re(1)O(4)-(1)
ref:21             10.Dec.97
      -166000.     -188200.       48.100
       8.6103      20.0581     -16.7541      -3.6081
      18.9300      -7.0800        .9004           -1.
Rh+3               Rh(+3)
Rh+3               Rh(1)+(3)
ref:21             15.Sep.97
        52450.       42830.      -71.600
      -3.2866     -15.8020      11.9492      -2.1256
      13.0231      -9.1862       2.6654           3.
Rn,aq              Rn(0)
Rn(aq)             Rn(1)+(0)
ref:3              13.Jul.87
        2790.       -5000.       16.000
       9.0862      14.4045        .0884      -3.3745
      52.5774      13.8725       -.2423           0.
RuO4-2             RuO4(-2)
RuO4-2             Ru(1)O(4)-(2)
ref:21             5.Jan.98
       -71600.     -110200.        6.600
       6.9502       9.1887       2.1387      -3.1588
       6.6707     -12.8325       3.1145           -2.
S2-2               S2(-2)
S2-2               S(2)-(2)
ref:2              3.Jul.87
       19000.        7200.        6.800
       5.5797       5.8426       3.4536      -3.0205
      -3.3496     -16.2955       3.1083           -2.
S203-2             S203(-2)
S203-2             S(2)O(3)-(2)
ref:2              3.Jul.87
      -124900.     -155000.       16.000
       6.6685      12.4951      -7.7281      -3.2955
      -0.0577     -14.7066       2.9694           -2.
S204-2             S204(-2)
S204-2             S(2)O(4)-(2)
ref:21             11.Sep.97
      -143500.     -180100.       22.000
       6.6784       8.5280       2.3917      -3.1314
       3.3115     -13.2399       2.8772           -2.
S205-2             S205(-2)
S205-2             S(2)O(5)-(2)
ref:21             11.Sep.97
      -189000.     -232000.       25.000
       7.3618      10.1945       1.7414      -3.2003
       3.9715     -12.8732       2.8343           -2.
S206-2             S206(-2)
S206-2             S(2)O(6)-(2)
ref:21             11.Sep.97
      -231000.     -280400.       30.000
       8.2257      12.3054        .9087      -3.2876
       5.0331     -12.2621       2.7587           -2.
S208-2             S208(-2)
S208-2             S(2)O(8)-(2)
ref:2              3.Jul.87
      -266500.     -321400.       58.400
      13.3622      24.8454      -4.0153      -3.8061
      12.9632      -8.1271       2.3281           -2.
S3-2               S3(-2)
S3-2               S(3)-(2)
ref:2              3.Jul.87
       17600.        6200.       15.800
       6.7661       8.7396       2.3150      -3.1403
       -.3595     -14.8288       2.9749           -2.
S306-2             S306(-2)
S306-2             S(3)O(6)-(2)
ref:21             11.Sep.97
      -229000.     -279000.       33.000
       8.4155      12.7691        .7268      -3.3068
       5.6683     -11.8954       2.7131           -2.
S4-2               S4(-2)
S4-2               S(4)-(2)
ref:2              3.Jul.87
       16500.        5500.       24.700
       7.9381      11.6012       1.1902      -3.2586
       2.6081     -13.3622       2.8390           -2.
S406-2             S406(-2)
S406-2             S(4)O(6)-(2)
ref:21             11.Sep.97
      -248700.     -292600.       61.500
      10.2672      17.2902      -1.0502      -3.4937
      11.7042      -8.4122       2.2805           -2.
S5-2               S5(-2)
S5-2               S(5)-(2)
ref:2              3.Jul.87
```

```
        15700.        5100.       33.600
       9.1107      14.4645       .0649      -3.3770
       5.5361     -11.9159      2.7051           -2.
S5O6-2                 S5O6(-2)
S5O6-2                 S(5)O(6)-(2)
ref:21                 11.Sep.97
      -229000.     -281000.      40.000
       8.8725      13.8806       .2986      -3.3527
       7.1576     -11.0399      2.6076           -2.
SO2,aq                 SO2(0)
SO2(aq)                S(1)O(2)+(0)
ref:3                  13.Jul.87
       -71980.      -77194.      38.700
       6.9502       9.1890       2.1383     -3.1589
      31.2101       6.4578       -.2461           0.
SO3-2                  SO3(-2)
SO3-2                  S(1)O(3)-(2)
ref:21                 11.Sep.97
      -116300.     -151900.      -7.000
       2.4632      -1.7691       6.4494     -2.7058
      -2.7967     -16.7843       3.3210           -2.
SO4-2                  SO4(-2)
SO4-2                  S(1)O(4)-(2)
ref:2                  3.Jun.87
      -177930.     -217400.       4.500
       8.3014      -1.9846      -6.2122     -2.6970
       1.6400     -17.9980       3.1463           -2.
SCN-                   SCN(-1)
SCN-                   S(1)C(1)N(1)-(1)
ref:21                 11.Sep.97
        22160.       18270.      34.500
       7.0244       9.3687       2.0708     -3.1662
      10.7414       -4.9900      1.1073           -1.
SbO2-                  SbO2(-1)
SbO2-                  Sb(1)O(2)-(1)
ref:21                 11.Sep.97
       -82400.     -110000.     -17.100
       -0.5113      -9.0269       9.2893     -2.4057
       -2.2802     -12.0177       1.8885           -1.
Sc+3                   Sc(+3)
Sc+3                   Sc(1)+(3)
ref:21                 5.Jan.98
      -140200.     -146800.     -61.000
       -2.1109     -12.9294      10.8170     -2.2444
       21.1134      -5.8456       2.5003           3.
ScOH+2                 ScOH(+2)
ScOH+2                 Sc(1)O(1)H(1)+(2)
ref:21                 11.Dec.97
       -19100.      -200700.     -15.700
       -0.4111      -8.7778       9.1827     -2.4160
        6.7806      -6.9659       1.2944           2.
ScO+                   ScO(+)
ScO+                   Sc(1)O(1)+(1)
ref:21                 11.Dec.97
      -183600.     -189800.      -3.600
        0.1089      -7.5069       8.6817     -2.4686
      -21.4773     -14.5843       0.6063           1.
ScO2-                  ScO2(-)
ScO2-                  Sc(1)O(2)-(1)
ref:21                 11.Dec.97
      -218100.     -234100.      19.200
        2.9831      -0.4979       5.9465     -2.7583
      -24.9439     -18.1287       1.3369           -1.
Sc(Ae)+2               ScCH3COO+2
Sc(Ae)+2               Sc(1)C(2)H(3)O(2)+(2)
ref:33                 10 Sep 92
      -233010.     -268100.      -42.400
        2.7175      -1.1437       6.1937     -2.7316
       60.3195      10.3398       1.7013           2.
Sc(Ae)2+               Sc(CH3COO)2+
Sc(Ae)2+               Sc(1)C(4)H(6)O(4)+(1)
ref:33                 10 Sep 92
      -324640.     -389320.      -27.500
        9.2794      14.8737       -0.0899    -3.3938
      106.5183      28.7370        0.9706          1.
Sc(Ae)3,aq             Sc(CH3COO)3
Sc(Ae)3,aq             Sc(1)C(6)H(9)O(6)
ref:33                 10 Sep 92
      -415370.     -511840.      -20.000
       16.5277      32.5748       -7.0539    -4.1255
      143.9346      44.9460       -0.0300          0.
SeO3-2                 SeO3(-2)
SeO3-2                 Se(1)O(3)-(2)
ref:21                 11.Sep.97
       -88400.     -121700.       3.100
        3.6149       1.0478       5.3323     -2.8222
        -.6517     -15.5417       3.1658           -2.
SeO4-2                 SeO4(-2)
SeO4-2                 Se(1)O(4)-(2)
ref:21                 11.Sep.97
      -105500.     -143200.      12.900
        5.7548       6.2678       3.2916     -3.0380
        1.3971     -14.3602       3.0192           -2.
SeCN-                  SeCN(-1)
SeCN-                  Se(1)C(1)N(1)-(1)
ref:21                 11.Sep.97
         19500.       18530.      46.600
        8.8752      13.8922        .2829     -3.3532
       13.0877      -3.5845        .9230           -1.
SiF6-2                 SiF6(-2)
SiF6-2                 Si(1)F(6)-(2)
ref:2                  16.Feb.88
      -525700.     -571000.      29.200
        8.5311      13.0492        .6211     -3.3185
        4.0970     -12.6289       2.7716           -2.
SiO2,aq                SiO2(0)
SiO2(aq)               Si(1)O(2)+(0)
ref:3                  13.Jan.89
      -199190.     -209775.      18.000
        1.9000       1.7000      20.0000     -2.7000
       29.1000     -51.2000        .1291           0.
Sm+2                   Sm(+2)
Sm+2                   Sm(1)+(2)
ref:21                 10.Dec.97
      -123000.     -120500.      -6.200
       -0.0353      -7.8592       8.8194     -2.4540
       10.5009      -5.2141       1.1512           2.
Sm+3                   Sm(+3)
Sm+3                   Sm(1)+(3)
ref:2                  13.Jul.87
      -159100.     -165200.      -50.700
       -3.2065     -15.6108      11.8857     -2.1337
        1.9385     -11.8548       2.2955           3.
SmOH+2                 SmOH+2
SmOH+2                 Sm(1)O(1)H(1)+(2)
ref:25                 1.Dec.95
      -204900.     -214600.       -4.9
        2.7076      -1.1676       6.2027     -2.7306
       -1.9523      -9.4714       1.1289           2.
SmO+                   SmO+
SmO+                   Sm(1)O(1)+(1)
ref:25                 1.Dec.95
      -193300.     -206500.        11.0
        2.8115      -0.9157       6.1076     -2.7410
      -33.2571     -17.9657       0.3837           1.
SmO2-                  SmO2-
SmO2-                  Sm(1)O(2)-(1)
ref:25                 1.Dec.95
      -224700.     -233500.       35.9
        4.9642       4.3393       4.0456     -2.9583
      -47.3681     -25.1156       1.0848           -1.
SmCl+2                 SmCl+2
SmCl+2                 Sm(1)Cl(1)+(2)
ref:25                 1.Dec.95
      -190900.     -201700.      -24.1
       -0.5006      -8.9988       9.2743     -2.4069
        8.5369      -6.7552       1.4192           2.
SmCl2+                 SmCl2+
SmCl2+                 Sm(1)Cl(2)+(1)
ref:25                 1.Dec.95
      -221800.     -240300.       -7.7
        2.5888      -1.4617       6.3276     -2.7185
       -9.2005     -10.5032       0.6644           1.
SmCl3,aq               SmCl3(aq)
SmCl3(aq)              Sm(1)Cl(3)
ref:25                 1.Dec.95
      -252700.     -281700.       -0.7
        6.0808       7.0673       2.9692     -3.0711
      -51.8359     -23.0986      -0.0300           0.
SmCl4-                 SmCl4-
SmCl4-                 Sm(1)Cl(4)-(1)
ref:25                 1.Dec.95
      -283500.     -326200.       -4.3
       10.8148      18.6261       -1.5732    -3.5489
      -97.6675     -44.5415        1.6917          -1.
SmF+2                  SmF+2
SmF+2                  Sm(1)F(1)+(2)
ref:25                 1.Dec.95
      -232400.     -239900.      -15.4
       -3.1578     -15.4843       11.8177    -2.1388
        9.7908      -5.9197        1.2944          2.
SmF2+                  SmF2+
SmF2+                  Sm(1)F(2)+(1)
ref:25                 1.Dec.95
      -304200.     -322200.      -11.2
       -2.9212     -14.9061       11.5895    -2.1627
       -2.9564      -8.5080        0.7191          1.
SmF3,aq                SmF3(aq)
SmF3(aq)               Sm(1)F(3)
ref:25                 1.Dec.95
      -374800.     -407700.      -21.2
       -2.6941     -14.3529       11.3752    -2.1856
      -41.8267     -19.6196       -0.0300          0.
SmF4-                  SmF4-
SmF4-                  Sm(1)F(4)-(1)
ref:25                 1.Dec.95
      -444800.     -497700.      -48.5
       -1.3502     -11.0723       10.0878    -2.3212
      -76.2703     -39.2546        2.3632          -1.
SmHCO3+2               SmHCO3+2
SmHCO3+2               Sm(1)H(1)C(1)O(3)+(2)
ref:25                 1.Dec.95
      -301800.     -327900.      -11.9
        0.3694      -6.8727       8.4365     -2.4948
       29.6747       1.1765       1.2366          2.
SmCO3+                 SmCO3+
SmCO3+                 Sm(1)C(1)O(3)+(1)
ref:25                 1.Dec.95
      -296000.     -308800.      -42.6
       -1.0455     -10.3293       9.7980     -2.3519
      -24.0049     -17.3342       1.1907          1.
SmH2PO4+2              SmH2PO4+2
SmH2PO4+2              Sm(1)H(2)P(1)O(4)+(2)
ref:25                 1.Dec.95
      -432300.     -477800.      -28.3
        1.3708      -4.4295       7.4801     -2.5958
       33.5675       1.7285       1.4867          2.
SmNO3+2                SmNO3+2
SmNO3+2                Sm(1)N(1)O(3)+(2)
ref:25                 1.Dec.95
      -186700.     -221600.      -35.4
        1.0908      -5.1124       7.7478     -2.5676
       24.2912      -1.8252       1.5897          2.
SmSO4+                 SmSO4+
SmSO4+                 Sm(1)S(1)O(4)+(1)
ref:25                 1.Dec.95
```

```
      -342000.    -377800.     -13.3
     -1.3885     -4.3882      7.4678     -2.5975
    -25.0918    -16.2954      0.7483           1.
Sm(Ae)+2          SmCH3COO+2
Sm(Ae)+2          Sm(1)C(2)H(3)O(2)+(2)
ref:33            17 Aug 92
      -251240.    -284550.     -27.800
      2.6264     -1.3667      6.2827     -2.7224
     47.8346      6.7190      1.4769           2.
Sm(Ae)2+          Sm(CH3COO)2+
Sm(Ae)2+          Sm(1)C(4)H(6)O(4)+(1)
ref:33            17 Aug 92
      -342190.    -403500.     -7.600
      9.1590     14.5839      0.0138     -3.3818
     83.3717     21.6725      0.6644           1.
Sm(Ae)3,aq        Sm(CH3COO)3
Sm(Ae)3,aq        Sm(1)C(6)H(9)O(6)
ref:33            10 Sep 92
      -432630.    -523910.      6.000
     16.5088     32.5307     -7.0412     -4.1237
    109.5807     33.0056     -0.0300           0.
Sm+4              Sm(+4)
Sm+4              Sm(1)+(4)
ref:21            10.Dec.97
       -39900.     -56400.    -101.100
      -4.2886    -18.2500     12.9154     -2.0244
      40.2222     -3.0752      3.7093           4.
Sn+2              Sn(+2)
Sn+2              Sn(1)+(2)
ref:21            11.Sep.97
        -6570.      -2100.      -4.000
         .0094     -7.7516      8.7810     -2.4584
        7.4160     -6.1919      1.1216           2.
SnO,aq            SnO
SnO(aq)           Sn(1)O(1)+(0)
ref:21            12.Sep.97
       -53600.     -60100.      14.800
      2.7401     -1.0905      6.1776     -2.7338
    -13.0981     -9.6344      -.0300           0.
SnOH+             SnOH(+1)
SnOH+             Sn(1)O(1)H(1)+(1)
ref:21            12.Sep.97
       -58600.     -63800.      19.200
      2.9337      -.6181      5.9928     -2.7533
       .9969     -5.6622       .2595           1.
Sr+2              Sr(+2)
Sr+2              Sr(1)+(2)
ref:2             1.Jul.87
      -134760.    -131670.     -7.530
       .7071    -10.1508      7.0027     -2.3594
     10.7452     -5.0818      1.1363           2.
SrOH+             SrOH(+1)
SrOH+             Sr(1)O(1)H(1)+(1)
ref:21            12.Sep.97
      -173300.    -180000.      14.600
      2.8620      -.7922      6.0586     -2.7462
      4.7576     -4.5826       .3306           1.
SrCl+             SrCl(+)
SrCl+             Sr(1)Cl(1)+(1)
ref:22            17.Sep.97
      -165800.    -169790.      11.000
      2.7719     -1.0104      6.1402     -2.7372
     16.6402      -.6227       .3837           1.
SrF+              SrF(+)
SrF+              Sr(1)F(1)+(1)
ref:22            17.Sep.97
      -202290.    -210670.     -6.200
       .2336     -7.2081      8.5761     -2.4810
     21.5706       .2471       .6472           1.
SrCO3,aq          SrCO3(0)
SrCO3(aq)         Sr(1)C(1)O(3)+(0)
ref:22            17.Sep.97

      -264860.    -288620.      8.500
      -.3332     -8.5922      9.1201     -2.4237
    -12.9961     -9.5733      -.0380           0.
Sr(Ae)+           SrCH3COO+
Sr(Ae)+           Sr(1)C(2)H(3)O(2)+(1)
ref:33            17 Aug 92
      -224510.    -247220.     20.000
      5.9602      6.7718      3.0884     -3.0588
     53.8109     12.7307      0.2482           1.
Sr(Ae)2,aq        Sr(CH3COO)2
Sr(Ae)2,aq        Sr(1)C(4)H(6)O(4)
ref:33            10 Sept 92
      -313610.    -363740.     42.200
     13.1015     24.2102     -3.7685     -3.7797
    109.4234     32.9508     -0.0300           0.
Sr(Ala)+          SrC3H6NO2)+
Sr(Ala)+          Sr(1)C(3)H(6)N(1)O(2)+(1)
ref:27            14.Aug.93
      -210430.    -247624.     42.695
      8.7700     13.6312      0.3947     -3.3424
     63.2691     17.1163     -0.0948           1.
Sr(Ala)2,aq       Sr(C3H6NO2)2
Sr(Ala)2,aq       Sr(1)C(6)H(12)N(2)O(4)
ref:27            14.Aug.93
      -285431.    -363933.     89.487
     19.2869     39.3109     -9.6990     -4.4040
    139.5534     43.4233     -0.0300           0.
Sr(But)+          SrCH3(CH2)2CO2+
Sr(But)+          Sr(1)C(4)H(7)O(2)+(1)
ref:27            26.Aug.93
      -219575.    -257725.     31.245
      9.9807     16.5869     -0.7651     -3.4646
     93.9079     27.2107      0.0785           1.
Sr(But)2,aq       Sr(CH3CH2CH2CO2)2
Sr(But)2,aq       Sr(1)C(8)H(17)O(4)
ref:27            26.Aug.93
      -303925.    -383903.     68.053
     21.7228     45.2592    -12.0373     -4.6499
    208.9047     67.5280     -0.0300           0.
Sr(For)+          SrCHO2+
Sr(For)+          Sr(1)C(1)H(1)O(2)+(1)
ref:27            26.Aug.93
      -220518.    -233167.     21.145
      3.9918      1.9636      4.9821     -2.8601
     22.9691      2.0692      0.2299           1.
Sr(For)2,aq       Sr(CHO2)2
Sr(For)2,aq       Sr(1)C(2)H(2)O(4)
ref:27            26.Aug.93
      -305513.    -335415.     44.736
      8.9529     14.0817      0.2091     -3.3610
     36.1759      7.4919     -0.0300           0.
Sr(Gly)+          Sr(C2H4NO2)+
Sr(Gly)+          Sr(1)C(2)H(4)N(1)O(2)+(1)
ref:27            27.Aug.93
      -211334.    -239307.     40.925
      6.3007      7.6019      2.7652     -3.0932
     36.9719      7.8914     -0.0684           1.
Sr(Gly)2,aq       Sr(C2H4NO2)2
Sr(Gly)2,aq       Sr(1)C(4)H(8)N(2)O(4)
ref:27            27.Aug.93
      -287199.    -347420.     85.401
     14.0476     26.5176     -4.6704     -3.8751
     76.1763     21.3950     -0.0300           0.
Sr(Glyc)+         SrCH3OCO2+
Sr(Glyc)+         Sr(1)C(2)H(3)O(3)+(1)
ref:27            30.Aug.93
      -257717.    -286078.     25.645
      5.8421      6.4821      3.2052     -3.0469
     53.3420     12.8441      0.1618           1.
Sr(Glyc)2,aq      Sr(CH3OCO2)2
Sr(Glyc)2,aq      Sr(1)C(4)H(6)O(6)
ref:27            30.Aug.93

      -380197.    -441109.     55.125
     12.9135     23.7481     -3.5809     -3.7606
    110.2025     33.2217     -0.0300           0.
Sr(Lac)+          SrCH3CH2OCO2+
Sr(Lac)+          Sr(1)C(3)H(5)O(3)+(1)
ref:27            30.Aug.93
      -258627.    -295697.     29.000
      8.0696     11.9219      1.0649     -3.2718
     74.8585     20.4811      0.1124           1.
Sr(Lac)2,aq       Sr(CH3CH2OCO2)2
Sr(Lac)2,aq       Sr(1)C(6)H(10)O(6)
ref:27            30.Aug.93
      -382098.    -459421.     65.215
     17.6581     35.3352     -8.1390     -4.2397
    162.6705     51.4582     -0.0300           0.
Sr(Pent)+         SrCH3(CH2)3CO2+
Sr(Pent)+         Sr(1)C(5)H(9)O(2)+(1)
ref:27            7.Sep.93
      -217114.    -263755.     37.745
     12.1383     21.8541     -2.8337     -3.6823
    130.3108     40.1784     -0.0199           1.
Sr(Pent)2,aq      Sr(CH3CH2CH2CH2CO2)2
Sr(Pent)2,aq      Sr(1)C(10)H(18)O(4)
ref:27            7.Sep.93
      -299073.    -395432.     83.059
     26.3546     56.5678    -16.4801     -5.1174
    297.9963     98.4940     -0.0300           0.
Sr(Prop)+         SrCH3CH2CO2+
Sr(Prop)+         Sr(1)C(3)H(5)O(2)+(1)
ref:27            15.Sep.93
      -221857.    -252548.     25.945
      7.9074     11.5294      1.2116     -3.2555
     79.8554     22.0690      0.1589           1.
Sr(Prop)2,aq      Sr(CH3CH2CO2)2
Sr(Prop)2,aq      Sr(1)C(6)H(10)O(4)
ref:27            15.Sep.93
      -308491.    -374036.     55.817
     17.2820     34.4174     -7.7796     -4.2017
    173.5798     55.2499     -0.0300           0.
Tb+2              Tb(+2)
Tb+2              Tb(1)+(2)
ref:21            10.Dec.97
       -79400.     -76200.      -2.900
       0.0294     -7.7042      8.7663     -2.4604
       9.6780     -5.3363      1.1000           2.
Tb+3              Tb(+3)
Tb+3              Tb(1)+(3)
ref:21            15.Sep.97
      -159500.    -166900.     -54.000
      -2.9245    -14.9162     11.5979     -2.1623
       7.1853    -10.3677      2.4007           3.
TbOH+2            TbOH+2
TbOH+2            Tb(1)O(1)H(1)+(2)
ref:25            1.Dec.95
      -205500.    -216700.      -9.3
      2.6348     -1.3451      6.2720     -2.7233
      1.6043     -8.4529      1.1969           2.
TbO+              TbO+
TbO+              Tb(1)O(1)+(1)
ref:25            1.Dec.95
      -194100.    -209000.       6.3
      2.7263     -1.1230      6.1877     -2.7325
    -29.4895    -16.8861      0.4555           1.
TbO2-             TbO2-
TbO2-             Tb(1)O(2)-(1)
ref:25            1.Dec.95
      -226200.    -236900.      30.5
      4.8006      3.9380      4.2071     -2.9417
    -40.1590    -22.8749      1.1676          -1.
TbCl+2            TbCl+2
TbCl+2            Tb(1)Cl(1)+(2)
ref:25            1.Dec.95
```

```
      -191200.    -203500.     -28.1
      -0.2034     -8.2736     8.9909     -2.4369
      18.7845     -3.4094     1.4867           2.
TbCl2+            TbCl2+
TbCl2+            Tb(1)Cl(2)+(1)
ref:25            1.Dec.95
      -222200.    -242400.     -12.6
       2.9196     -0.6498     5.9993     -2.7520
      10.2630     -3.9752     0.7384           1.
TbCl3,aq          TbCl3(aq)
TbCl3(aq)         Tb(1)Cl(3)
ref:25            1.Dec.95
      -253000.    -284300.      -7.2
       6.4214      7.8972     2.6479     -3.1054
     -20.0913    -12.0650     -0.0300           0.
TbCl4-            TbCl4-
TbCl4-            Tb(1)Cl(4)-(1)
ref:25            1.Dec.95
      -283800.    -329400.     -13.2
      11.2397     19.6657     -1.9861     -3.5919
     -47.9171    -27.6788      1.8257          -1.
TbF+2             TbF+2
TbF+2             Tb(1)F(1)+(2)
ref:25            1.Dec.95
      -233200.    -241600.     -17.6
      -2.8718    -14.7859     11.5438     -2.1677
      19.7334     -2.5739      1.3288           2.
TbF2+             TbF2+
TbF2+             Tb(1)F(2)+(1)
ref:25            1.Dec.95
      -305300.    -324300.     -13.3
      -2.6056    -14.1355     11.2872     -2.1945
      16.0944     -1.9800      0.7483           1.
TbF3,aq           TbF3(aq)
TbF3(aq)          Tb(1)F(3)
ref:25            1.Dec.95
      -376100.    -410200.     -24.0
      -2.3534    -13.5233     11.0536     -2.2198
     -10.0820     -8.5860     -0.0300           0.
TbF4-             TbF4-
TbF4-             Tb(1)F(4)-(1)
ref:25            1.Dec.95
      -446300.    -500900.     -53.2
      -0.9496    -10.0938      9.7025     -2.3616
     -27.1819    -22.3919      2.4254          -1.
TbHCO3+2          TbHCO3+2
TbHCO3+2          Tb(1)H(1)C(1)O(3)+(2)
ref:25            1.Dec.95
      -302100.    -335300.     -34.3
       0.7596     -5.9232      8.0699     -2.5340
      42.4558      4.5223      1.5790           2.
TbCO3+            TbCO3+
TbCO3+            Tb(1)C(1)O(3)+(1)
ref:25            1.Dec.95
      -296500.    -310400.     -46.7
       1.5196     -4.0643      7.3324     -2.6109
     -20.3354    -14.8084      0.8002           1.
TbH2PO4+2         TbH2PO4+2
TbH2PO4+2         Tb(1)H(2)P(1)O(4)+(2)
ref:25            1.Dec.95
      -432600.    -479900.     -33.1
       1.6693     -3.7077      7.2115     -2.6256
      43.8497      5.0743      1.5579           2.
TbNO3+2           TbNO3+2
TbNO3+2           Tb(1)N(1)O(3)+(2)
ref:25            1.Dec.95
      -186700.    -223800.     -41.6
       1.3991     -4.3601      7.4524     -2.5987
      34.8389      1.5205      1.6897           2.
TbSO4+            TbSO4+
TbSO4+            Tb(1)S(1)O(4)+(1)
ref:25            1.Dec.95
      -342400.    -379600.     -17.1
       1.5192     -4.0691      7.3424     -2.6107
     -20.2352    -14.8084      0.8111           1.
Tb(Ae)+2          TbCH3COO+2
Tb(Ae)+2          Tb(1)C(2)H(3)O(2)+(2)
ref:33            10 Sep 92
      -251390.    -286400.     -32.500
       2.9247     -0.6382      5.9963     -2.7525
      52.1779      8.0023      1.5475           2.
Tb(Ae)2+          Tb(CH3COO)2+
Tb(Ae)2+          Tb(1)C(4)H(6)O(4)+(1)
ref:33            10 Sep 92
      -342250.    -405780.     -14.000
       9.4965     15.4094      -0.3132     -3.4159
      91.4417     24.1763       0.7584           1.
Tb(Ae)3,aq        Tb(CH3COO)3
Tb(Ae)3,aq        Tb(1)C(6)H(9)O(6)
ref:33            10 Sep 92
      -432390.    -526470.      -2.300
      16.8495     33.3603      -7.3624     -4.1580
     121.7569     37.2376      -0.0300           0.
Tb+4              Tb(+4)
Tb+4              Tb(1)+(4)
ref:21            10.Dec.97
       -88200.    -105900.    -104.200
      -4.3164    -18.3144     12.9330     -2.0218
      39.9963     -3.2789      3.7484           4.
TcO4-             TcO4(-1)
TcO4-             Tc(1)O(4)-(1)
ref:21            30.Apr.97
      -151100.    -173200.      47.500
       8.6135     18.7256     -13.3543     -3.5530
      18.9500     -5.9500       .9101          -1.
Th+2              Th(+2)
Th+2              Th(1)+(2)
ref:36            16.Jan.98
       -19700.     -13500.       2.500
       0.1521     -7.4017      8.6408     -2.4729
       8.2741     -5.5604      1.0176           2.
Th+3              Th(+3)
Th+3              Th(1)+(3)
ref:36            16.Jan.98
       -82200.     -85100.     -43.700
      -2.7582    -14.5095     11.4370     -2.1791
       5.2821    -10.5307      2.2450           3.
Th+4              Th(+4)
Th+4              Th(1)+(4)
ref:21            11.Sep.97
      -168500.    -183800.    -101.000
      -4.2886    -18.2500     12.9154     -2.0244
      40.2222     -3.0752      3.7093           4.
Tl+               Tl(+)
Tl+               Tl(1)+(1)
ref:21            12.Dec.97
        -7740.      1280.       30.000
       4.2884      2.6903      4.6910     -2.8901
       4.6024     -3.8900      0.0974           1.
TlOH,aq           TlOH
TlOH(aq)          Tl(1)O(1)H(1)+(0)
ref:21            11.Dec.97
       -65550.     -66660.      32.500
       5.1759      4.8579      3.8372     -2.9797
     -10.5781      -8.7585     -0.0300           0.
TlCl,aq           TlCl(0)
TlCl(aq)          Tl(1)Cl(1)+(0)
ref:22            5.Jan.98
       -39815.     -37819.      48.690
       8.1182     12.0440      1.0092     -3.2768
      -6.2744     -7.2370      -0.0380           0.
TlF,aq            TlF(0)
TlF(aq)           Tl(1)F(1)+(0)
ref:22            6.Jan.98
       -75216.     -77118.      33.180
       5.4909      5.6287      3.5307     -3.0116
      -3.7726     -6.3675      -0.0380           0.
Tl(Ae),aq         TlCH3COO
Tl(Ae),aq         Tl(1)C(2)H(3)O(2)
ref:33            17 Aug 92
       -95860.     -113350.     55.200
      11.2955     19.8003      -2.0347     -3.5974
      32.4138      6.1843      -0.0300           0.
Tl(Ae)2-          Tl(CH3COO)2-
Tl(Ae)2-          Tl(1)C(4)H(6)O(4)-(1)
ref:33            20 Sept 92
      -183600.    -230620.      70.300
      19.3516     39.4721      -9.7684     -4.4107
      76.8519     19.7269       0.5643          -1.
Tl+3              Tl(+3)
Tl+3              Tl(1)+(3)
ref:21            12.Dec.97
       51300.      47000.      -46.000
      -1.1607    -10.6078      9.9017     -2.3404
      27.0098     -3.0752      2.2752           3.
TlOH+2            TlOH(+2)
TlOH+2            Tl(1)O(1)H(1)+(2)
ref:21            11.Dec.97
       -4500.     -18800.      -23.700
       2.3952     -1.9341      6.5118     -2.6989
      13.2638     -5.1122      1.4192           2.
TlO+              TlO(+)
TlO+              Tl(1)O(1)+(1)
ref:21            11.Dec.97
       -3200.      -5150.      17.700
       2.9144     -0.6673      6.0161     -2.7513
     -38.6952    -19.5342      0.2832           1.
TlO2-             TlO2(-)
TlO2-             Tl(1)O(2)-(1)
ref:21            11.Dec.97
       -41600.     -52500.      43.500
       5.1854      4.8830      3.8238     -2.9808
     -57.6278    -28.3137      0.9699          -1.
TlCl+2            TlCl(+2)
TlCl+2            Tl(1)Cl(1)+(2)
ref:22            5.Jan.98
        9375.        671.      -18.520
      -0.2904     -8.4877      9.0790     -2.4281
      13.4748     -4.7774      1.3375           2.
Tm+2              Tm(+2)
Tm+2              Tm(1)+(2)
ref:21            10.Jul.97
      -107600.    -105600.      -6.700
      -0.0464     -7.8863      8.8296     -2.4529
      10.6286     -5.1937      1.1587           2.
Tm+3              Tm(+3)
Tm+3              Tm(1)+(3)
ref:2             13.Jul.87
      -159900.    -168500.     -58.100
      -3.2967    -15.8312     11.9724     -2.1245
       8.4826    -10.0215      2.4333           3.
TmOH+2            TmOH+2
TmOH+2            Tm(1)O(1)H(1)+(2)
ref:25            1.Dec.95
      -206100.    -219000.     -14.7
       2.5389     -1.5805      6.3673     -2.7136
       5.9225     -7.2104      1.2776           2.
TmO+              TmO+
TmO+              Tm(1)O(1)+(1)
ref:25            1.Dec.95
      -194900.    -211600.        0.5
       2.6339     -1.3489      6.2767     -2.7231
     -24.7834    -15.5417      0.5464           1.
TmO2-             TmO2-
TmO2-             Tm(1)O(2)-(1)
ref:25            1.Dec.95
```

```
      -228700.    -241400.      23.9
       4.6152      3.4877      4.3792      -2.9231
     -31.2152    -20.0842      1.2669           -1.
TmCl+2              TmCl+2
TmCl+2              Tm(1)Cl(1)+(2)
ref:25              1.Dec.95
      -191600.    -205300.     -33.0
      -0.6062     -9.2588      9.3810      -2.3961
      21.6825     -2.6303      1.5579            2.
TmCl2+              TmCl2+
TmCl2+              Tm(1)Cl(2)+(1)
ref:25              1.Dec.95
      -222600.    -244600.     -18.7
       2.4761     -1.7342      6.4282      -2.7072
      15.5119     -2.4550      0.8334            1.
TmCl3,aq            TmCl3(aq)
TmCl3(aq)           Tm(1)Cl(3)
ref:25              1.Dec.95
      -253400.    -287000.     -15.3
       5.8915      6.6023      3.1580      -3.0518
     -12.6987     -9.4955     -0.0300            0.
TmCl4-              TmCl4-
TmCl4-              Tm(1)Cl(4)-(1)
ref:25              1.Dec.95
      -284200.    -333100.     -24.2
      10.7064     18.3610     -1.4676      -3.5379
     -35.0588    -23.7519      1.9951           -1.
TmF+2               TmF+2
TmF+2               Tm(1)F(1)+(2)
ref:25              1.Dec.95
      -233800.    -243000.     -20.3
      -3.2867    -15.8018     11.9486      -2.1257
      22.3012     -1.7948      1.3642            2.
TmF2+               TmF2+
TmF2+               Tm(1)F(2)+(1)
ref:25              1.Dec.95
      -306000.    -325800.     -16.0
      -3.0673    -15.2659     11.7377      -2.1478
      20.8477     -0.4598      0.7895            1.
TmF3,aq             TmF3(aq)
TmF3(aq)            Tm(1)F(3)
ref:25              1.Dec.95
      -376900.    -412000.     -27.5
      -2.8834    -14.8179     11.5640      -2.1663
      -2.6893     -6.0166     -0.0300            0.
TmF4-               TmF4-
TmF4-               Tm(1)F(4)-(1)
ref:25              1.Dec.95
      -447200.    -503600.     -59.0
      -1.5097    -11.4594     10.2349      -2.3052
     -15.0561    -18.4650      2.5152           -1.
TmHCO3+2            TmHCO3+2
TmHCO3+2            Tm(1)H(1)C(1)O(3)+(2)
ref:25              1.Dec.95
      -302600.    -332200.     -22.4
       0.2724     -7.1116      8.5345      -2.4849
      43.0537      5.3015      1.4006            2.
TmCO3+              TmCO3+
TmCO3+              Tm(1)C(1)O(3)+(1)
ref:25              1.Dec.95
      -297300.    -312700.     -51.6
      -1.0611    -10.3695      9.8181      -2.3502
     -17.4772    -15.5009      1.3268            1.
TmH2PO4+2           TmH2PO4+2
TmH2PO4+2           Tm(1)H(2)P(1)O(4)+(2)
ref:25              1.Dec.95
      -433100.    -482200.     -39.1
       1.2716     -4.6688      7.5680      -2.5859
      46.8875      5.8534      1.6444            2.
TmNO3+2             TmNO3+2
TmNO3+2             Tm(1)N(1)O(3)+(2)
ref:25              1.Dec.95
      -186700.    -226000.     -49.3
       1.0128     -5.3011      7.8182      -2.5598
      38.1891      2.2996      1.8100            2.
TmSO4+              TmSO4+
TmSO4+              Tm(1)S(1)O(4)+(1)
ref:25              1.Dec.95
      -342700.    -381120.     -21.2
      -1.3743     -4.4228      7.4814      -2.5961
     -18.7119    -14.0000      0.8683            1.
Tm(Ae)+2            TmCH3COO+2
Tm(Ae)+2            Tm(1)C(2)H(3)O(2)+(2)
ref:33              11 Sept 92
      -251770.    -288500.     -38.300
       2.5268     -1.6112      6.3814      -2.7123
      61.1431     10.8439      1.6332            2.
Tm(Ae)2+            Tm(CH3COO)2+
Tm(Ae)2+            Tm(1)C(4)H(6)O(4)+(1)
ref:33              11 Sept 92
      -342620.    -408490.     -21.900
       9.0621     14.3448      0.1131      -3.3719
     108.5166     29.7206      0.8803            1.
Tm(Ae)3,aq          Tm(CH3COO)3
Tm(Ae)3,aq          Tm(1)C(6)H(9)O(6)
ref:33              11 Sept 92
      -432750.    -529900.     -12.700
      16.3195     32.0657      -6.8520      -4.1045
     148.7181     46.6086      -0.0300            0.
Tm+4                Tm(+4)
Tm+4                Tm(1)+(4)
ref:21              10.Dec.97
       -30100.     -48300.    -105.600
      -4.3349    -18.3596     12.9511      -2.0199
      40.0047     -3.3604      3.7747            4.
U+2                 U(+2)
U+2                 U(1)+(2)
ref:36              16.Jan.98
       -48800.     -42900.       0.600
       0.1087     -7.5126      8.6950      -2.4683
       8.8177     -5.4789      1.0512            2.
U+3                 U(+3)
U+3                 U(1)+(3)
ref:21              11.Sep.97
      -113550.    -116900.     -46.100
      -2.8438    -14.7220     11.5280      -2.1703
       5.7945    -10.4492      2.2752            3.
UOH+2               UOH(+2)
UOH+2               U(1)O(1)H(1)+(2)
ref:37              20.Jan.98
      -161800.    -167700.       1.200
       2.8136     -0.9087      6.1004      -2.7413
      -6.8963    -10.8973      1.0376            2.
UO+                 UO(+)
UO+                 U(1)O(1)+(1)
ref:37              20.Jan.98
      -152900.    -153900.      17.500
       2.9158     -0.6648      6.0168      -2.7514
     -38.5403    -19.4935      0.2873            1.
UO2-                UO2(-)
UO2-                U(1)O(2)-(1)
ref:37              20.Jan.98
      -183700.    -193600.      43.300
       5.1728      4.8473      3.8491      -2.9793
     -57.3622    -28.2322      0.9733           -1.
U(Ae)+2             UCH3COO+2
U(Ae)+2             U(1)C(2)H(3)O(2)+(2)
ref:33              17 Aug 92
      -205480.    -235460.     -21.300
       4.8662      4.1031      4.1308      -2.9485
     103.6659     26.4274      1.3823            2.
U(Ae)2+             U(CH3COO)2+
U(Ae)2+             U(1)C(4)H(6)O(4)+(1)
ref:33              17 Aug 92
      -296950.    -354230.       1.300
      11.6455     20.6554     -2.3718      -3.6328
     192.7896     60.1258      0.5324            1.
U(Ae)3,aq           U(CH3COO)3
U(Ae)3,aq           U(1)C(6)H(9)O(6)
ref:33              17 Aug 92
      -387360.    -473790.      17.700
      19.3290     39.4128     -9.7374      -4.4082
     296.5739     97.9996     -0.0300            0.
U(But)+2            UCH3(CH2)2CO2+2
U(But)+2            U(1)C(4)H(7)O(2)+(2)
ref:27              14.Aug.93
      -202157.    -247566.     -10.070
       7.1485      9.6738      1.9467      -3.1788
      95.4995     24.1323      1.2126            2.
U(But)2+            U(CH3CH2CH2CO2)2+
U(But)2+            U(1)C(8)H(14)O(4)+(1)
ref:27              14.Aug.93
      -289537.    -376461.      27.782
      18.1945     36.6443     -8.6523      -4.2938
     194.4029     61.9728      0.1308            1.
U(For)+2            UCHO2+2
U(For)+2            U(1)C(1)H(1)O(2)+(2)
ref:27              26.Aug.93
      -201409.    -221316.     -20.170
       1.1596     -4.9432      7.6782      -2.5745
      24.5615     -1.0091      1.3642            2.
U(For)2+            U(CHO2)2+
U(For)2+            U(1)C(2)H(2)O(4)+(1)
ref:27              26.Aug.93
      -288791.    -325806.       3.911
       5.5468      5.7644      3.4796      -3.0172
      25.0070      1.9367      0.4925            1.
U(Pent)+2           UCH3(CH2)3CO2+2
U(Pent)+2           U(1)C(5)H(9)O(2)+(2)
ref:27              31.Aug.93
      -200147.    -254046.      -3.570
       9.3061     14 .9410     -0.1209      -3.3966
     131.9035     37.1000      1.1144            2.
U(Prop)+2           UCH3CH2CO2+2
U(Prop)+2           U(1)C(3)H(5)O(2)+(2)
ref:27              15.Sep.93
      -204317.    -242266.     -15.370
       5.0757      4.6150      3.9293      -2.9697
      81.4601     18.9905      1.2944            2.
U(Prop)2+           U(CH3CH2CO2)2+
U(Prop)2+           U(1)C(6)H(10)O(4)+(1)
ref:27              15.Sep.93
      -293529.    -366108.      15.255
      13.8181     25.9582     -4.4517      -3.8520
     160.8356     49.6947      0.3215            1.
U+4                 U(+4)
U+4                 U(1)+(4)
ref:21              11.Sep.97
      -126650.    -141300.     -99.600
      -4.2836    -18.2319     12.8955      -2.0252
      40.2193     -2.9938      3.6835            4.
UOH+3               UOH(+3)
UOH+3               U(1)O(1)H(3)+(3)
ref:37              18.Jan.98
      -182600.    -198400.     -47.800
       2.1611     -2.5064      6.7390      -2.6753
      37.5484      0.4894      2.3058            3.
UO+2                UO(+2)
UO+2                U(1)O(1)+(2)
ref:37              20.Jan.98
      -180600.    -192100.     -33.400
       2.2403     -2.3083      6.6513      -2.6835
       7.3127     -7.6585      1.5684            2.
UO2,aq              UO2(0)
UO2(aq)             U(1)O(2)+(0)
ref:37              20.Jan.98
```

```
       -233800.     -259700.      -26.000
        2.4664      -1.7587        6.4404      -2.7062
       17.0840       0.8561       -0.0300            0.
UO2+                  UO2(+1)
UO2+                  U(1)O(2)+(1)
ref:21                11.Sep.97
       -229690.     -245000.      -6.000
        3.3767        .4614        5.5725      -2.7980
        -.9002      -7.5363         .6388            1.
UO2OH,aq              UO2OH(0)
UO2OH(aq)             U(1)O(3)H(1)+(0)
ref:37                20.Jan.98
       -261600.     -295900.      -13.900
        3.7390       1.3467        5.2242      -2.8346
       20.4246       2.0172       -0.0300            0.
UO3-                  UO3(-1)
UO3-                  U(1)O(3)-(1)
ref:37                20.Jan.98
       -236600.     -273600.      -19.500
        4.1388       2.3272        4.8294      -2.8751
       27.8024      -1.6697        1.9223           -1.
UO2+2                 UO2(+2)
UO2+2                 U(1)O(2)+(2)
ref:21                11.Sep.97
       -227680.     -243550.      -23.500
        3.0256      -4.1084       15.3326      -2.6091
       21.0700        .4300        1.4099            2.
UO2OH+                UO2OH(+)
UO2OH+                U(1)O(3)H(1)+(1)
ref:37                20.Jan.98
       -277250.     -301500.        4.100
        4.7640       3.8529        4.2318      -2.9382
       13.2240      -2.1586        0.4925            1.
UO3,aq                UO3(0)
UO3(aq)               U(1)O(3)+(0)
ref:37                20.Jan.98
       -270300.     -299600.      -12.900
        3.7801       1.4512        5.1736      -2.8389
        5.4213      -3.1975       -0.0300            0.
UO4-2                 UO4(-2)
UO4-2                 U(1)O(4)-(2)
ref:37                20.Jan.98
       -296000.     -346200.      -27.100
        5.0964       4.6606        3.9223      -2.9716
       13.5130     -12.0788        3.6219           -2.
UO2(Ae)+              UO2CH3COO+
UO2(Ae)+              U(1)C(2)H(3)O(4)+(1)
ref:33                17 Aug 92
       -320100.     -363520.      -1.700
        9.5990      15.6588       -0.4099      -3.4262
       83.5297      22.0118        0.5756            1.
UO2(Ae)2,aq           UO2(CH3COO)2
UO2(Ae)2,aq           U(1)C(4)H(6)O(6)
ref:33                17 Aug 92
       -411840.     -484700.       13.700
       17.0325      33.8044       -7.5309      -4.1764
      161.5228      51.0592       -0.0300            0.
UO2(Ae)3-             UO2(CH3COO)3-
UO2(Ae)3-             U(1)C(6)H(9)O(8)-(1)
ref:33                17 Aug 92
       -502400.     -607960.       18.300
       26.0101      55.7294      -16.1571      -5.0828
      275.3211      86.1855        1.3526           -1.
V+2                   V(+2)
V+2                   V(1)+(2)
ref:21                5.Jan.98
        -52000.      -54000.      -31.000
       -1.6188      -11.7289       10.3473      -2.2940
       13.8458       -5.2548        1.5269            2.
VOH+                  VOH(+)
VOH+                  V(1)O(1)H(1)+(1)
ref:21                11.Dec.97
        -99800.     -114100.      -16.400
       -1.5223      -11.4950       10.2591      -2.3037
       29.7729        2.6079        0.8002            1.
V+3                   V(+3)
V+3                   V(1)+(3)
ref:21                5.Jan.98
        -57900.      -62000.      -55.000
       -1.7304      -11.9981       10.4465      -2.2829
       23.4604       -4.7456        2.4115            3.
VOH+2                 VOH(+2)
VOH+2                 V(1)O(1)H(1)+(2)
ref:21                11.Dec.97
       -111500.     -119400.      -10.600
       -0.1213       -8.0707        8.9058      -2.4453
        2.7011       -8.1474        1.2206            2.
VO+                   VO(+)
VO+                   V(1)O(1)+(1)
ref:21                11.Dec.97
       -106100.     -109400.        4.900
       -3.1084      -15.3641       11.7711      -2.1437
      -28.3270      -16.5602        0.4799            1.
VOOH+                 VOOH(+)
VOOH+                 V(1)O(2)H(1)+(1)
ref:21                11.Dec.97
       -155700.     -177600.      -17.700
       -1.5696      -11.6082       10.2984      -2.2990
       30.8543        2.9134        0.8222            1.
VO+2                  VO(+2)
VO+2                  V(1)O(1)+(2)
ref:21                5.Jan.98
       -106700.     -116300.      -32.000
       -1.2971      -10.9431       10.0377      -2.3265
       38.8261        3.3616        1.5475            2.
VO2+                  VO2(+)
VO2+                  V(1)O(2)+(1)
ref:21                5.Jan.98
       -140300.     -155300.      -10.100
        3.2606        0.1790        5.6817      -2.7863
        4.5892       -5.8252         .7003            1.
VO4-3                 VO4(-3)
VO4-3                 V(1)O(4)-(3)
ref:21                5.Jan.98
       -214900.     -270600.      -35.200
        1.2579       -4.7015        7.5797      -2.5845
       77.6555        4.7060        5.3424           -3.
WO4-2                 WO4(-2)
WO4-2                 W(1)O(4)-(2)
ref:21                15.Sep.97
       -218500.     -236500.        9.700
        7.2074        8.7933        4.4891      -3.1424
        8.3308      -12.0991        3.0657           -2.
Xe,aq                 Xe(0)
Xe(aq)                Xe(1)+(0)
ref:3                 13.Jul.87
          3225.        -4510.       14.620
        7.5196       10.5793        1.5919      -3.2163
       42.1036       10.1652        -.2214            0.
Y+3                   Y(+3)
Y+3                   Y(1)+(3)
ref:21                5.Jan.98
       -163800.     -170900.      -60.000
       -2.0463      -12.7741       10.7611      -2.2508
       21.5366       -5.6622        2.4890            3.
YOH+2                 YOH(+2)
YOH+2                 Y(1)O(1)H(1)+(2)
ref:21                12.Dec.97
       -210000.     -220900.      -17.200
        2.4985       -1.6806        6.4099      -2.7094
        8.0136       -6.6196        1.3201            2.
YO+                   YO(+)
YO+                   Y(1)O(1)+(1)
ref:21                12.Dec.97
       -198100.     -204600.      -2.200
        2.5778       -1.4890        6.3393      -2.7173
      -22.6289      -14.9102        0.5831            1.
YO2-                  YO2(-1)
YO2-                  Y(1)O(2)-(1)
ref:21                12.Dec.97
       -227400.     -243600.       20.800
        4.5219        3.2579        4.4729      -2.9136
      -27.0256      -18.7805        1.3145           -1.
Y(Ae)+2               YCH3COO+2
Y(Ae)+2               Y(1)C(2)H(3)O(2)+(2)
ref:33                10 Sep 92
       -255670.     -291130.      -41.000
        2.8774       -0.7576        6.0516      -2.7476
       59.7114       10.2023        1.6782            2.
Y(Ae)2+               Y(CH3COO)2+
Y(Ae)2+               Y(1)C(4)H(6)O(4)+(1)
ref:33                10 Sep 92
       -346520.     -411420.      -25.600
        9.4572       15.3127       -0.2736      -3.4119
      105.4982       28.4687        0.9437            1.
Y(Ae)3,aq             Y(CH3COO)3
Y(Ae)3,aq             Y(1)C(6)H(9)O(6)
ref:33                10 Sep 92
       -436650.     -533170.      -17.500
       16.7359       33.0838       -7.2550      -4.1466
      142.6300       44.4926       -0.0300            0.
Yb+2                  Yb(+2)
Yb+2                  Yb(1)+(2)
ref:21                10.Dec.97
       -128500.     -126800.      -11.200
       -0.1323       -8.0980        8.9173      -2.4441
       11.7413       -5.0308        1.2285            2.
Yb+3                  Yb(+3)
Yb+3                  Yb(1)+(3)
ref:2                 13.Jul.87
       -153000.     -160300.      -56.900
       -3.4983      -16.3233       12.1658      -2.1042
        7.3533      -10.4493        2.4443            3.
YbOH+2                YbOH+2
YbOH+2                Yb(1)O(1)H(1)+(2)
ref:25                1.Dec.95
       -199300.     -210700.      -13.1
        2.5716       -1.5040        6.3438      -2.7167
        4.6390       -7.5770        1.2528            2.
YbO+                  YbO+
YbO+                  Yb(1)O(1)+(1)
ref:25                1.Dec.95
       -188200.     -203400.        2.2
        2.6656       -1.2698        6.2422      -2.7264
      -26.1516      -15.9287        0.5188            1.
YbO2-                 YbO2-
YbO2-                 Yb(1)O(2)-(1)
ref:25                1.Dec.95
       -221800.     -232900.       25.8
        4.6743        3.6324        4.3212      -2.9291
      -33.8142      -20.8990        1.2392           -1.
YbCl+2                YbCl+2
YbCl+2                Yb(1)Cl(1)+(2)
ref:25                1.Dec.95
       -184600.     -196900.      -31.5
       -0.8419       -9.8331        9.6042      -2.3724
       18.7222       -3.5928        1.5372            2.
YbCl2+                YbCl2+
YbCl2+                Yb(1)Cl(2)+(1)
ref:25                1.Dec.95
       -215400.     -236000.      -16.9
        2.2137       -2.3759        6.6832      -2.6807
        9.9034       -4.3329        0.8111            1.
YbCl3,aq              YbCl3(aq)
YbCl3(aq)             Yb(1)Cl(3)
ref:25                1.Dec.95
```

```
      -246100.    -278100.     -12.9
       5.6076      5.9109      3.4260     -3.0233
     -12.8306    -12.6696     -0.0300          0.
YbCl4-            YbCl4-
YbCl4-            Yb(1)Cl(4)-(1)
ref:25            1.Dec.95
      -276900.    -323800.     -21.0
      10.3734     17.5486     -1.1496     -3.5044
     -49.4701    -28.6028      1.9457         -1.
YbF+2             YbF+2
YbF+2             Yb(1)F(1)+(2)
ref:25            1.Dec.95
      -226900.    -234900.     -19.5
      -3.5184    -16.3679     12.1716     -2.1023
      19.4495     -2.7572      1.3552          2.
YbF2+             YbF2+
YbF2+             Yb(1)F(2)+(1)
ref:25            1.Dec.95
      -299100.    -317700.     -15.2
      -3.3257    -15.8931     11.9766     -2.1219
      15.3476     -2.3377      0.7790          1.
YbF3,aq           YbF3(aq)
YbF3(aq)          Yb(1)F(3)
ref:25            1.Dec.95
      -370100.    -403900.     -26.5
      -3.1673    -15.5093     11.8317     -2.1377
     -11.8214     -9.1906     -0.0300          0.
YbF4-             YbF4-
YbF4-             Yb(1)F(4)-(1)
ref:25            1.Dec.95
      -440400.    -495300.     -57.3
      -1.8339    -12.2511     10.5461     -2.2724
     -29.2268    -23.3159      2.4920         -1.
YbHCO3+2          YbHCO3+2
YbHCO3+2          Yb(1)H(1)C(1)O(3)+(2)
ref:25            1.Dec.95
      -295792.    -323900.     -20.7
       0.0344     -7.6923      8.7622     -2.4609
      40.0319      4.3390      1.3732          2.
YbCO3+            YbCO3+
YbCO3+            Yb(1)C(1)O(3)+(1)
ref:25            1.Dec.95
      -290500.    -305400.     -50.2
      -1.0611    -10.3695      9.8181     -2.3502
     -17.4772    -15.5009      1.3268          1.
YbH2PO4+2         YbH2PO4+2
YbH2PO4+2         Yb(1)H(2)P(1)O(4)+(2)
ref:25            1.Dec.95
      -426300.    -473900.     -37.31
       1.0354     -5.2480      7.8010     -2.5619
      43.9143      4.8910      1.6222          2.
YbNO3+2           YbNO3+2
YbNO3+2           Yb(1)N(1)O(3)+(2)
ref:25            1.Dec.95
      -179800.    -217600.     -47.0
       0.7716     -5.8922      8.0541     -2.5353
      35.0774      1.3371      1.7728          2.
YbSO4+            YbSO4+
YbSO4+            Yb(1)S(1)O(4)+(1)
ref:25            1.Dec.95
      -335800.    -37200.      -20.1
      -1.2745     -4.6665      7.5772     -2.5860
     -20.0516    -14.8899      0.8565          1.
Yb(Ae)+2          YbCH3COO+2
Yb(Ae)+2          Yb(1)C(2)H(3)O(2)+(2)
ref:33            17 Aug 92
      -244760.    -280040.     -36.600
       2.2906     -2.1905      6.6154     -2.6883
      58.1718      9.8814      1.6113          2.
Yb(Ae)2+          Yb(CH3COO)2+
Yb(Ae)2+          Yb(1)C(4)H(6)O(4)+(1)
ref:33            17 Aug 92

      -335520.    -399750.     -19.600
       8.7953     13.6959      0.3628     -3.3451
     102.7868     27.8427      0.8449          1.
Yb(Ae)3,aq        Yb(CH3COO)3
Yb(Ae)3,aq        Yb(1)C(6)H(9)O(6)
ref:33            10 Sep 92
      -425590.    -520890.     -9.700
      16.0356     31.3743     -6.5843     -4.0759
     139.5859     43.4346     -0.0300          0.
Yb(But)+2         YbCH3(CH2)2CO2+2
Yb(But)+2         Yb(1)C(4)H(7)O(2)+(2)
ref:27            26.Aug.93
      -241293.    -291999.     -25.387
       6.3100      7.6274      2.7480     -3.0942
      98.2368     24.3614      1.4382          2.
Yb(But)2+         Yb(CH3CH2CH2CO2)2+
Yb(But)2+         Yb(1)C(8)H(14)O(4)+(1)
ref:27            26.Aug.93
      -328536.    -422417.      6.898
      17.2830     34.4210     -7.7836     -4.2019
     198.6263     62.4199      0.4496          1.
Yb(For)+2         YbCHO2+2
Yb(For)+2         Yb(1)C(1)H(1)O(2)+(2)
ref:27            26.Aug.93
      -240545.    -265749.     -35.487
       0.3247     -6.9803      8.4752     -2.4903
      27.3976     -0.7799      1.6005          2.
Yb(For)2+         Yb(CHO2)2+
Yb(For)2+         Yb(1)C(2)H(2)O(4)+(1)
ref:27            26.Aug.93
      -327027.    -370998.     -16.973
       4.6352      3.5352      4.3629     -2.9250
      29.2285      2.3838      0.8111          1.
Yb(Pent)+2        YbCH3(CH2)3CO2+2
Yb(Pent)+2        Yb(1)C(5)H(9)O(2)+(2)
ref:27            7.Sep.93
      -239283.    -298479.     -18.887
       8.4697     12.9016      0.6745     -3.3123
     134.7001     37.3291      1.3464          2.
Yb(Pent)2+        Yb(CH3CH2CH2CH2CO2)2+
Yb(Pent)2+        Yb(1)C(10)H(18)O(4)+(1)
ref:27            7.Sep.93
      -324503.    -434659.      22.260
      21.8358     45.5373     -12.1516     -4.6614
     285.5660     93.3859      0.2160          1.
Yb(Prop)+2        YbCH3CH2CO2+2
Yb(Prop)+2        Yb(1)C(3)H(5)O(2)+(2)
ref:27            15.Sep.93
      -243276.    -286522.     -30.687
       4.2395      2.5689      4.7426     -2.8851
      84.2616     19.2197      1.5269          2.
Yb(Prop)2+        Yb(CH3CH2CO2)2+
Yb(Prop)2+        Yb(1)C(6)H(10)O(4)+(1)
ref:27            15.Sep.93
      -332543.    -412078.     -5.628
      12.9061     23.7300     -3.5735     -3.7599
     165.0447     50.1419      0.6388          1.
Yb+4              Yb(+4)
Yb+4              Yb(1)+(4)
ref:21            10.Dec.97
         3800.     -13600.     -106.600
      -4.3441    -18.3854     12.9683     -2.0188
      39.9511     -3.4215      3.7880          4.
Zn+2              Zn(+2)
Zn+2              Zn(1)+(2)
ref:21            15.Sep.97
       -35200.     -36660.     -26.200
      -1.0676     -8.9290      6.1282     -2.4098
      18.7400     -5.3700      1.4574          2.
ZnOH+             ZnOH(+1)
ZnOH+             Zn(1)O(1)H(1)+(1)
ref:21            16.Sep.97

       -81190.     -86990.      15.000
       1.1499     -4.9677      7.6896     -2.5735
      15.0306      -.9975       .3260          1.
ZnO,aq            ZnO(0)
ZnO(aq)           Zn(1)O(1)+(0)
ref:21            16.Sep.97
       -67420.     -78290.     -2.000
      -1.2418    -10.8072      9.9819     -2.3321
       .0295     -5.0715      -.0300          0.
ZnO2-2            ZnO2(-2)
ZnO2-2            Zn(1)O(2)-(2)
ref:21            17.Sep.97
       -93290.    -132100.     -40.000
       -.5559     -9.1347      9.3301     -2.4013
      32.5837     -6.0900      3.8216         -2.
ZnCl+             ZnCl(+)
ZnCl+             Zn(1)Cl(1)+(1)
ref:22            17.Sep.97
       -66850.     -66240.      23.000
       1.6583     -3.7293      7.2088     -2.6248
      19.6947      1.0191       .2025          1.
ZnCl2,aq          ZnCl2(0)
ZnCl2(aq)         Zn(1)Cl(2)+(0)
ref:22            17.Sep.97
       -98300.    -109080.      27.030
       5.1486      4.7929      3.8592     -2.9771
      26.1528      4.0338      -.0380          0.
ZnCl3-            ZnCl3(-)
ZnCl3-            Zn(1)Cl(3)-(1)
ref:22            17.Sep.97
      -129310.    -151060.      25.000
       9.5636     15.5732      -.3779     -3.4227
      42.2912      5.5147      1.2513         -1.
ZnCl4-2           ZnCl4(-2)
ZnCl4-2           Zn(1)Cl(4)-(2)
ref:5             JAN.91
      -161890.    -195200.      36.000
      14.6628     28.0213     -5.2636     -3.9374
      56.1061      5.7856      2.6662         -2.
ZnF+              ZnF(+)
ZnF+              Zn(1)F(1)+(1)
ref:22            6.Jan.98
      -104109.    -116131.     -21.810
       -0.7395    -9.5843      9.5101     -2.3827
       28.5991     1.9435      0.8803          1.
Zn(Ae)+           Zn(CH3COOH)(+)
Zn(Ae)+           Zn(1)C(2)H(3)O(2)+(1)
ref:22            17.Sep.97
      -125660.    -155120.      9.400
       4.8484      4.0600      4.1473     -2.9468
      60.4626     14.5244       .4100          1.
Zn(Ae)2,aq        Zn(CH3COOH)2(0)
Zn(Ae)2(aq)       Zn(1)C(4)H(6)O(4)+(0)
ref:22            17.Sep.97
      -216450.    -271500.      22.470
      11.7443     20.8978     -2.4707     -3.6429
     119.1022     36.3407      -.0380          0.
Zn(Ae)3-          Zn(CH3COO)3(-)
Zn(Ae)3-          Zn(1)C(6)H(9)O(6)-(1)
ref:22            17.Sep.97
      -305740.    -394090.      25.000
      20.0332     41.1373     -10.4257     -4.4796
     203.1827     61.4365      1.2513         -1.
Zn(Ala)+          Zn(C3H6NO2)+
Zn(Ala)+          Zn(1)C(3)H(6)N(1)O(2)+(1)
ref:27            14.Aug.93
      -116613.    -161048.      17.000
       7.8514     11.3891      1.2746     -3.2497
      71.8106     18.8350      0.2956          1.
Zn(Ala)2,aq       Zn(C3H6NO3)2
Zn(Ala)2,aq       Zn(1)C(6)H(12)N(2)O(6)
ref:27            14.Aug.93
```

```
      -197112.    -283389.      60.000
      18.1164     36.4558     -8.5823     -4.2860
      149.2015    46.7767     -0.0300           0.
Zn(But)+          ZnCH3(CH2)2CO2+
Zn(But)+          Zn(1)C(4)H(7)O(2)+(1)
ref:27            26.Aug.93
      -121815.    -166539.      5.790
       9.0597     14.3386      0.1167     -3.3717
      102.3810    28.9294      0.4615           1.
Zn(But)2,aq       Zn(CH3CH2CH2CO2)2
Zn(But)2,aq       Zn(1)C(8)H(14)O(4)
ref:27            26.Aug.93
      -207667.    -296560.     34.741
      20.5524     42.4038    -10.9205     -4.5319
      218.5528    70.8814     -0.0300           0.
Zn(For)+          ZnCHO2+
Zn(For)+          Zn(1)C(1)H(1)O(2)+(1)
ref:27            26.Aug.93
      -121477.    -140698.     -4.310
       3.0712     -0.2795      5.8532     -2.7673
      31.4547      3.7879      0.6143           1.
Zn(For)2,aq       Zn(CHO2)2
Zn(For)2,aq       Zn(1)C(2)H(2)O(4)
ref:27            26.Aug.93
      -206908.    -245726.     11.424
       7.7824     11.2204      1.3417     -3.2428
      45.8240     10.8453     -0.0300           0.
Zn(Gly)+          Zn(C2H4NO2)+
Zn(Gly)+          Zn(1)C(2)H(4)N(1)O(2)+(1)
ref:27            27.Aug.93
      -117818.    -151609.     18.000
       5.3677      5.3226      3.6628     -2.9989
      45.1185     9.6102       0.2792           1.
Zn(Gly)2,aq       Zn(C2H4NO2)2
Zn(Gly)2,aq       Zn(1)C(2)H(8)N(2)O(4)
ref:27            27.Aug.93
      -199139.    -267408.     55.000
      12.8771     23.6625     -3.5537     -3.7571
      85.8243     24.7484     -0.0300           0.
Zn(Glyc)+         ZnCH3OCO2+
Zn(Glyc)+         Zn(1)C(2)H(3)O(3)+(1)
ref:27            30.Aug.93
      -159617.    -194550.      0.190
       4.9216      4.2387      4.0776     -2.9541
      61.8303     14.5628      0.5464           1.
Zn(Glyc)2,aq      Zn(CH3OCO2)2
Zn(Glyc)2,aq      Zn(1)C(4)H(6)O(6)
ref:27            30.Aug.93
      -283311.    -353139.     21.813
      11.7430     20.8930     -2.4643     -3.6426
      119.8505    36.5751     -0.0300           0.
Zn(Lac)+          ZnCH3CH2OCO2+
Zn(Lac)+          Zn(1)C(3)H(5)O(3)+(1)
ref:27            30.Aug.93
      -160731.    -200064.     18.000
       7.0755      9.4969      2.0126     -3.1715
      81.3400     22.1998      0.2792           1.
Zn(Lac)2,aq       Zn(CH3CH2OCO2)2
Zn(Lac)2,aq       Zn(1)C(6)H(10)O(6)
ref:27            30.Aug.93
      -285376.    -364728.     55.000
      16.4877     32.4799     -7.0229     -4.1216
      172.3186    54.8116     -0.0300           0.
Zn(Pent)+         ZnCH3(CH2)3CO2+
Zn(Pent)+         Zn(1)C(5)H(9)O(2)+(1)
ref:27            7.Sep.93
      -119683.    -172896.     12.290
      11.2174     19.6055     -1.9494     -3.5894
      138.7888    41.8971      0.3636           1.
Zn(Pent)2,aq      Zn(CH3CH2CH2CH2CO2)2
Zn(Pent)2,aq      Zn(1)C(10)H(18)O(4)
ref:27            7.Sep.93
      -203415.    -308690.     49.747
      25.1842     53.7125     -15.3636     -4.9994
      307.6444    101.8474     -0.0300           0.
Zn(Prop)+         ZnCH3CH2CO2+
Zn(Prop)+         Zn(1)C(3)H(5)O(2)+(1)
ref:27            15.Sep.93
      -123675.    -160939.      0.490
       6.9879      9.2834      2.0962     -3.1627
      88.3708     23.7877      0.5464           1.
Zn(Prop)2,aq      Zn(CH3CH2CO2)2
Zn(Prop)2,aq      Zn(1)C(6)H(10)O(4)
ref:27            15.Sep.93
      -211455.    -285915.     22.506
      16.1116     31.5558     -6.6473     -4.0834
      183.2279    58.6033     -0.0300           0.
Zr+4              Zr(+4)
Zr+4              Zr(1)+(4)
ref:21            11.Sep.97
      -133270.    -150330.    -110.300
      -4.3670    -18.4377     12.9811     -2.0167
      39.7423     -3.6660      3.8417           4.
ZrOH+3            ZrOH(+3)
ZrOH+3            Zr(1)O(1)H(1)+(3)
ref:21            1.May.97
      -190400.    -212500.     -71.600
        .9279     -5.5093      7.9015     -2.5511
      56.7436      6.0097      2.6654           3.
ZrO+2             ZrO(+2)
ZrO+2             Zr(1)O(1)+(2)
ref:21            1.May.97
      -187600.    -204300.     -53.400
       1.9014     -3.1364      6.9769     -2.6492
      23.3712     -3.0141      1.8611           2.
ZrO2,aq           ZrO2
ZrO2(aq)          Zr(1)O(2)+(0)
ref:21            1.May.97
      -233400.    -263800.     -43.700
       1.8643     -3.2264      7.0119     -2.6455
      38.4166      8.2708      -.0300           0.

 143  minerals that do not undergo phase transition (nmin1)
  33  minerals that undergo one phase transition    (nmin2)
  17  minerals that undergo two phase transitions   (nmin3)
   2  minerals that undergo three phase transitions (nmin4)
  16  gases                                         (ngas)
1147  aqueous species                               (naqs)
    ----  ----------------------------
    1358  total

     258  comment lines preceed top of min1 block
```

Appendix B: Listing of the PHREEQE.JNC Database

(see Tables 5.3.1_1 - 5.3.1_3 for formatting and unit conventions)

```
ELEMENTS
Ca          4   40.078          Ca+2
Mg          5   24.305          Mg+2
Na          6   22.9898         Na+
K           7   39.0983         K+
Fe          8   55.847          Fe+2
Mn          9   54.9380         Mn+2
Al         10   26.9815         Al+3
Ba         11   137.327         Ba+2
Sr         12   87.62           Sr+2
Si         13   60.0843         SiO2
Cl         14   35.4527         Cl-
C          15   44.0098         CO2
S          16   96.064          SO4-2
N          17   62.0049         NO3-
B          18   10.811          B
P          19   94.9714         PO4-3
F          20   18.9984         F-
Li         21    6.941          Li+
Br         22   79.904          Br-
I          23   126.9045        I-
Bi         25   208.9804        Bi+3
Cs         27   132.9054        Cs+
Ni         29   58.6934         Ni+2
Pb         32   207.2           Pb+2
Sb         35   153.756         SbO2-
Se         37   142.96          SeO4-2
Sn         39   118.710         Sn+2
Th         41   232.0381        Th+4
U          42   238.0289        U+4
Zr         43   91.224          Zr+4

SPECIES
  1
H+          101 1.0       0.0       9.0       9.0                 -1.0
 0.0       0.0
  1 1.0
  2
E-          100 -1.0      0.0       0.0                           0.0
 0.0       0.0
  2 1.0
  3
H2O         100 0.0       0.0       0.0                           0.0
 0.0       0.0
  3 1.0
  4
Ca+2        101 2.0       0.0       6.0       5.0       0.165     0.0
 0.0       0.0
  4 1.0
  5
Mg+2        101 2.0       0.0       8.0       5.5       0.20      0.0
0.0       0.0
  5 1.0
  6
Na+         101 1.0       0.0       4.0       4.0       0.075     0.0
0.0       0.0
  6 1.0
  7
K+          101 1.0       0.0       3.0       3.5       0.015     0.0
0.0       0.0
  7 1.0
  8
Fe+2        100 2.0       2.0       6.0                           0.0
0.0       0.0
  8 1.0
  9
Mn+2        100 2.0       2.0       6.0                           0.0
 0.0       0.0
  9 1.0
 10
Al+3        100 3.0       0.0       9.0                           0.0
 0.0       0.0
 10 1.0
 11
Ba+2        100 2.0       0.0       5.0                           0.0
 0.0       0.0
 11 1.0
 12
Sr+2        101 2.0       0.0       5.0       5.26      0.121     0.0
 0.0       0.0
 12 1.0
 13
H4SiO4      100 0.0       0.0       0.0                           0.0
 0.0       0.0
 13 1.0
 14
Cl-         101 -1.0      0.0       3.0       3.5       0.015     0.0
 0.0       0.0
 14 1.0
 15
CO3-2       101 -2.0      4.0       4.5       5.4       0.0       2.0
 0.0       0.0
 15 1.0
 16
SO4-2       101 -2.0      6.0       4.0       5.0       -0.04     0.0
 0.0       0.0
 16 1.0
 17
NO3-        100 -1.0      5.0       3.0                           0.0
 0.0       0.0
 17 1.0
 18
H3BO3       100 0.0       0.0       0.0                           0.0
0.0       0.0
 18 1.0
 19
PO4-3       100 -3.0      0.0       4.0                           2.0
 0.0       0.0
 19 1.0
 20
F-          100 -1.0      0.0       3.5                           0.0
 0.0       0.0
 20 1.0
 21
Li+         100 1.0       0.0       6.0                           0.0
0.0       0.0
 21 1.0
 22
Br-         100 -1.0      0.0       3.0                           0.0
0.0       0.0
 22 1.0
 23
I-          100 -1.0      -1.0      3.0                           0.0
0.0       0.0
```

```
 23 1.0
 25
Bi+3          100 3.0        0.0        0.0                              0.0
0.0         0.0
 25 1.0
 27
Cs+           100 1.0        0.0        2.5                              0.0
0.0         0.0
 27 1.0
 29
Ni+2          100 2.0        0.0        6.0                              0.0
0.0         0.0
 29 1.0
 32
Pb+2          100 2.0        0.0        4.5                              0.0
 0.0        0.0
 32 1.0
 33
Pd+2          100 2.0        0.0        0.0                              0.0
 0.0        0.0
 33 1.0
 35
SbO2-         100 -1.0       0.0        0.0                              0.0
 0.0        0.0
 35 1.0
 37
SeO4-2        100 -2.0       6.0        4.0                              0.0
 0.0        0.0
 37 1.0
 39
Sn+2          100 2.0        2.0        6.0                              0.0
 0.0        0.0
 39 1.0
 41
Th+4          100 4.0        4.0       11.0                              0.0
0.0         0.0
 41 1.0
 42
U+4           100 4.0        4.0        0.0                              0.0
0.0         0.0
 42 1.0
 43
Zr+4          100 4.0        0.0        0.0                              0.0
0.0         0.0
 43 1.0
100
OH-           210    -1.000      .000     3.500      .000      .000     1.000
   -13.995     13.340    -814.968 -.135133969    41130.89     296.229
-2639175.4
  3  1.000  1 -1.000
101
O2 AQ         310      .000     4.000      .000      .000      .000      .000
   -86.003    133.734     508.521  .078341650   -53472.79    -184.907
1689617.4
  3  2.000  1 -4.000  2 -4.000
102
H2 AQ         210      .000    -2.000      .000      .000      .000      .000
    -3.105     -1.000     238.732  .041950712   -15527.16     -86.009
938463.7
  1  2.000  2  2.000
103
HCO3-         211    -1.000     4.000     4.500     5.400      .000     1.000
    10.329     -3.513     988.487  .164396835   -52292.14    -358.627
3165965.0
 15  1.000  1  1.000
104
H2CO3         310      .000     4.000      .000      .000      .000      .000
    16.673     -5.832    1961.123  .327901516  -105318.32    -712.077
6490384.7
 15  1.000  1  2.000  3 -1.000
105
HSO4-         210    -1.000     6.000      .000      .000      .000      .000
     1.979      4.900    1031.228  .167740348   -57682.75    -373.661
3449687.8
 16  1.000  1  1.000
106
HS-           410    -1.000    -2.000     3.500      .000      .000     1.000
    33.690    -59.717     877.665  .157143140   -42510.55    -316.250
3048568.3
 16  1.000  1  9.000  2  8.000  3 -4.000
107
H2S           410      .000    -2.000      .000      .000      .000      .000
    40.677    -64.868    1796.831  .312081279   -91103.02    -651.361
6054543.5
 16  1.000  1 10.000  2  8.000  3 -4.000
108
H2S2O3        410      .000     4.000      .000      .000      .000    -2.000
    40.739    -57.184    3064.125  .522179413  -160696.36   -1112.631
10048214.3
 16  2.000  1 12.000  2  8.000  3 -5.000
109
HS2O3-        410    -1.000     4.000      .000      .000      .000    -1.000
    40.153    -60.684    2403.048  .410787847  -125499.26    -871.141
8101435.5
 16  2.000  1 11.000  2  8.000  3 -5.000
110
H2S2O4        410      .000     6.000      .000      .000      .000    -2.000
    13.407    -13.767    2885.921  .488097780  -159685.80   -1046.904
9604362.5
 16  2.000  1 10.000  2  6.000  3 -4.000
111
HS2O4-        410    -1.000     6.000      .000      .000      .000    -1.000
    13.041    -17.567    2586.186  .437111025  -142733.53    -938.290
8622370.3
 16  2.000  1  9.000  2  6.000  3 -4.000
112
HSO3-         410    -1.000     4.000     4.000      .000      .000    -1.000
     3.583      -.587    1003.072  .167352354   -56521.75    -362.744
3358039.7
 16  1.000  1  3.000  2  2.000  3 -1.000
113
HSO5-         410    -1.000     8.000      .000      .000      .000      .000
   -60.288    100.337    1643.797  .263756937  -109486.70    -596.329
5340127.2
 16  1.000  3  1.000  2 -2.000  1 -1.000
114
H2BO3-        210    -1.000      .000      .000      .000      .000     1.000
    -9.249      3.907    -749.560 -.118300018    40652.28     269.835
-2529481.4
 18  1.000  1 -1.000
115
HPO4-2        210    -2.000      .000     4.000      .000      .000     1.000
    12.322     -3.515    1118.483  .185856870   -59072.19    -405.509
3552188.0
```

```
 19  1.000  1  1.000
116
H2PO4-       210    -1.000      .000     4.500      .000      .000      .000
    19.527    -4.520    1835.861  .305075586   -97715.09    -665.229
5912355.3
 19  1.000  1  2.000
117
HF AQ        210      .000      .000      .000      .000      .000    -1.000
     3.168     3.315     502.317  .085310800   -27798.71    -181.851
1656258.1
  1  1.000 20  1.000
118
HF2-         210    -1.000      .000      .000      .000      .000    -2.000
     2.551     4.960     621.371  .105034434   -33039.06    -226.098
1790449.1
  1  1.000 20  2.000
119
H3SiO4-      210    -1.000      .000      .000      .000      .000     1.000
    -9.585     4.220    2517.724  .359699913  -143036.87    -909.042
8405688.6
 13  1.000  1 -1.000
120
H2SiO4-2     210 -2.0      0.0       0.0                              2.0
  -23.0     17.6      -294.0184   -0.072650   11204.49    108.18466
-1119669.0
 13 1.0      1 -2.0
121
HCl          210      .000      .000      .000      .000      .000    -1.000
     -.710     9.648     214.218  .054464831   -10517.85     -82.749
788406.1
  1  1.000 14  1.000
122
HNO3         210      .000     5.000      .000      .000      .000      .000
    -1.303     4.019     671.846  .112252371   -36724.24    -245.315
2095373.3
  1  1.000 17  1.000
123
H3PO4        210      .000      .000      .000      .000      .000      .000
    21.697    -2.620    2316.714  .386099144  -123813.98    -840.013
7440311.8
 19  1.000  1  3.000
124
HIO3         410      .000     5.000      .000      .000      .000    -1.000
  -110.518   168.050     576.193  .089398004   -61456.94    -212.617
1677277.5
 23  1.000  3  3.000  1 -5.000  2 -6.000
125
HSbO2        210      .000      .000      .000      .000      .000      .000
    10.995    -6.600     205.995  .036144163    -9032.29     -73.725
617370.9
 35  1.000  1  1.000
127
HSe-         410    -1.000    -2.000      .000      .000      .000      .000
    81.181  -126.267     677.195  .128654474   -16648.95    -244.559
2365666.7
 37  1.000  1  9.000  2  8.000  3 -4.000
128
HSeO3-       410    -1.000     4.000      .000      .000      .000      .000
    36.304   -48.097     958.119  .162509198   -43513.48    -347.650
3192628.3
 37  1.000  1  3.000  2  2.000  3 -1.000
129
H2SeO3       410      .000     4.000      .000      .000      .000    -1.000
    38.877   -46.407    1466.667  .248458421   -70758.45    -532.712
4766215.5
 37  1.000  1  4.000  2  2.000  3 -1.000
130
HSeO4-       210    -1.000     6.000      .000      .000      .000    -1.000
     1.906     4.200    1109.489  .183362040   -60980.15    -403.400
3596961.1
 37  1.000  1  1.000
300
AlOH+2       310     2.000      .000      .000      .000      .000     1.000
    -4.957    11.902     518.723  .087307679   -30187.23    -188.639
1627784.5
 10  1.000  3  1.000  1 -1.000
301
AlOH2+       310     1.000      .000      .000      .000      .000     2.000
   -10.594    23.490     635.697  .106955890   -38498.51    -230.700
1937490.5
 10  1.000  3  2.000  1 -2.000
302
AlOH3        310      .000      .000      .000      .000      .000     3.000
   -16.433    34.585    1026.675  .168585830   -61549.69    -372.496
3091927.9
 10  1.000  3  3.000  1 -3.000
303
AlOH4-       310    -1.000      .000      .000      .000      .000     4.000
   -22.883    43.236     254.968  .037464280   -21866.23     -89.941
610777.9
325
BaOH+        310     1.000      .000      .000      .000      .000     1.000
   -13.500    20.917    -149.785 -.023556399     5059.36     54.248
-701773.9
 11  1.000  3  1.000  1 -1.000
326
BaCl+        210     1.000      .000      .000      .000      .000      .000
     -.498     3.110     551.818  .096853934   -30344.23    -201.966
1807602.8
 11  1.000 14  1.000
327
BaF+         210     1.000      .000      .000      .000      .000      .000
     -.183     2.140     773.520  .131270194   -41996.15    -282.807
2471505.7
 11  1.000 20  1.000
328
BaCO3        210      .000     4.000      .000      .000      .000     2.000
     2.645     4.035    1202.115  .204575449   -63300.94    -439.639
3529649.3
 11  1.000 15  1.000
350
BiOH+2       310     2.000      .000      .000      .000      .000     1.000
    -1.105     4.157     -15.546 -.004256649     1633.32      5.617
-326041.0
 25  1.000  3  1.000  1 -1.000
351
BiOH2+       310     1.000      .000      .000      .000      .000     2.000
    -3.304    18.657    -701.450 -.113390384    38819.53    256.574
-2944397.0
 25  1.000  3  2.000  1 -2.000
352
BiOH3        310      .000      .000      .000      .000      .000     3.000
    -8.206    30.974   -1395.429 -.228640541    76549.91    509.901
-5606920.9
```

```
 25  1.000  3  3.000  1 -3.000
353
BiOH4-       310    -1.000      .000      .000      .000      .000     4.000
   -21.107    45.674   -1262.701 -.209757822    64579.44     462.127
-4975299.5
 25  1.000  3  4.000  1 -4.000
400
CaOH+        310     1.000      .000      .000      .000      .000     1.000
   -12.833    18.517     48.057  .008051439    -5894.27    -17.763
38295.7
  4  1.000  3  1.000  1 -1.000
401
CaCl+        210     1.000      .000      .000      .000      .000      .000
     -.292     1.126     756.098  .130939275   -40791.05    -277.128
2410655.5
  4  1.000 14  1.000
402
CaCl2        210      .000      .000      .000      .000      .000      .000
     -.644    -1.394    1589.350  .272060292   -84643.89    -583.386
5008097.6
  4  1.000 14  2.000
403
CaF+         210     1.000      .000      .000      .000      .000      .000
      .682     1.350    1067.673  .178933274   -57839.51    -389.929
3423074.0
  4  1.000 20  1.000
404
CaHCO3+      311     1.000     4.000      .000     5.400      .000     1.000
    11.376    -3.165    2048.601  .339363192  -110541.90    -744.834
6702119.6
  4  1.000 15  1.000  1  1.000
405
CaCO3        210      .000     4.000      .000      .000      .000     2.000
     3.327     3.795    1266.919  .215696046   -66449.82    -463.382
3696159.4
  4  1.000 15  1.000
406
CaSO4        210      .000     6.000      .000      .000      .000      .000
     2.111     1.300    1286.832  .216006198   -67690.42    -470.850
3822460.9
  4  1.000 16  1.000
410
CaH3SiO4     310     1.000      .000      .000      .000      .000     1.000
    -8.575     4.783    3799.621  .572165180  -211848.92   -1377.281
12422706.4
  4  1.000 13  1.000  1 -1.000
425
CH4 AQ       410      .000    -4.000      .000      .000      .000      .000
    38.194   -64.575    1957.295  .335797111  -100765.85    -709.737
6662566.5
 15  1.000  1 10.000  2  8.000  3 -3.000
450
CsOH         310      .000      .000      .000      .000      .000     1.000
   -15.685    17.687    -269.095 -.049506083    11122.83     97.848
-1000453.9
 27  1.000  3  1.000  1 -1.000
451
CsCl         210      .000      .000      .000      .000      .000      .000
     -.139      .653     456.846  .075746038   -24335.19    -166.885
1333328.4
 27  1.000 14  1.000
452
CsBr         210      .000      .000      .000      .000      .000      .000
      .022     2.220     383.709  .063348834   -20432.13    -140.117
1125972.7
 27  1.000 22  1.000
453
CsI          210      .000      .000      .000      .000      .000      .000
      .982    -2.550     224.949  .038641780   -11614.28     -82.453
665976.8
 27  1.000 23  1.000
500
FeOH+        310     1.000     2.000      .000      .000      .000     1.000
    -9.315    12.287     458.740  .072604481   -27012.31    -167.456
1356234.5
  8  1.000  3  1.000  1 -1.000
501
FeOH2        310      .000     2.000      .000      .000      .000     2.000
   -20.405    27.417     180.811  .028793639   -14872.42     -66.543
421087.1
  8  1.000  3  2.000  1 -2.000
502
FeOH3-       310    -1.000     2.000      .000      .000      .000     3.000
   -29.207    32.984     428.934  .059826568   -31339.83    -156.140
1377230.6
  8  1.000  3  3.000  1 -3.000
503
FeCl+        210     1.000     2.000      .000      .000      .000      .000
     -.161      .723     876.802  .147143826   -47742.47    -320.423
2858795.1
  8  1.000 14  1.000
504
FeCl2        210      .000     2.000      .000      .000      .000      .000
    -8.172    23.426    1624.758  .273351854   -91791.49    -591.719
5121162.5
  8  1.000 14  2.000
505
FeF+         210     1.000     2.000      .000      .000      .000      .000
     1.427      .748    1006.203  .166186287   -54475.98    -366.935
3230866.7
  8  1.000 20  1.000
514
Fe+3         210     3.000     3.000     9.000      .000      .000      .000
   -13.011    10.200    -101.736 -.017163759     3781.73     34.213
-311058.6
  8  1.000  2 -1.000
515
FeOH+2       410     2.000     3.000      .000      .000      .000     1.000
   -15.216    20.367     113.510  .015220631    -9193.40    -42.482
239182.9
  8  1.000  3  1.000  2 -1.000  1 -1.000
516
FeOH2+       410     1.000     3.000      .000      .000      .000     2.000
   -18.661    29.367    -469.648 -.078431304    21664.30    170.453
-1783755.2
  8  1.000  3  2.000  1 -2.000  2 -1.000
517
FeOH3        410      .000     3.000      .000      .000      .000     3.000
   -25.029    38.384    -642.841 -.108881515    29996.50    234.158
-2644016.6
  8  1.000  3  3.000  1 -3.000  2 -1.000
518
FeOH4-       410    -1.000     3.000      .000      .000      .000     4.000
   -34.631    47.984    -619.528 -.109884387    24467.08    226.853
```

```
-2287898.8
  8  1.000  3  4.000  1 -4.000  2 -1.000
521
FeCl+2       310     2.000     3.000      .000      .000      .000      .000
   -11.531    11.163     686.031  .115696727   -38860.60   -253.292
2225664.2
  8  1.000 14  1.000  2 -1.000
524
FeF+2        310     2.000     3.000      .000      .000      .000      .000
    -7.011    15.059     848.998  .139466396   -48129.57   -309.804
2704569.6
  8  1.000 20  1.000  2 -1.000
550
IO3-         410    -1.000     5.000     4.500      .000      .000      .000
  -111.324   165.650     -80.344 -.019674636   -25739.47    26.554
-399135.9
 23  1.000  3  3.000  1 -6.000  2 -6.000
551
IO4-         410    -1.000     7.000     3.500      .000      .000      .000
  -165.044   250.667     285.173  .036433312   -61406.97   -106.000
637400.5
 23  1.000  3  4.000  1 -8.000  2 -8.000
575
KOH          310      .000      .000      .000      .000      .000     1.000
   -14.895    16.483     349.824  .050960980   -21962.98   -128.042
940603.2
  7  1.000  3  1.000  1 -1.000
576
KCl          210      .000      .000      .000      .000      .000      .000
    -1.751     2.803     941.395  .149125852   -52074.36   -342.358
3039483.1
  7  1.000 14  1.000
577
KBr          210      .000      .000      .000      .000      .000      .000
    -1.737     2.990     242.347  .042919392   -13652.55    -88.844
777675.4
  7  1.000 22  1.000
578
KI           210      .000      .000      .000      .000      .000      .000
    -1.598     2.041     231.496  .042873438   -12537.22    -85.636
717633.6
  7  1.000 23  1.000
579
KHSO4        310      .000     6.000      .000      .000      .000    -1.000
  -179.909   277.670    1488.638  .241725974  -132606.48   -545.199
4729756.6
  7  1.000 16  1.000  1  1.000
580
KSO4-        210    -1.000     6.000      .000      .000      .000      .000
      .880      .690    1102.996  .179334687   -59776.88   -401.927
3506858.5
  7  1.000 16  1.000
582
KAlOH4       410      .000      .000      .000      .000      .000     4.000
   -24.224    50.603    1193.112  .186224965   -72937.50   -430.881
3374636.9
  7  1.000 10  1.000  3  4.000  1 -4.000
600
LiOH         310      .000      .000      .000      .000      .000     1.000
   -13.649    13.369     -20.761 -.006191102    -1294.13     6.302
-203984.6
 21  1.000  3  1.000  1 -1.000
601
LiCl         210      .000      .000      .000      .000      .000      .000
    -1.511      .805     526.414  .090058339   -28586.59   -193.139
1690109.2
 21  1.000 14  1.000
625
MgOH+        310     1.000      .000      .000      .000      .000     1.000
   -11.682    26.729     636.776  .098556534   -38168.05   -231.461
2036313.2
  5  1.000  3  1.000  1 -1.000
626
MgCl+        210     1.000      .000      .000      .000      .000      .000
     -.135     .367    1088.098  .180272411   -58882.26   -397.534
3483003.2
  5  1.000 14  1.000
627
MgF+         210     1.000      .000      .000      .000      .000      .000
     1.352     .567    1284.027  .208518452   -70287.10   -467.329
4202395.6
  5  1.000 20  1.000
628
MgHCO3+      310     1.000     4.000      .000      .000      .000     1.000
    11.365   -2.998    2477.682  .404496646  -133861.26   -900.524
8030882.7
  5  1.000  1  1.000 15  1.000
629
MgCO3        210      .000     4.000      .000      .000      .000     2.000
     2.979    2.182    1363.900  .226965746   -72097.13   -498.117
4069666.6
  5  1.000 15  1.000
635
MgH3SiO4     310     1.000      .000      .000      .000      .000     1.000
    -8.325    3.759    4051.337  .608609927  -225649.90  -1468.304
13239398.7
  5  1.000 13  1.000  1 -1.000
650
MnOH+        310     1.000     2.000      .000      .000      .000     1.000
   -10.620   14.417     287.434  .044885174   -18036.78   -104.992
787107.2
  9  1.000  3  1.000  1 -1.000
651
MnOH2        310      .000     2.000      .000      .000      .000     2.000
   -22.201   22.117      -3.606 -.000866611    -4831.90      .247
-243738.1
  9  1.000  3  2.000  1 -2.000
652
MnOH3-       310    -1.000     2.000      .000      .000      .000     3.000
   -34.800   39.634      10.159 -.007005930    -9359.18    -4.313
-71771.5
  9  1.000  3  3.000  1 -3.000
653
MnOH4-2      310    -2.000     2.000      .000      .000      .000     4.000
   -48.287   56.234   -1067.057 -.186190332    45507.93   388.739
-3578904.8
  9  1.000  3  4.000  1 -4.000
654
MnCl+        210     1.000     2.000      .000      .000      .000      .000
     -.139    4.553     965.727  .162105090   -52863.14   -352.225
3081470.6
  9  1.000 14  1.000
657
MnF+         210     1.000     2.000      .000      .000      .000      .000
```

```
      .880      .596    1194.770  .197973966   -64321.91    -436.301
3770819.7
  9  1.000 20  1.000
660
MnSO4         210      .000     8.000      .000      .000      .000      .000
     1.913     3.550    1452.985  .241233096   -76839.40    -531.000
4324641.8
  9  1.000 16  1.000
662
Mn+3          210     3.000     3.000      .000      .000      .000      .000
   -25.509    22.200    -350.610 -.057782802    14257.71    123.895
-1072167.2
  9  1.000  2 -1.000
663
MnO4-2        410    -2.000     6.000      .000      .000      .000      .000
   -118.345   169.567    -942.744 -.173063096    18728.17    343.932
-3365013.4
  9  1.000  3  4.000  1 -8.000  2 -4.000
675
NaOH          310      .000      .000      .000      .000      .000     1.000
   -14.795    12.823     416.532  .065022580   -25700.92    -153.295
1316230.2
  6  1.000  3  1.000  1 -1.000
676
NaCl          210      .000      .000      .000      .000      .000      .000
     -.777     1.206     435.280  .072276061   -24040.10    -158.876
1435884.1
  6  1.000 14  1.000
677
NaF           210      .000      .000      .000      .000      .000      .000
     -.998     1.723     886.198  .145078346   -47509.85    -323.890
2697174.5
  6  1.000 20  1.000
678
NaBr          210      .000      .000      .000      .000      .000      .000
    -1.357     1.643     632.427  .104303732   -34380.69    -231.113
1982896.3
  6  1.000 22  1.000
679
NaI           210      .000      .000      .000      .000      .000      .000
    -1.540     1.932     570.484  .095763909   -30846.25    -209.002
1781773.4
  6  1.000 23  1.000
682
NaSO4-        210    -1.000     6.000      .000      .000      .000      .000
      .923     -.647    1469.473  .235914956   -79536.64    -535.343
4671368.2
  6  1.000 16  1.000
684
NaAlOH4       410      .000      .000      .000      .000      .000     4.000
   -23.627    45.489    1448.202  .230900017   -86305.07    -525.223
4304910.5
  6  1.000 10  1.000  3  4.000  1 -4.000
685
NaB(OH)4      410      .000      .000      .000      .000      .000     1.000
      .278     -.147     191.667  .036737069   -10360.30     -70.778
670417.5
  6  1.000 18  1.000  3  1.000  1 -1.000
686
NaH3SiO4      310      .000      .000      .000      .000      .000     1.000
    -7.754     1.631    3757.083  .561173967  -208056.83   -1362.488
12183994.2
  6  1.000 13  1.000  1 -1.000
725
NiOH+         310     1.000      .000      .000      .000      .000     1.000
   -10.803    13.567     621.981  .097869700   -37136.99    -226.372
2021226.0
 29  1.000  3  1.000  1 -1.000
726
NiOH2         310      .000      .000      .000      .000      .000     2.000
   -20.706    24.987     595.585  .096080522   -39053.07    -215.168
1641594.0
 29  1.000  3  2.000  1 -2.000
727
NiOH3-        310    -1.000      .000      .000      .000      .000     3.000
   -31.003    30.774     657.860  .096381627   -44762.59    -239.867
2317425.3
 29  1.000  3  3.000  1 -3.000
728
NiOH4-2       310    -2.000      .000      .000      .000      .000     4.000
   -44.036    47.734    -444.237 -.085913899    11439.71     162.328
-1264209.3
 29  1.000  3  4.000  1 -4.000
729
NiCl+         210     1.000      .000      .000      .000      .000      .000
     -.996     1.433     860.735  .145492560   -46393.90    -315.232
2712784.2
 29  1.000 14  1.000
730
NiF+          210     1.000      .000      .000      .000      .000      .000
     1.120      .735     938.690  .154645514   -50955.26    -342.182
3016570.8
 29  1.000 20  1.000
775
NH3 AQ        410      .000    -3.000      .000      .000      .000     1.000
   109.906   -174.961     362.506  .075072550    10293.78    -131.497
1410912.7
 17  1.000  1  9.000  2  8.000  3 -3.000
776
NH4+          410     1.000    -3.000     2.500      .000      .000      .000
   119.147   -187.371     549.591  .103123837     3037.58    -199.394
1956469.2
 17  1.000  1 10.000  2  8.000  3 -3.000
778
N2 AQ         410      .000      .000      .000      .000      .000      .000
   207.269   -313.538    1494.655  .267559947   -24081.60    -544.108
5331034.3
 17  2.000  1 12.000  2 10.000  3 -6.000
779
NO2-          410    -1.000     3.000     3.000      .000      .000      .000
    27.767    -43.888     -81.292 -.009696531    12033.72      29.920
-217519.0
 17  1.000  1  2.000  2  2.000  3 -1.000
825
PbOH+         310     1.000      .000      .000      .000      .000     1.000
    -6.192     -.803     -61.676 -.012242871     3789.23      20.182
-312443.6
 32  1.000  3  1.000  1 -1.000
826
PbOH2         310      .000      .000      .000      .000      .000     2.000
   -16.894    23.397     -338.453 -.056356175    14784.26     122.803
-1341649.3
 32  1.000  3  2.000  1 -2.000
827
```

```
PbOH3-        310    -1.000       .000       .000       .000       .000     3.000
   -27.917     32.214    -752.526 -.130113036    35175.17     273.305
-2742511.3
 32  1.000  3  3.000  1 -3.000
830
PbCl+         210     1.000       .000       .000       .000       .000       .000
     1.437      1.083     783.284  .132501234   -42110.09    -286.110
2475238.9
 32  1.000 14  1.000
831
PbCl2         210       .000       .000       .000       .000       .000       .000
     2.003      1.946    1297.314  .220894673   -69252.17    -474.537
4028009.6
 32  1.000 14  2.000
832
PbCl3-        210    -1.000       .000       .000       .000       .000       .000
     1.688      1.879    1648.091  .279928337   -87854.47    -603.200
5100824.5
 32  1.000 14  3.000
833
PbCl4-2       210    -2.000       .000       .000       .000       .000       .000
     1.430       .303    1647.021  .280297498   -87799.03    -603.213
5149501.2
 32  1.000 14  4.000
834
PbF+          210     1.000       .000       .000       .000       .000       .000
     2.060      -.661     996.558  .165226865   -53308.67    -363.815
3135515.6
 32  1.000 20  1.000
835
PbF2          210       .000       .000       .000       .000       .000       .000
     3.420     -2.703    1599.953  .265609161   -85547.60    -584.360
5081486.3
 32  1.000 20  2.000
836
PbHS2         510       .000    -2.000       .000       .000       .000     2.000
    82.089   -134.805    3557.832  .611454222  -178989.38   -1289.641
11859835.6
 32  1.000 16  2.000  1 18.000  2 16.000  3 -8.000
837
PbHS3-        510    -1.000     -2.000       .000       .000       .000     3.000
   117.078   -196.525    4841.737  .832664974  -244229.09   -1753.096
16369938.4
 32  1.000 16  3.000  1 27.000  2 24.000  3-12.000
850
PdOH+         310     1.000       .000       .000       .000       .000     1.000
    -1.091      -.763     415.150  .064184337   -22633.86    -151.298
1325776.4
 33  1.000  3  1.000  1 -1.000
851
PdOH2         310       .000       .000       .000       .000       .000     2.000
    -2.190      1.537     256.363  .041558345   -12866.44     -94.705
582292.2
 33  1.000  3  2.000  1 -2.000
852
PdCl+         210     1.000       .000       .000       .000       .000       .000
     6.099     -7.647     959.383  .161106997   -50353.56    -350.611
3123209.3
 33  1.000 14  1.000
853
PdCl2         210       .000       .000       .000       .000       .000       .000
    10.733    -15.814    1819.284  .305982103   -95522.32    -665.417
5967755.9
 33  1.000 14  2.000
854
PdCl3-        210    -1.000       .000       .000       .000       .000       .000
    13.094    -24.281    2572.586  .427939382  -135633.62    -940.824
8519672.8
 33  1.000 14  3.000
855
PdCl4-2       210    -2.000       .000       .000       .000       .000       .000
    15.162    -36.348    2795.782  .465087629  -146547.22   -1024.014
9430857.8
 33  1.000 14  4.000
901
S2-2          410    -2.000    -2.000       .000       .000       .000       .000
    57.645   -104.534    1451.874  .264883400   -69953.19    -523.794
5112593.0
 16  2.000  1 16.000  2 14.000  3 -8.000
902
S3-2          410    -2.000    -2.000       .000       .000       .000       .000
    94.457   -161.401    2907.217  .517957838  -142258.09   -1051.762
9997170.3
 16  3.000  1 24.000  2 20.000  3 -12.000
903
S4-2          410    -2.000    -2.000       .000       .000       .000       .000
   131.049   -217.968    4346.529  .767958213  -213906.87   -1573.717
14850442.5
 16  4.000  1 32.000  2 26.000  3 -16.000
904
S5-2          410    -2.000    -2.000       .000       .000       .000       .000
   167.422   -274.235    5580.331  .983261211  -275274.95   -2020.000
19162497.9
 16  5.000  1 40.000  2 32.000  3-20.000
905
S2O3-2        410    -2.000     4.000     4.000       .000       .000       .000
    38.467    -61.784    1536.132  .266874951   -77744.80    -555.799
5227983.1
 16  2.000  1 10.000  2  8.000  3 -5.000
906
S2O4-2        410    -2.000     6.000     5.000       .000       .000       .000
    10.549    -18.567    1611.209  .275984254   -89406.41    -583.562
5414621.5
 16  2.000  1  8.000  2  6.000  3 -4.000
907
S2O5-2        410    -2.000     8.000       .000       .000       .000       .000
     2.348     -2.150    1819.335  .306422449  -101699.51    -660.365
5936649.9
 16  2.000  1  6.000  2  4.000  3 -3.000
908
S2O6-2        410    -2.000    10.000     4.000       .000       .000       .000
    -8.418     17.766    1701.044  .282382169   -98348.05    -616.986
5591123.9
 16  2.000  1  4.000  2  2.000  3 -2.000
909
S2O8-2        210    -2.000    14.000     4.000       .000       .000       .000
   -65.501    113.400    1950.999  .315193634  -128651.93    -707.231
6313368.3
 16  2.000  2 -2.000
910
S3O6-2        410    -2.000    10.000       .000       .000       .000       .000
    25.902    -36.701    3334.767  .565013805  -179919.23   -1211.070
10919710.6
 16  3.000  1 12.000  2  8.000  3 -6.000
```

```
911
S4O6-2        410    -2.000    10.000      .000      .000      .000      .000
    76.128  -106.168    4830.090  .823862961  -251911.60   -1751.763
15995568.7
 16  4.000  1 20.000  2 14.000  3-10.000
912
S5O6-2        410    -2.000    10.000      .000      .000      .000      .000
    97.474  -150.435    5922.101 1.016944428  -307733.36   -2149.155
19757256.1
 16  5.000  1 28.000  2 20.000  3-14.000
913
SO3-2         410    -2.000     4.000     4.500      .000      .000      .000
    -3.623    -2.817     -76.012 -.011796480     1877.60     28.569
-96236.1
 16  1.000  1  2.000  2  2.000  3 -1.000
914
SO2           410      .000     4.000      .000      .000      .000      .000
     5.443     3.572    1826.363  .308250395  -101820.26   -662.569
6059447.6
 16  1.000  1  4.000  2  2.000  3 -2.000
925
SeO3-2        410    -2.000     4.000      .000      .000      .000     1.000
    29.018   -46.817     -49.881 -.003537584    11119.27     17.864
-137209.0
 37  1.000  1  2.000  2  2.000  3 -1.000
975
SnOH+         310     1.000      .000      .000      .000      .000     1.000
    -3.414     6.617     144.023  .020579352    -8438.16    -52.041
311262.2
 39  1.000  3  1.000  1 -1.000
976
SnOH2         310      .000      .000      .000      .000      .000     2.000
    -7.079    10.317    -150.092 -.025521383     7295.27     54.228
-713824.4
 39  1.000  3  2.000  1 -2.000
977
SnOH3-        310    -1.000      .000      .000      .000      .000     3.000
   -16.599    16.634    -369.411 -.068739688    17082.04    134.129
-1411683.5
 39  1.000  3  3.000  1 -3.000
1000
SrOH+         311     1.000      .000     5.000     5.000      .000     1.000
   -13.302    19.987      99.133  .014069720    -8839.39    -35.913
167232.5
 12  1.000  3  1.000  1 -1.000
1001
SrCl+         210     1.000      .000      .000      .000      .000      .000
     -.248     1.813     940.954  .158962656   -50551.22   -344.352
2936080.2
 12  1.000 14  1.000
1002
SrF+          210     1.000      .000      .000      .000      .000      .000
     .139     1.150    1046.500  .173031837   -56581.59   -382.094
3315152.4
 12  1.000 20  1.000
1004
SrCO3         210      .000     4.000      .000      .000      .000     2.000
     2.865     4.435    1395.434  .233818757   -73753.32   -509.674
4110630.5
 12  1.000 15  1.000
1025
SiF6-2        410    -2.000      .000      .000      .000      .000    -4.000
    26.275   -16.959    6090.487  .959294846  -328137.72   -2210.280
19516155.2
 13  1.000  1  4.000 20  6.000  3 -4.000
1075
Th+2          210     2.000     2.000      .000      .000      .000      .000
  -109.071   170.300     226.627  .040869947   -47591.17    -77.397
288991.6
 41  1.000  2  2.000
1076
Th+3          210     3.000     3.000      .000      .000      .000      .000
   -63.258    98.700    -252.869 -.038257331    -5884.17     94.546
-1172965.8
 41  1.000  2  1.000
1100
U+2           210     2.000     2.000      .000      .000      .000      .000
   -57.065    98.400     145.999  .026809334   -27966.70    -47.805
91846.8
 42  1.000  2  2.000
1101
U+3           210     3.000     3.000      .000      .000      .000      .000
    -9.602    24.400    -209.792 -.031242733     8072.53     78.494
-1048770.8
 42  1.000  2  1.000
1102
UOH+2         410     2.000     3.000      .000      .000      .000     1.000
   -15.787    41.917      26.700  .006081412    -6457.05     -6.425
-599625.4
 42  1.000  3  1.000  2  1.000  1 -1.000
1103
UOH2+         410     1.000     3.000      .000      .000      .000     2.000
   -22.311    55.717    -462.825 -.072635741    18599.63    172.365
-2375169.5
 42  1.000  3  2.000  2  1.000  1 -2.000
1104
UOH3          410      .000     3.000      .000      .000      .000     3.000
   -30.805    72.834   -1180.441 -.192069636    56299.60    434.517
-5076801.9
 42  1.000  3  3.000  2  1.000  1 -3.000
1105
UOH4-         410    -1.000     3.000      .000      .000      .000     4.000
   -41.287    84.334   -1077.185 -.177428469    46716.58    397.355
-4544090.4
 42  1.000  3  4.000  2  1.000  1 -4.000
1106
UOH+3         310     3.000     4.000      .000      .000      .000     1.000
     -.541    11.217     379.997  .059338534   -21825.06   -136.117
1047519.1
 42  1.000  3  1.000  1 -1.000
1107
UOH2+2        310     2.000     4.000      .000      .000      .000     2.000
    -2.007    17.517     -6.700 -.001285081     -305.81      4.530
-453944.4
 42  1.000  3  2.000  1 -2.000
1108
UOH3+         310     1.000     4.000      .000      .000      .000     3.000
    -5.003    23.134     586.501  .093017064   -32834.64   -211.604
1288275.0
 42  1.000  3  3.000  1 -3.000
1109
UOH4          310      .000     4.000      .000      .000      .000     4.000
    -4.563    18.234     653.911  .106053771   -36035.34   -237.333
1603178.3
```

```
 42  1.000  3  4.000  1 -4.000
1110
UOH5-       310    -1.000     4.000      .000      .000      .000     5.000
   -16.576    25.050    1001.671  .151691166   -60056.11   -362.685
3146386.8
 42  1.000  3  5.000  1 -5.000
1111
UO2+        410     1.000     5.000      .000      .000      .000      .000
    -7.576    32.934     227.164  .035074896   -13864.38    -80.552
55431.6
 42  1.000  3  2.000  2 -1.000  1 -4.000
1112
UO2OH       410      .000     5.000      .000      .000      .000     1.000
   -25.738    50.350     794.224  .124922917   -49435.17   -288.371
1969210.6
 42  1.000  3  3.000  2 -1.000  1 -5.000
1113
UO2OH2-     410    -1.000     5.000      .000      .000      .000     2.000
   -44.063    72.650     398.946  .056001524   -34140.25   -143.222
817387.5
 42  1.000  3  4.000  2 -1.000  1 -6.000
1114
UO2+2       410     2.000     6.000      .000      .000      .000      .000
    -9.049    34.384     606.976  .092741480   -35609.11   -218.681
1499467.2
 42  1.000  3  2.000  2 -2.000  1 -4.000
1115
UO2OH+      410     1.000     6.000      .000      .000      .000     1.000
   -14.267    44.750     502.746  .074921403   -31206.93   -180.266
1011014.0
 42  1.000  3  3.000  2 -2.000  1 -5.000
1116
UO2OH2      410      .000     6.000      .000      .000      .000     2.000
   -19.361    46.650     448.930  .068968459   -28298.55   -162.731
775796.2
 42  1.000  3  4.000  2 -2.000  1 -6.000
1117
UO2OH3-     410    -1.000     6.000      .000      .000      .000     3.000
   -28.295    51.667     626.678  .088689559   -41071.67   -226.717
1541177.4
 42  1.000  3  5.000  2 -2.000  1 -7.000
1118
UO2OH4-2    410    -2.000     6.000      .000      .000      .000     4.000
   -42.075    68.367    -245.020 -.055519263     3375.35     90.568
-1415944.2
 42  1.000  3  6.000  2 -2.000  1 -8.000
1150
ZrOH+3      310     3.000      .000      .000      .000      .000     1.000
      .324     6.147     656.392  .103728549   -37020.84   -237.085
2117953.6
 43  1.000  3  1.000  1 -1.000
1151
ZrOH2+2     310     2.000      .000      .000      .000      .000     2.000
    -1.728    14.347     264.855  .042403809   -15352.91    -94.571
558087.9
 43  1.000  3  2.000  1 -2.000
1152
ZrOH3+      310     1.000      .000      .000      .000      .000     3.000
    -5.091    21.664    1410.055  .225286719   -79446.00   -511.653
4462372.5
 43  1.000  3  3.000  1 -3.000
1153
ZrOH4       310      .000      .000      .000      .000      .000     4.000
    -9.709    23.164    1191.054  .192686380   -67348.64   -433.022
3481201.9
 43  1.000  3  4.000  1 -4.000
1154
ZrOH5-      310    -1.000      .000      .000      .000      .000     5.000
   -16.004    21.980     934.554  .141916041   -56184.39   -337.646
2760831.4
 43  1.000  3  5.000  1 -5.000

LOOK MIN
Akerman     5          .000    45.319   -68.970      1
   1 -6.0          3  -1.0          4 2.0          5 1.0          13 2.0
  -7479.300-1.127733552   427046.53    2707.535 -24097829.2
Alaband     3          .000      .045    -5.750      1
   9 1.0          106 1.0          1 -1.0
    -990.802 -.164530798    53531.70     361.330  -2998374.8
Albite      4          .000   -20.119    30.843      1
   6 1.0          303 1.0          13 3.0          3 -8.0
  -10348.331-1.555244968   567564.23    3746.228 -33913353.5
Alb-high    4          .000   -18.800    28.213      1
   6 1.0          303 1.0          13 3.0          3 -8.0
  -10436.474-1.569454292   572661.25    3778.291 -34156627.7
Alunite     5        12.000     -.348    -55.414      1
  10 3.0          3 6.0          1 -6.0          7 1.0          16 2.0
   -5507.427 -.916819492   300187.74    2003.800 -16416616.0
Analcime    5          .000     6.948    -20.421      1
   1 -4.0          3 -1.0          6 1.0         10 1.0          13 2.0
   -7446.063-1.119406059   415245.43    2693.508 -24080007.2
Andalus     4          .000    15.944    -56.221      1
   1 -6.0          3 1.0          10 2.0         13 1.0
   -4851.444 -.747867671   274825.20    1753.752 -15196130.6
Anglesit    2        6.000    -7.853     2.690      1
  32 1.0          16 1.0
   -1757.967 -.290646263    94363.84     640.089  -5652288.5
Anhydrit    2        6.000    -4.306    -4.440      1
   4 1.0          16 1.0
-1732.6926   -0.29047750  93359.2040  631.641790 -5430711.9
Annite      5        6.000    29.469    -62.132      1
   1 -10.0         7  1.00         8 3.00         10 1.00         13 3.0
  -11924.617-1.804025576   668489.65    4316.082 -38226809.4
Anorth      4          .000   -19.189    14.044      1
   4 1.0          303 2.0          13 2.0          3 -8.0
   -7859.229-1.202238613   429124.33    2847.113 -25405419.4
Anthophy    4          .000    66.796   -115.554      1
   1 -14.0         3 -8.0          5 7.0          13 8.0
  -29526.408-4.431294078  1655352.19   10683.925 -95503064.9
Antig       4          .000   477.194   -804.099      1
   1 -96.0         5 48.0         13 34.0         3 11.0
 -135487.825-20.36302000  7617232.16   49043.019-432537669.9
Aragonit    2        4.000    -8.336    -2.654      1
  15 1.0          4 1.0
   -1875.816 -.316393683    99680.75     683.927  -5764723.1
Artinite    4        4.000     9.327   -27.660      1
   1 -2.0          5 2.0          15 1.0          3 5.0
   -2478.304 -.399899523   136957.56     901.577  -7412746.9
Barite      2        6.000    -9.971     6.200      1
  11 1.0          16 1.0
   -1846.064 -.310722479    97011.28     674.192  -5768118.7
Na-Beid     5          .000     5.647   -37.253      1
   3 -2.68         1 -7.32         6 0.33         10 2.33         13 3.67
  -13722.572-2.073105312   764018.99    4963.790 -44339021.5
```

```
K-Beid     5          .000     5.309   -36.055     1
   3 -2.68         1 -7.32         7 0.33        10 2.33          13 3.67
  -13794.274-2.086296955   767361.09    4990.575 -44533824.3
Ca-Beid    5          .000     5.591   -38.820     1
   3 -2.68         1 -7.32         4 0.165       10 2.33          13 3.67
  -13676.962-2.067368826   761750.04    4947.070 -44196302.6
Mg-Beid    5          .000     5.554   -39.550     1
   3 -2.68         1 -7.32         5 0.165       10 2.33          13 3.67
  -13675.311-2.065894557   761987.31    4945.951 -44210057.9
Berndtit   5        -2.000   -92.228   146.334     1
   3 -8.0         39 1.0          16 2.0          1 16.0           2 14.0
   -3338.034 -.577782924   162045.35    1212.010 -11064594.2
Boehmite   3          .000     7.564   -27.075     1
   1 -3.0         10 1.0          3 2.0
    -885.683 -.143391305    51203.55     320.101   -2471843.0
Brucite    3          .000    16.298   -26.611     1
   1 -2.0          5 1.0          3 2.0
    -452.893 -.06887724     29129.29     163.991   -1223060.0
Bunsenit   3          .000    12.472   -23.917     1
   1 -2.0         29 1.0          3 1.0
    -666.525 -.106871087    39719.19     242.020   -1886279.7
CaAlpyrx   5          .000    35.976   -86.411     1
   1 -8.0          3 2.0          4 1.0          10 2.0           13 1.00
   -5136.742 -.793286373   296156.66    1857.336 -15994942.7
Calcite    2         4.000    -8.480    -2.633     1
  15 1.0           4 1.0
   -1599.510 -.270987115    85519.84     582.500   -5010794.3
Cassiter   4         2.000    -3.163      .066     1
   1 -4.0          2 -2.0         39 1.0          3 2.0
    -664.775 -.103903817    32909.93     243.842   -1880950.7
Celadon    6          .000     7.457   -17.786     1
   1 -6.0          3 -4.0          5 1.0          7 1.0            10 1.0
  13  4.0
  -14328.054-2.150756077   795968.52    5185.065 -46494406.6
Celestit   2         6.000    -5.677    -1.770     1
  12 1.0          16 1.0
   -1818.393 -.301055879    98130.55     662.153   -5787958.5
Cerussit   2         4.000   -13.538     6.835     1
  15 1.0          32 1.0
   -1848.113 -.308591128    97339.27     673.154   -5828973.4
Chalcedy   2          .000    -3.728     7.507     1
  13 1.0          3 -2.0
   -3123.761 -.465693023   172688.44    1129.990 -10347838.8
Chm-7A     5         4.000    32.842   -87.051     1
   1 -10.0         8 2.0          10 2.0          13 1.0           3 5.0
   -5840.044 -.902158261   332564.88    2112.780 -17912014.6
Chlorite   5          .000   -87.115    43.063     1
   3 -10.0         5 5.0          303 2.0         13 3.0         100 8.0
  -19991.001-3.133247435  1077279.97    7250.236 -63592949.0
Chrysotl   4          .000    31.125   -52.112     1
   3 1.0           1 -6.0          13 2.0          5 3.0
  -8098.4599-1.21792980   455736.100   2931.70270 -25791661.0
Cnc-7A     5          .000    70.612  -150.126     1
   1 -16.0         5 5.0          10 2.0          13 3.0           3 6.0
  -14087.645-2.140140582   798424.08    5097.978 -44108901.7
Cnc-14A    5          .000    67.239  -146.359     1
   1 -16.0         5 5.0          10 2.0          13 3.0           3 6.0
  -14162.235-2.152335846   801753.94    5124.825 -44353020.9
Czo        5          .000    43.257  -109.404     1
   1 -13.0         4 2.0          10 3.0          13 3.0           3 1.0
  -12642.665-1.929004296   714177.92    4573.839 -40177450.4
Cordier    5          .000    52.303  -149.668     1
   1 -16.0         3 -2.00         5 2.00         10 4.00          13 5.0
  -20252.193-3.073237500  1142309.32    7322.248 -64800136.6
Corundum   3          .000    18.312   -61.812     1
   1 -6.0         10 2.0          3 3.0
   -1807.728 -.294292276   106064.49     652.820   -5095360.1
a-Crs      2          .000    -3.449     6.980     1
  13 1.0           3 -2.0
   -3109.751 -.463608807   172039.14    1124.875 -10304943.3
b-Crs      2          .000    -3.005     5.900     1
  13 1.0           3 -2.0
   -3223.421 -.482555307   177782.61    1166.693 -10569625.9
Dph-7A     5        10.000    55.655   -127.234     1
   1 -16.0         8 5.0          10 2.0          13 3.0           3 6.0
  -13593.925-2.072201691   767343.59    4920.092 -42732843.3
Dph-14A    5        10.000    50.365   -120.147     1
   1 -16.0         8 5.0          10 2.0          13 3.0           3 6.0
  -13619.951-2.076289129   767594.51    4929.156 -42849750.2
Diaspore   3          .000     7.160    -26.391     1
   1 -3.0         10 1.0          3 2.0
    -980.072 -.159069041    55862.29     354.813   -2726112.4
Diopside   5          .000    20.964    -31.973     1
   1 -4.0          3 -2.0          4 1.0          5 1.0            13 2.00
   -7122.056-1.070227146   400510.90    2577.775 -23089799.4
Dolomite   3         8.000   -18.144    -7.306     1
   4 1.0           5 1.0          15 2.0
   -3657.993 -.612488930   195522.75    1331.265 -11329561.5
Ord-Dol    3         8.000   -18.144    -7.306     1
   4 1.0           5 1.0          15 2.0
   -3677.022 -.615681181   196492.78    1338.260 -11381374.3
Dis-Dol    3         8.000   -16.600   -10.233     1
   4 1.0           5 1.0          15 2.0
   -3580.249 -.599514810   192169.62    1302.489 -11117943.9
Enstatit   4          .000    11.327   -19.773     1
   1 -2.0          3 -1.0          5 1.0          13 1.00
   -3818.110 -.574363172   214630.23    1381.763 -12291481.2
Epidote    6         3.000    32.930   -92.362     1
   1 -13.0         4 2.0          514 1.0         10 2.00          13 3.0
   3  1.0
  -12602.342-1.922159744   707991.75    4560.056 -39985393.7
Ord-ep     6         3.000    32.930   -92.338     1
   1 -13.0         4 2.0          514 1.0         10 2.00          13 3.0
   3  1.0
  -12691.663-1.935137259   712918.44    4592.331 -40269334.2
Fayalite   3         4.000    19.111   -36.390     1
   1 -4.0          8 2.0          13 1.0
   -4152.095 -.629499494   235235.02    1502.800 -13215977.6
K-fs       5          .000     -.448    -5.486     1
   1 -4.0          3 -4.0          7 1.0          10 1.0           13 3.0
  -10567.643-1.592335431   585341.68    3825.157 -34348101.0
FeO        3         2.000    13.532   -25.347     1
   1 -2.0          8 1.0          3 1.0
    -364.484 -.056961006    24454.74     131.220   -1041733.9
Fluorite   2          .000   -10.037     2.900     1
   4 1.0          20 2.0
   -1722.337 -.288926229    90264.70     628.331   -5250972.6
Forsteri   3         0.000    19.111   -36.390     1
   1 -4.0          5 2.0          13 1.0
   -4152.095 -.629499494   235235.02    1502.800 -13215977.6
Galena     5        -2.000   -48.544    79.587     1
   3 -4.0         32 1.0          16 1.0          1 8.0            2 8.0
   -1759.170 -.302652609    85853.89     638.116   -5873232.6
Gehlenit   5          .000    56.300   -117.096    1
```

```
   1 -10.0         3  3.0         4 2.0          10 2.0          13 1.0
   -5452.296 -.844960385   318834.33     1972.405 -16839986.2
Gibbsite   3          .000      7.756    -24.566      1
  10 1.0          3 3.0          1 -3.0
   -1035.632 -.167985591    58000.08      376.073   -2811524.2
Graphite   4          .000    -32.159     43.565      1
   3 -3.0         15 1.0          1 6.0          2 4.0
   -1279.976 -.223805226    63446.79      464.655   -4268148.1
Grn        4         6.000     22.670    -39.510      1
   1 -6.0          8 3.0         13 2.0          3 1.0
   -7780.486-1.173213917   436236.99     2816.853 -24918143.6
Halite     2          .000      1.585       .894      1
   6 1.0          14 1.0
    -661.998 -.110080533    35472.55      242.853   -2088650.8
Halloysi   4          .000      8.266    -38.201      1
   1 -6.0          3 1.0         13 2.0         10 2.0
   -8053.662-1.224137760   448994.88     2913.681 -25667467.9
Hd         5         2.000     19.606    -29.758      1
   1 -4.0          3 -2.0          4 1.0          8 1.0          13 2.00
   -7126.053-1.073940699   399968.50     2580.012 -23087063.4
Hematite   3         6.000      .109     -30.930      1
 514 2.0          3 3.0          1 -6.0
   -1436.588 -.230339374    80055.00      517.950   -3979539.1
Huntite    3        16.000    -31.014     -26.841      1
   4 1.0          5 3.0         15 4.0
   -7439.772-1.239652579   400664.70     2705.258 -23064297.0
Hydr-mgs   4        16.000    -10.461     -55.186      1
   1 -2.0          5 5.0         15 4.0          3 6.0
   -8331.097-1.368707717   453917.27     3028.087 -25470794.2
Illite     6          .000    -43.606     58.384      1
   3 -11.2         7 0.6          5 0.25       303 2.3          13 3.5
   1 1.2
  -12794.603-1.939187958   694687.37     4634.697 -41698245.6
Fe(c)      2          .000     16.031    -22.050      1
   8 1.0          2 2.0
    -475.935 -.077889507    31501.05      171.825   -1389856.8
Jadeite    5          .000      8.389    -20.182      1
   1 -4.0          3 -2.0          6 1.0         10 1.0          13 2.00
   -7574.843-1.143280623   421692.17     2741.870 -24431462.4
Kaolinit   4          .000      6.810    -36.275      1
   1 -6.0          3 1.0         13 2.0         10 2.0
   -8286.561-1.262845831   460406.93     2999.259 -26294093.0
Kyanite    4          .000     15.674    -55.190      1
   1 -6.0          3 1.0         10 2.0         13 1.0
   -4743.347 -.729179993   269292.11     1713.973 -14924987.2
Lmt        4          .000     13.667    -44.132      1
   1 -8.0          4 1.0         10 2.0         13 4.0
  -14714.624-2.217489144   820687.64     5323.100 -47542555.1
Lawsonit   5          .000     22.213    -58.509      1
   1 -8.0          4 1.0         10 2.0         13 2.0          3 2.0
   -8332.911-1.268250104   468146.76     3015.253 -26487073.6
Lime       3          .000     18.581    -32.987      1
   1 -1.0          4 1.0        100 1.0
   -1178.684 -.195360728    69659.25      429.388   -3610840.6
Magnesit   2         4.000     -8.035     -7.122      1
   5 1.0          15 1.0
   -2074.278 -.344113358   111341.02      754.505   -6362306.1
Magnetit   4         8.000     10.472    -51.767      1
   1 -8.0        514 2.0          8 1.0          3 4.0
   -2027.628 -.324745692   115078.19      732.416   -5632950.5
Mng        3         2.000      4.369    -15.807      1
   1 -1.0          9 1.0        100 1.0
   -1135.067 -.185282737    63919.91      412.142   -3513780.6
Margarit   5          .000     41.066    -124.805      1
   1 -14.0         4 1.0         10 4.0         13 2.0          3 4.0
  -10063.791-1.551460700   570971.57     3639.291 -31362453.8
Merwinit   4          .000     68.514    -102.788      1
   1 -8.0          4 3.0          5 1.0         13 2.00
   -7887.939-1.195224658   455128.87     2857.088 -25190378.6
Max-mc     5          .000      -.448      -5.486      1
   1 -4.0          3 -4.0          7 1.0         10 1.0          13 3.0
  -10609.943-1.597968871   587973.57     3840.169 -34525302.1
Mnn        4         6.000     13.981     -25.151      1
   1 -6.0          3 -4.0          8 3.0         13 4.0
  -14021.559-2.102326013   782168.43     5073.166 -45715584.5
Mtc        4          .000     29.585     -46.776      1
   1 -4.0          4 1.0          5 1.0         13 1.0
   -4134.594 -.626378004   236613.20     1497.400 -13146403.8
Na-Mont    6          .000      2.484     -22.284      1
   3 -4.0          1 -6.0          6 0.33         5 0.33          10 1.67
  13  4.0
  -14342.806-2.158849015   797303.81     5188.598 -46585806.2
K-Mont     6          .000      2.142     -21.082      1
   3 -4.0          1 -6.0          7 0.33         5 0.33          10 1.67
  13  4.0
  -14334.449-2.158810234   796739.44     5185.874 -46592829.1
Ca-Mont    6          .000      2.495     -23.942      1
   3 -4.0          1 -6.0          4 0.165        5 0.33          10 1.67
  13  4.0
  -14345.021-2.160786176   797538.22     5189.374 -46577188.5
Mg-Mont    5          .000      2.388     -24.529      1
   3 -4.0          1 -6.0          5 0.495       10 1.67          13 4.0
  -14294.860-2.151283400   795281.01     5170.446 -46461250.8
Muscovit   4          .000     14.050     -57.895      1
  10 3.0          13 3.0          7 1.0          1 -10.0
  -12152.686-1.847242051   678653.92     4396.344 -38863206.8
Nephelin   4          .000     13.801     -32.282      1
   1 -4.0          6 1.0         10 1.0         13 1.0
   -4370.329 -.664264106   245846.09     1581.632 -13870692.1
Nesqueh    2         4.000     -5.333      -5.126      1
   5 1.0          15 1.0          3 3.0
   49851.470 7.653242489 -2688423.62    -18120.452 152568176.4
Ni(c)      2        -2.000      7.990     -12.900      1
  29 1.0          2 2.0
    -421.178 -.068444742    26903.17      151.035   -1278704.3
Na-Nont    6         6.000    -11.526      -7.550      1
   3 -2.68         1 -7.32         6 0.33         514 2.00         10 0.33
  13  3.67
  -13454.443-2.025559977   743668.89     4866.612 -43517908.0
K-Nont     6         6.000    -11.865      -6.358      1
   3 -2.68         1 -7.32         7 0.33         514 2.00         10 0.33
  13  3.67
  -13467.076-2.029747569   743836.79     4871.933 -43534605.6
Ca-Nont    6         6.000    -11.582      -9.120      1
   3 -2.68         1 -7.32         4 0.165        514 2.00         10 0.33
  13  3.67
  -13507.124-2.036717794   746289.43     4886.171 -43627645.0
Mg-Nont    6         6.000    -11.620      -9.847      1
   3 -2.68         1 -7.32         5 0.165        514 2.00         10 0.33
  13  3.67
  -13573.212-2.045849257   750111.05     4909.747 -43839568.1
Paragoni   4          .000     17.522     -65.739      1
   1 -10.0         6 1.0          10 3.0         13 3.0
  -12224.958-1.856130652   683757.75     4421.870 -39030905.0
```

```
Pargasit   6          .000   101.994  -210.371     1
   1 -22.0        6 1.0          4 2.0          5 4.0          10 3.0
  13 6.0
  -24800.265-3.757500513  1403655.86    8973.054 -78987142.2
Pd(c)      2         -2.000   -30.933    42.080     1
  33 1.0          2 2.0
    -391.307 -.064011947    13062.76     140.850   -1144809.2
PdO        3          .000      .064     -5.837     1
   1 -2.0        33 1.0          3 1.0
    -557.284 -.088194330    29888.63     202.315   -1530740.2
Periclas   3          .000     7.340   -22.544     1
   1 -1.0         5 1.0         100 1.0
   -1297.046 -.209430861    73987.99     470.249   -3993898.9
Phlogopi   5          .000    37.267   -73.975     1
   1 -10.0         7 1.0          5 3.0         10 1.0          13 3.0
  -12259.827-1.850841351   688872.78    4436.987 -39166474.0
Prehnite   4          .000    32.931   -74.539     1
   1 -10.0         4 2.0         10 2.0         13 3.0
  -11829.504-1.796157920   665091.71    4281.148 -37885439.1
Pyrite     4          .000   -16.231    11.250     1
   1 -2.0          2 -2.0         8 1.0         106 2.0
   -1548.858 -.259099104    77697.68     566.855   -4743914.2
Pyrophyl   4          .000      .440   -24.416     1
   1 -6.0          3 -4.0        10 2.0         13 4.0
  -14331.760-2.159302294   796991.87    5183.719 -46571317.3
Pyrrhot    3          .000    -3.719    -1.900     1
   8 1.0         106 1.0          1 -1.0
   -1025.621 -.172010922    54305.77     374.152   -3090835.2
Quartz     2          .000    -3.999     7.875     1
  13 1.0          3 -2.0
   -3119.839 -.464968292   172433.11    1128.522 -10340602.0
Rhodochr   2         6.000   -10.082    -1.764     1
   9 1.0          15 1.0
   -1697.910 -.284421270    90619.33     617.635   -5298772.0
Hi-sa      5          .000      .751    -8.136     1
   1 -4.0          3 -4.0         7 1.0         10 1.0          13 3.0
  -10603.862-1.596705488   588225.89    3837.627 -34508836.6
Sepiolit   4          .000    15.222   -18.801     1
   5 2.0          13 3.0          1 -4.0          3  -0.5
  -10839.905-1.622706355   603023.20    3924.346 -35037234.6
Siderite   2         6.000   -10.521    -4.262     1
   8 1.0          15 1.0
   -1965.635 -.328101570   104973.89     714.917   -6059054.5
Silliman   4          .000    16.308   -56.988     1
   1 -6.0          3 1.0         10 2.0         13 1.0
   -4987.000 -.769270055   282118.80    1803.157 -15588136.2
Sn(c)      2         -2.000     4.816    -2.100     1
  39 1.0          2 2.0
    -467.216 -.075720505    27571.64     169.223   -1475424.2
SnO        3          .000     1.318    -2.077     1
   1 -2.0         39 1.0          3 1.0
    -332.250 -.050717303    18657.56     120.450   -1060842.3
SnS        5         -2.000   -49.312    79.231     1
   3 -4.0         39 1.0         16 1.0          1 8.0           2 8.0
   -1937.432 -.332181853    95083.09     703.165   -6372481.6
Strontit   2         4.000   -10.643     1.545     1
  12 1.0          15 1.0
   -1992.808 -.333033249   105442.71     726.315   -6170664.1
Sylvite    2          .000      .846     4.167     1
   7 1.0          14 1.0
    -590.444 -.100416932    31258.87     217.463   -1930064.5
Talc       4          .000   -62.832    44.491     1
   3 -10.0         5 3.0         13 4.0         100 6.0
  -19416.602-2.992242873  1056811.85    7035.287 -62848878.0
Tremolit   5          .000    61.237   -97.131     1
   1 -14.0         3 -8.0         4 2.0          5 5.0           13 8.0
  -28763.041-4.316868131  1610956.14   10409.407 -93268346.2
Uraninit   3         4.000    -4.827   -18.614     1
   1 -4.0         42 1.0          3 2.0
    -522.960 -.084066499    28482.59     186.188   -1159366.4
Wairakit   5          .000    18.076   -56.830     1
   1 -8.0          3 -2.0         4 1.0         10 2.0          13 4.0
  -14790.873-2.233044351   827113.64    5349.918 -47775054.1
Witherit   2         4.000   -13.325     7.615     1
  11 1.0          15 1.0
   -1596.724 -.269593183    83916.36     581.785   -5090742.0
Wollast    4          .000    13.761   -18.302     1
   1 -2.0          3 -1.0         4 1.0         13 1.00
   -3496.501 -.526508819   197363.48    1266.189 -11362479.4
Zoisite    5          .000    43.302  -109.494     1
   1 -13.0         4 2.0         10 3.0         13 3.0           3 1.0
  -12711.565-1.940677793   717652.86    4599.215 -40357316.6
PCO2       1         4.000    -1.469    -4.849     1
 104 1.0
     601.628  .098938252   -32950.42    -220.638   2122221.1
O2 gas     1         4.000    -2.898    -2.900     1
 101 1.0
     340.129  .057594960   -19638.01    -125.175   1369242.5
H2 gas     1        -2.000    -3.105    -1.000     1
 102 1.0
     323.711  .054983622   -18216.82    -119.338   1172092.5
N2 gas     1          .000    -3.186    -2.495     1
 778 1.0
     662.955  .111292748   -36151.15    -243.796   2238739.5
H2S gas    1        -2.000     -.988    -4.070     1
 107 1.0
     395.925  .068107112   -21036.57    -146.269   1357485.8
CH4 gas    1        -4.000    -2.850    -3.130     1
 425 1.0
     644.123  .107080467   -35748.80    -236.314   2288661.1
NH3 gas    1        -3.000     1.797    -8.419     1
 775 1.0
    -303.189 -.045603086    17285.59     108.962    -801252.8

END

_
```

Appendix C: Calculated and Experimental Equilibrium Constants of Mineral and Gas Solubility Reactions as Functions of Pressure and Temperature

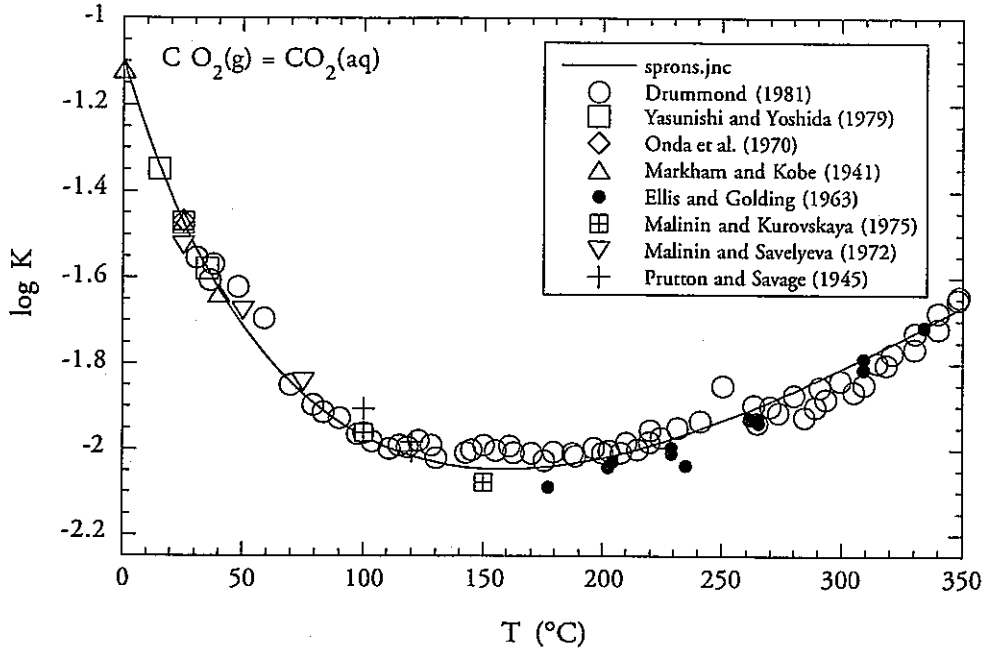


Fig. C.1: Logarithm of the equilibrium constant for the reaction $CO_2(g) \rightleftharpoons CO_2(aq)$ between 0 and 350°C at *Psat*.

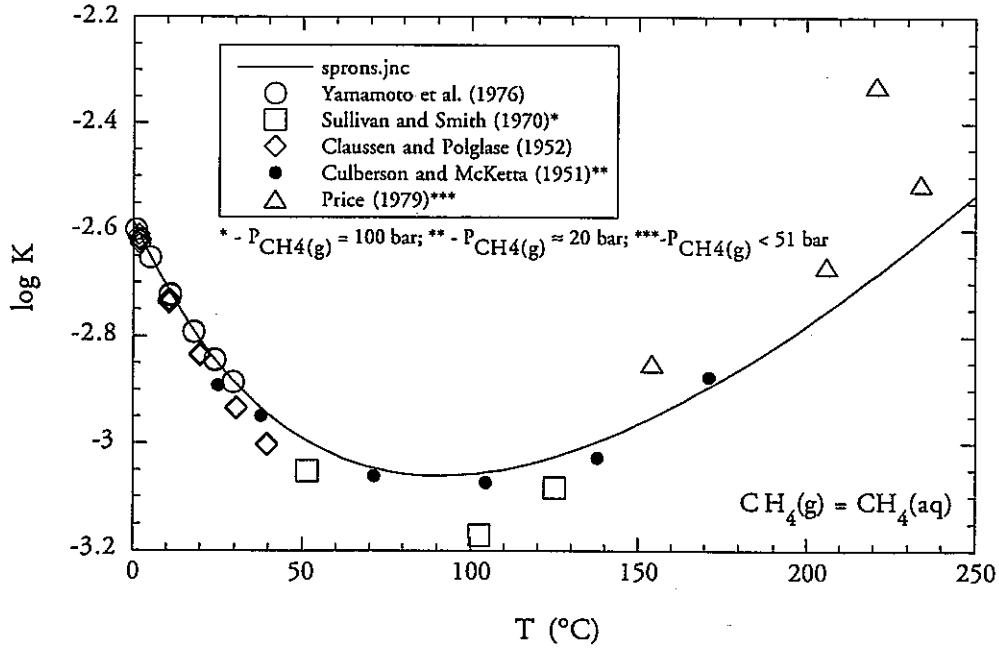


Fig. C.2: Logarithm of the equilibrium constant for the reaction $CH_4(g) \rightleftharpoons CH_4(aq)$ between 0 and 250°C, and pressures from *Psat* to 100 bars.

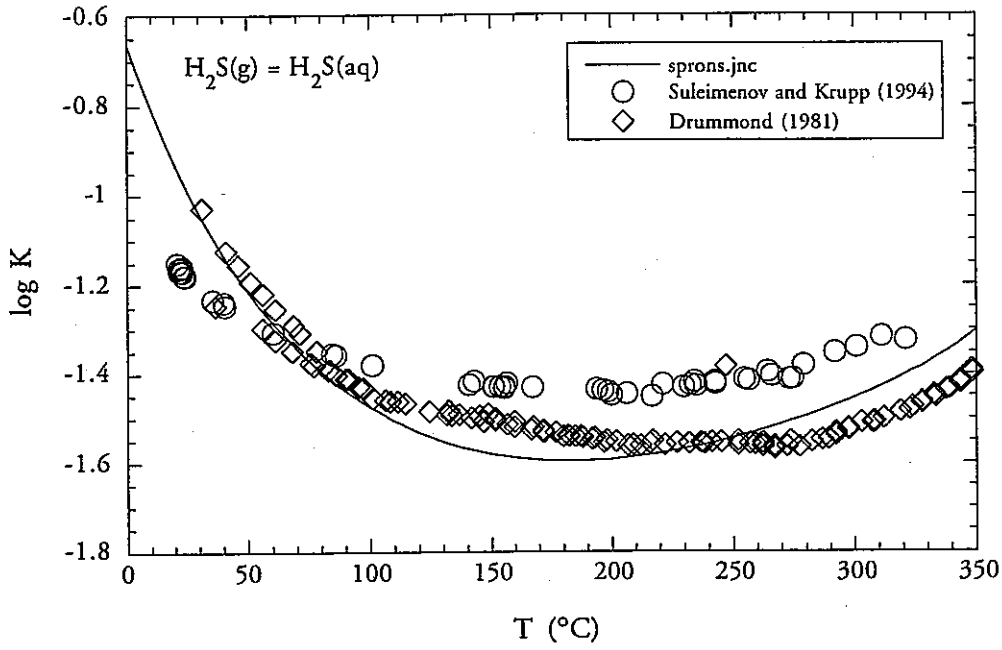


Fig. C.3: logarithm of the equilibrium constant for the reaction $H_2S(g) \rightleftharpoons H_2S(aq)$ between 0 and 350°C at *Psat*.

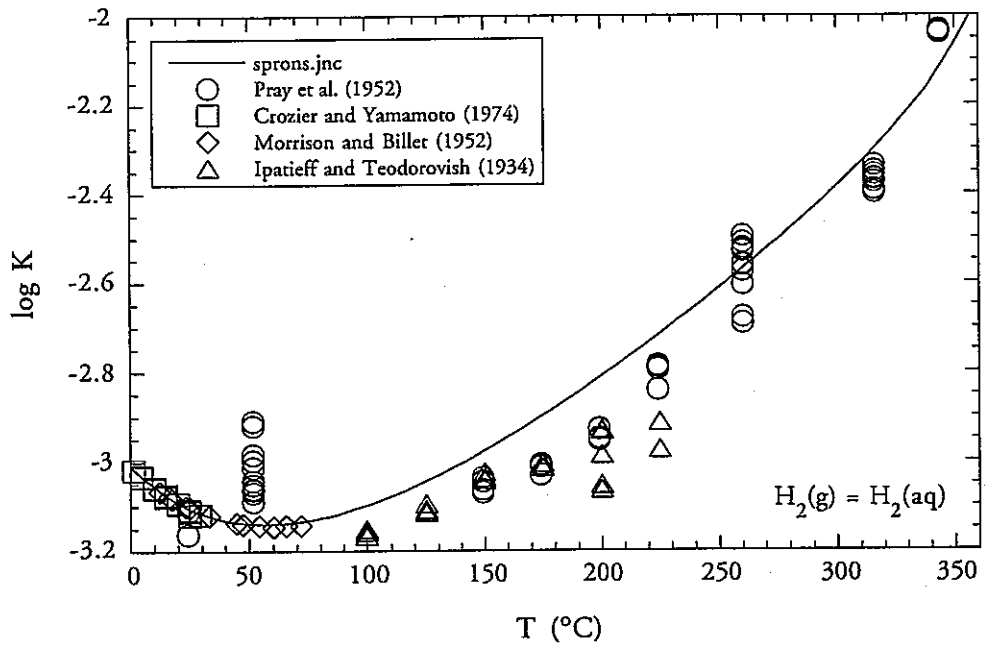


Fig. C.4: Logarithm of the equilibrium constant for the reaction $H_2(g) \rightleftharpoons H_2(aq)$ between 0 and 350°C at *Psat*.

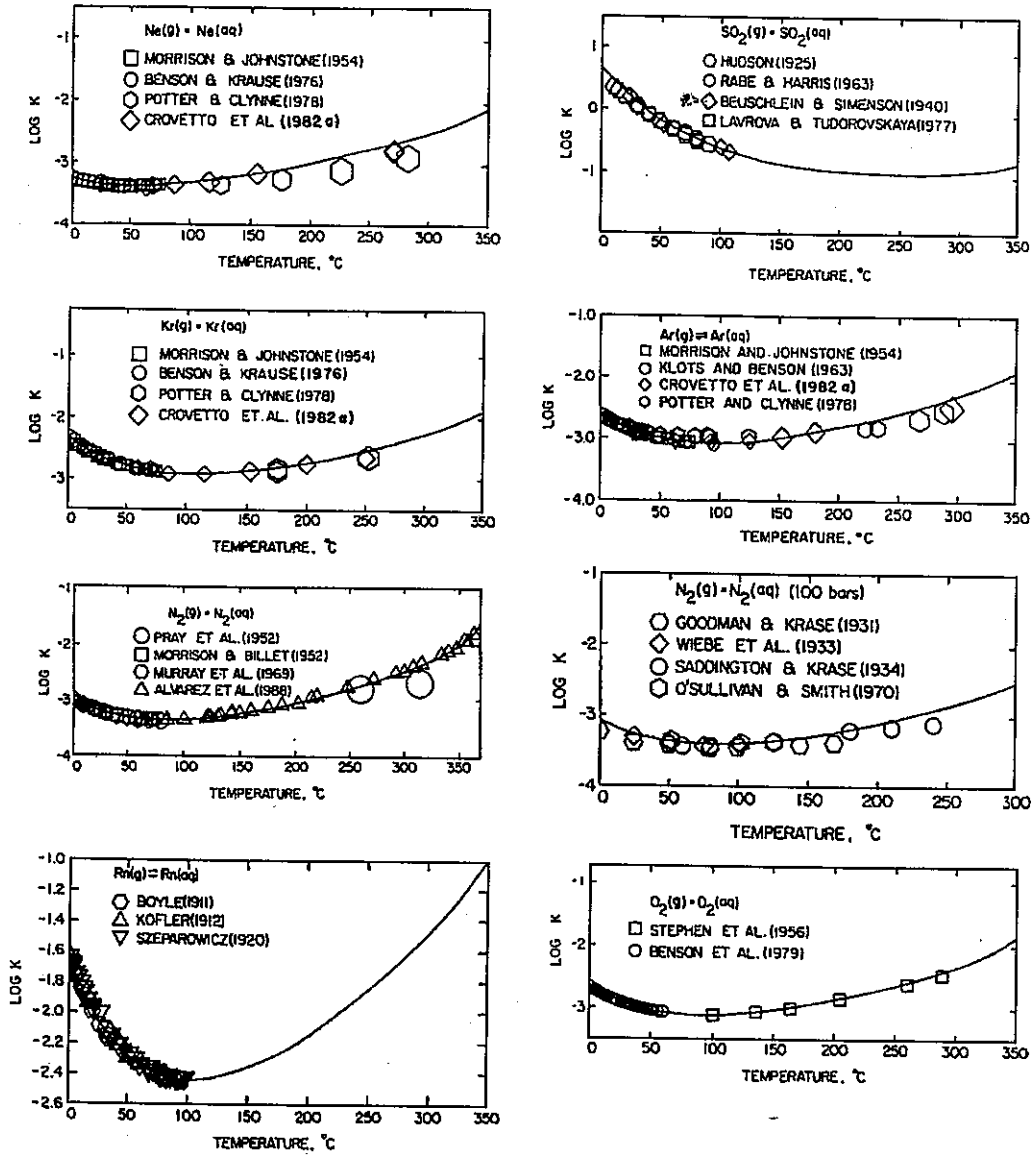


Fig. C.5: Logarithms of the equilibrium constants of gas solubility reactions as functions of temperature at *Psat* [and at 100 bars for the reaction $N_2(g) \rightleftharpoons N_2(aq)$]. The figures were generated by Shock *et al.* (1989) using thermodynamic data for gas and aqueous species that are included in SPRONS.JNC.

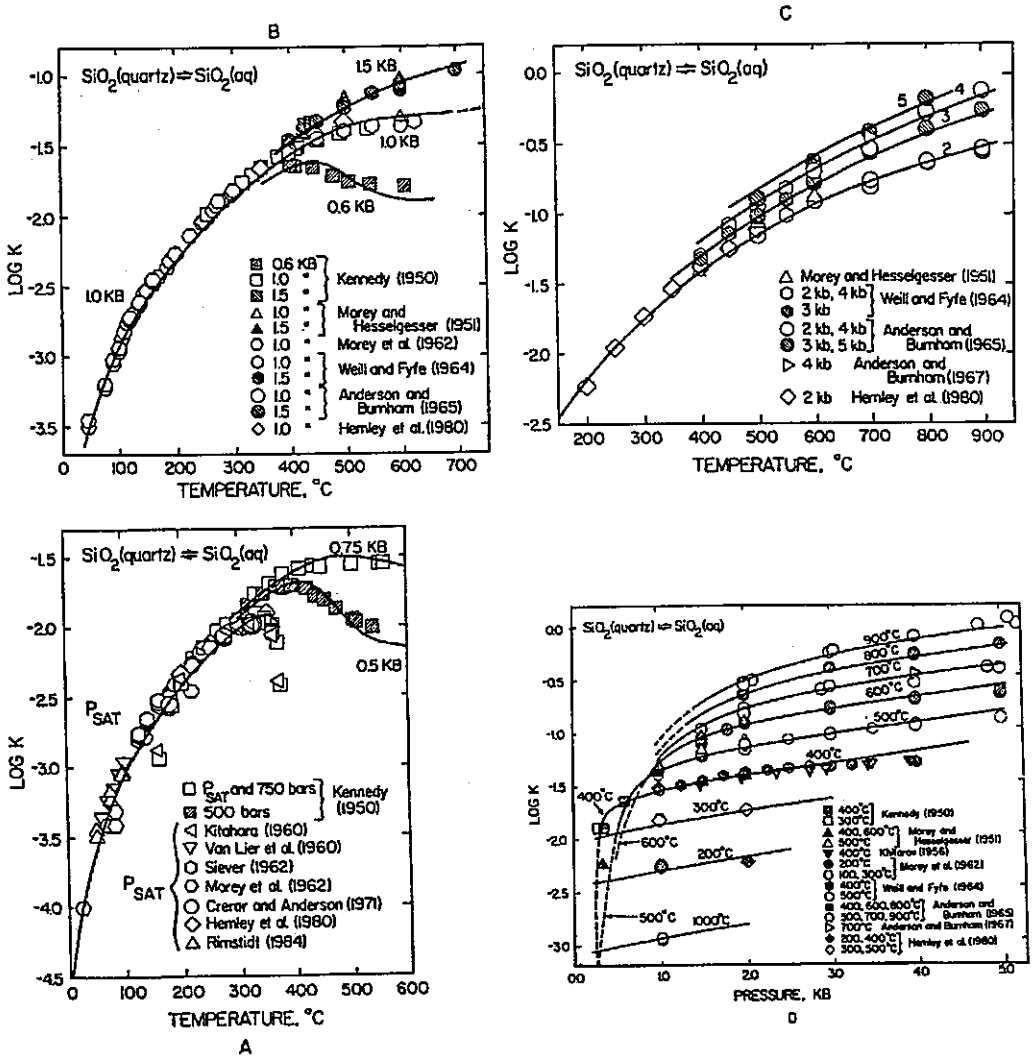


Fig. C.6: Logarithms of the equilibrium constant for the reaction SiO_2 (quartz) ⇌ SiO_2*(aq)* as a function of temperature at *Psat* and constant pressure (diagrams A, B and C), and pressure at constant temperature (diagram D) [from Shock *et al.*, 1989].

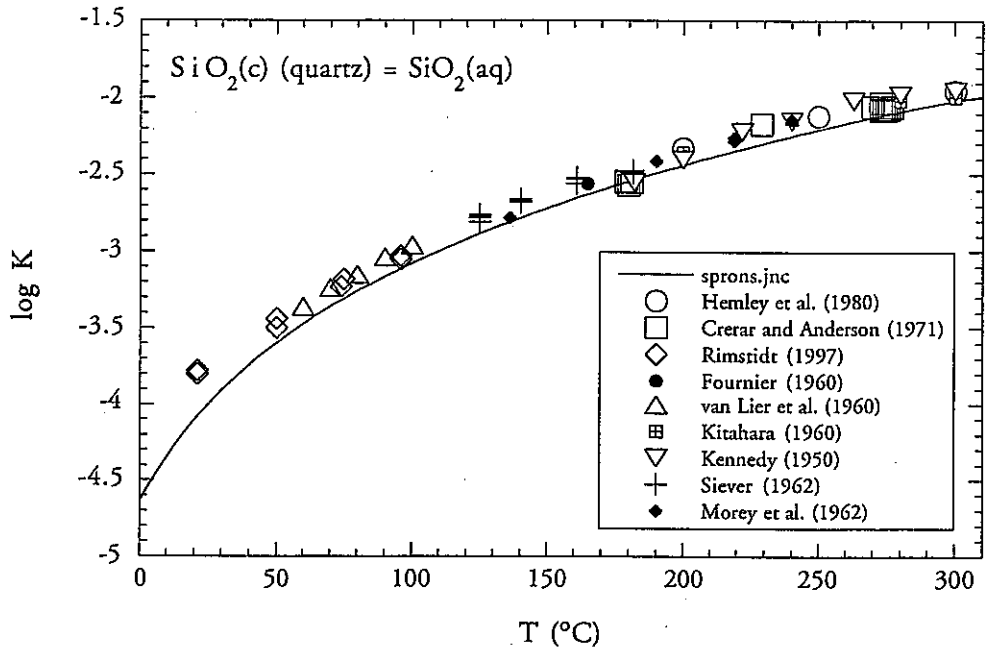


Fig. C.7: Calculated and experimental silica molalities (≈ log *K*) in solutions equilibrated with quartz between 0 and 300°C at *Psat*. Data from "unequilibrated" experiments by Fournier (1960) and Morey *et al.* (1962) at temperatures < 100°C not shown (see Fig. C.8).

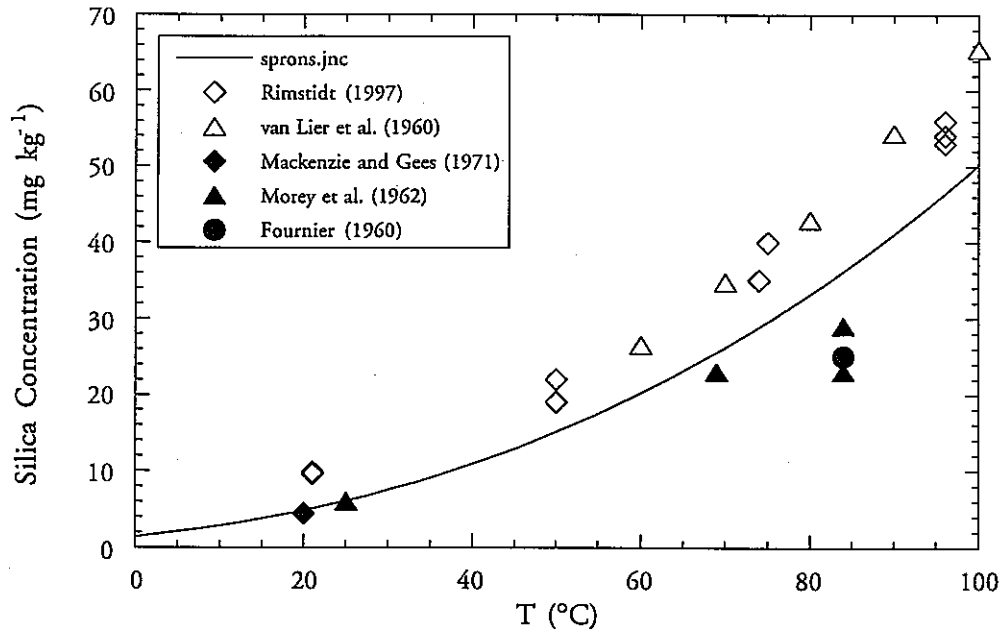


Fig. C.8: Calculated and experimental silica concentrations in solutions coexisting with quartz between 0 and 100°C at 1 bar. [open symbols denote equilibrated experiments; filled symbols refer to unequilibrated experiments (see text)].

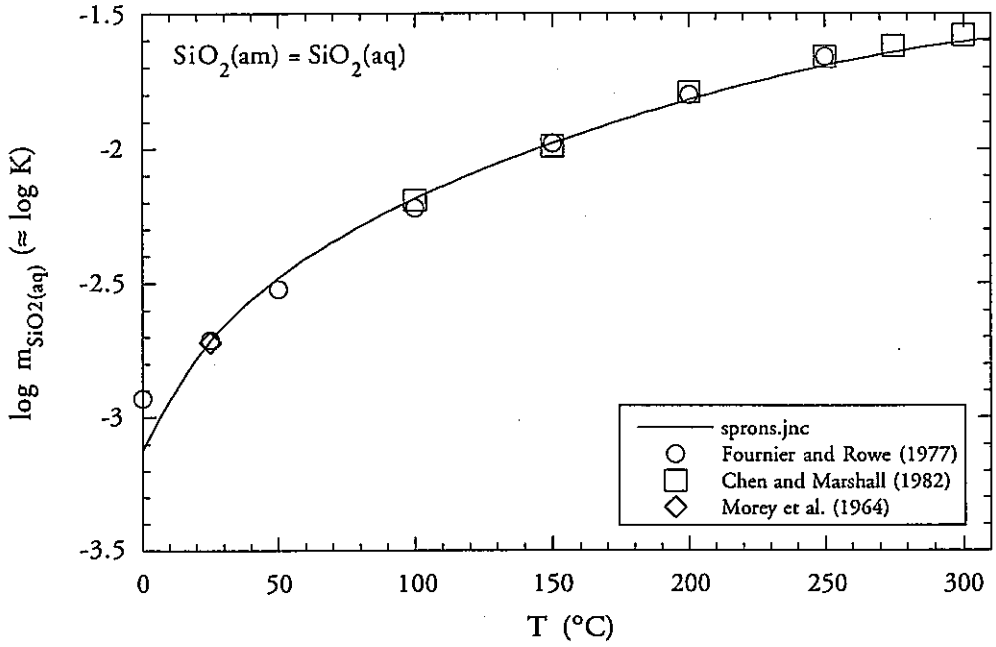


Fig. C.9: Calculated and experimental silica molalities (≈ log K) in solutions equilibrated with amorphous silica between 0 and 300°C at *Psat*.

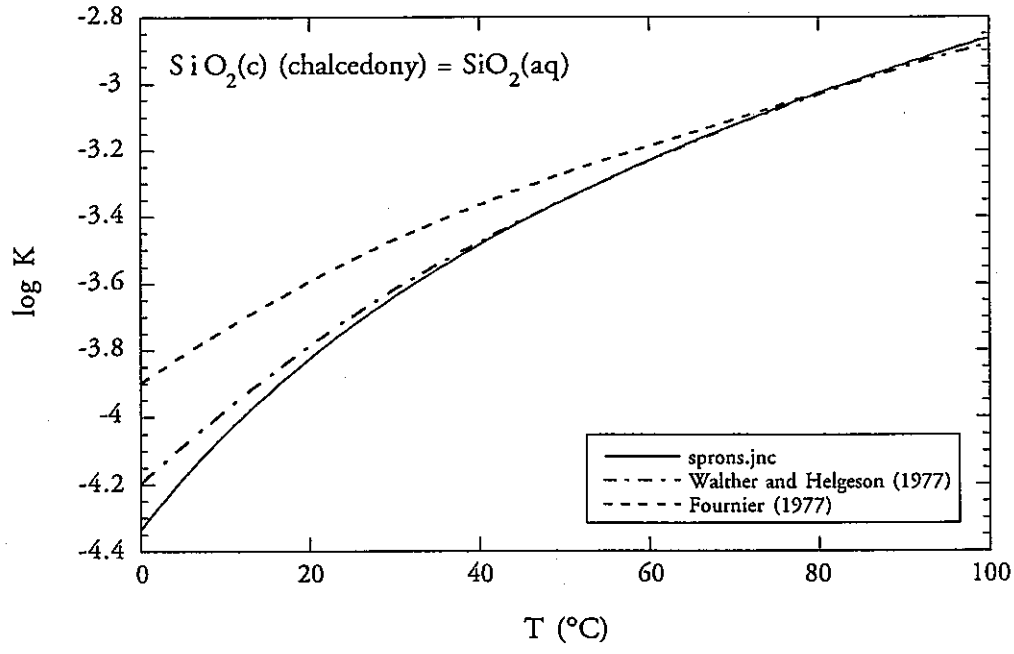


Fig. C.10: Solubility of chalcedony between 0 and 100°C at 1 bar calculated using temperature functions from Walther and Helgeson (1977) and Fournier (1977), which are based on experimental solubilities between 92 and 259°C determined by Fournier and Rowe (1966) and Fournier (1973).

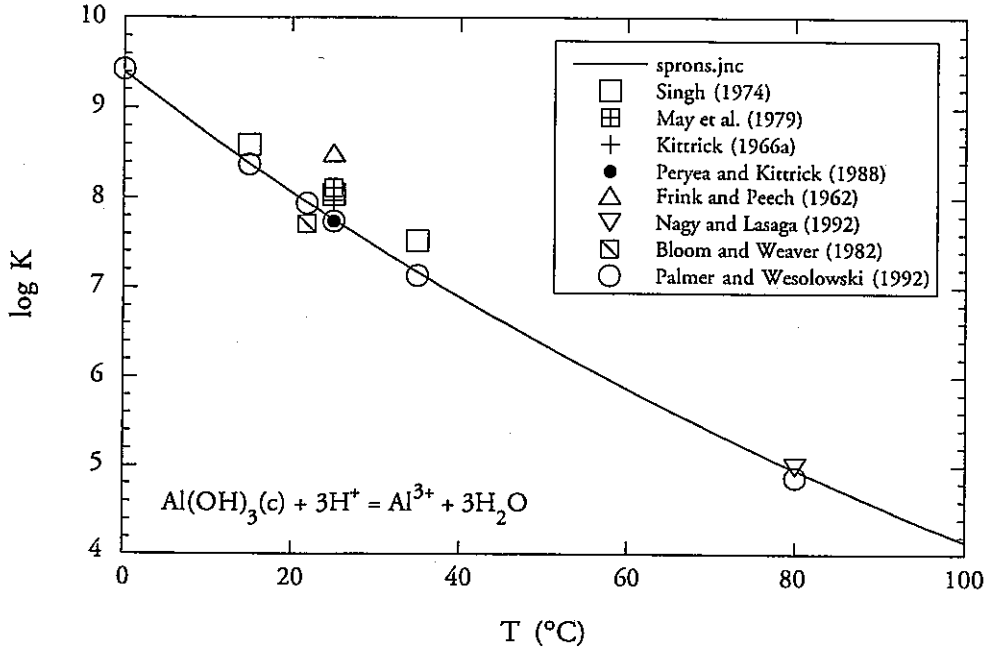


Fig. C.11: Logarithm of the equilibrium constant for the reaction gibbsite + $3H^+ \rightleftharpoons Al^{3+} + 3H_2O(l)$ between 0 and 100°C at 1 bar.

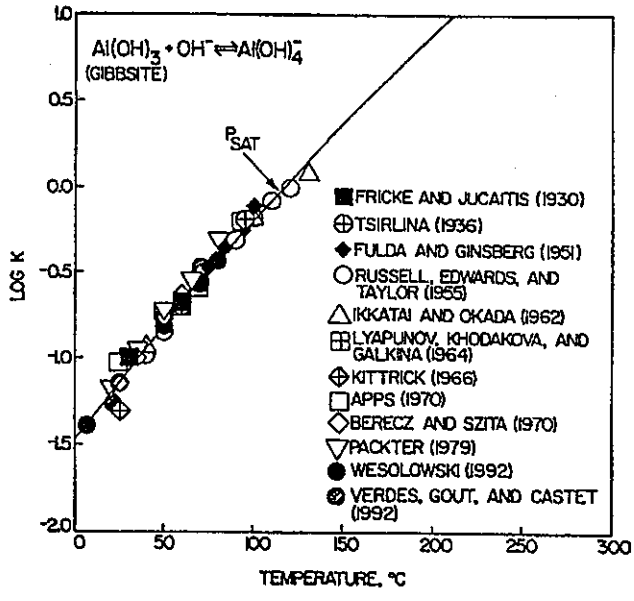


Fig. C.12: Logarithm of the equilibrium constant for the reaction gibbsite + $OH^- \rightleftharpoons Al(OH)_4^-$ between 0 and 300°C at *Psat* (from Pokrovskii and Helgeson, 1995).

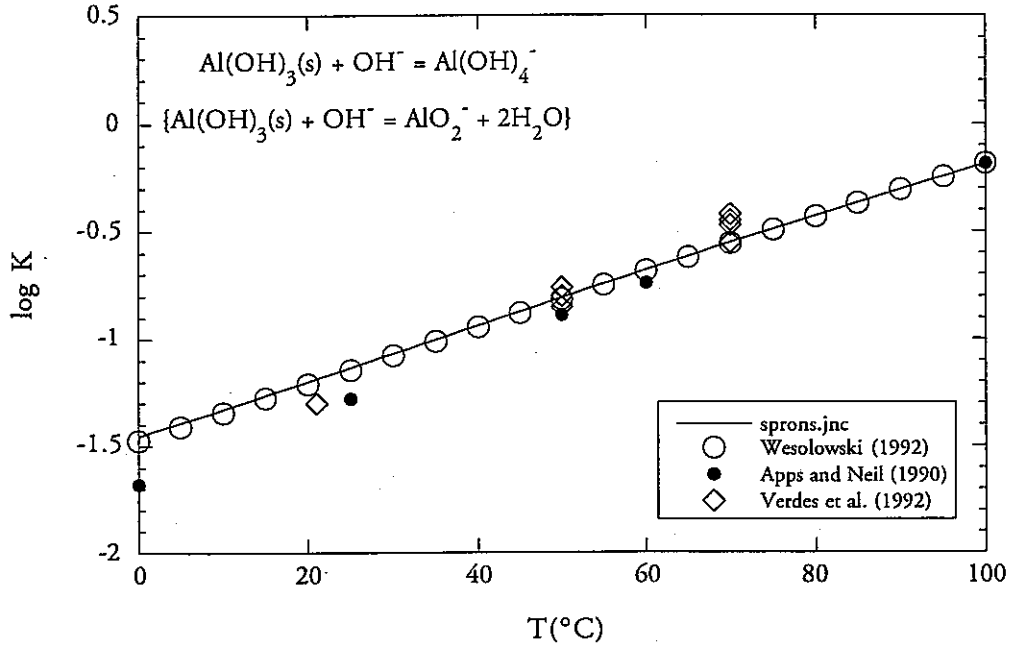


Fig. C.13: Logarithm of the equilibrium constant for the reaction gibbsite + $OH^- \rightleftharpoons Al(OH)_4^-$ between 0 and 100°C at 1 bar.

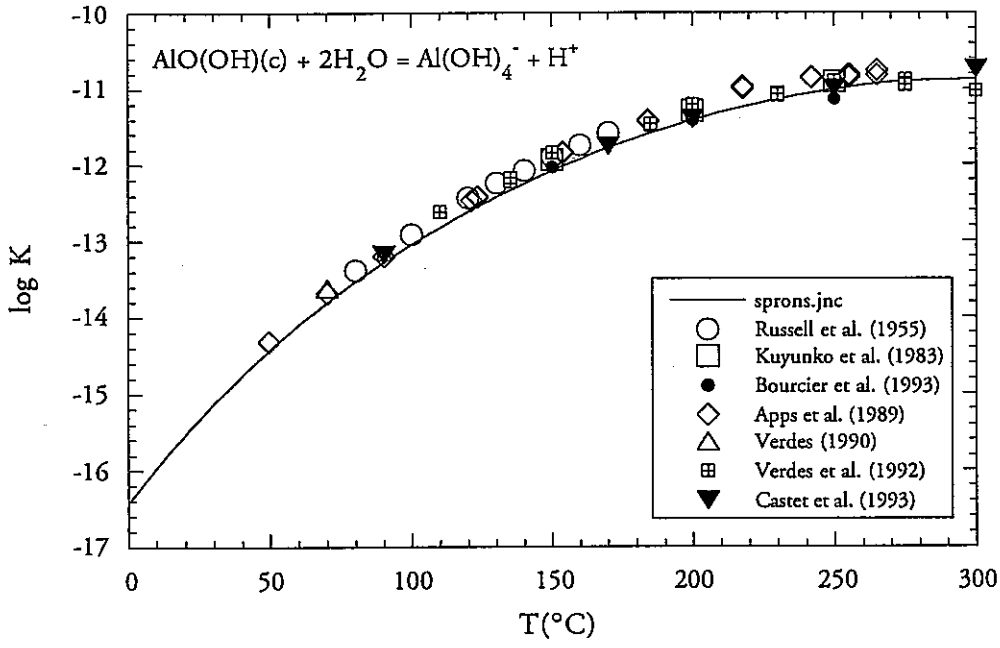


Fig. C.14: Logarithm of the equilibrium constant for the reaction boehmite + $2H_2O(l) \rightleftharpoons Al(OH)_4^-$ between 0 and 300°C at *Psat*.

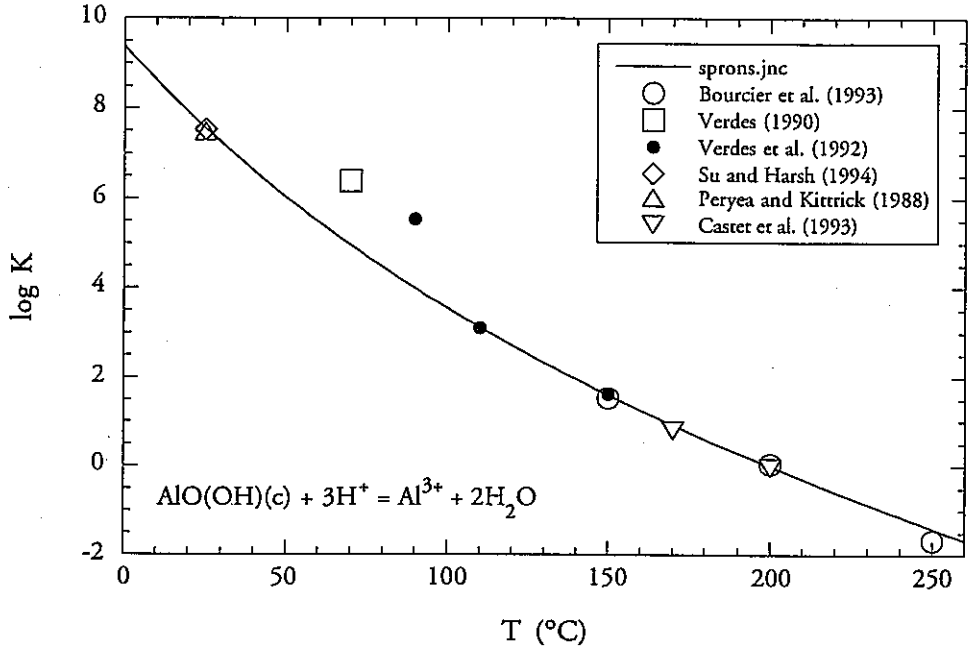


Fig. C.15: Logarithm of the equilibrium constant for the reaction boehmite + $3H^+ \rightleftharpoons Al^{3+} + 2H_2O(l)$ between 0 and 250°C at *Psat*.

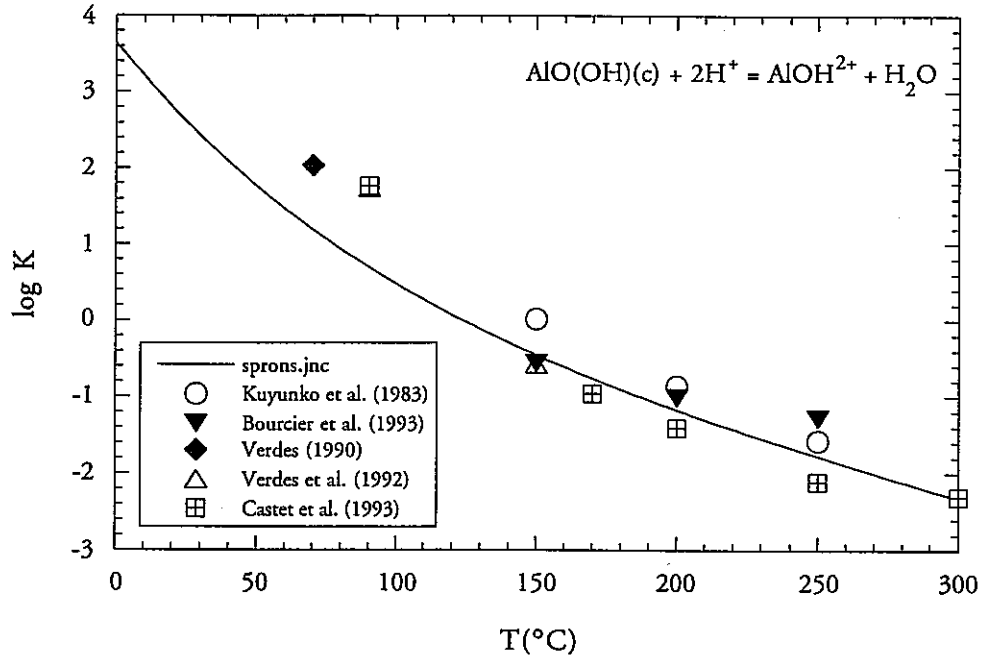


Fig. C.16: Logarithm of the equilibrium constant for the reaction boehmite + $2H^+ \rightleftharpoons AlOH^{2+} + H_2O(l)$ between 0 and 300°C at *Psat*.

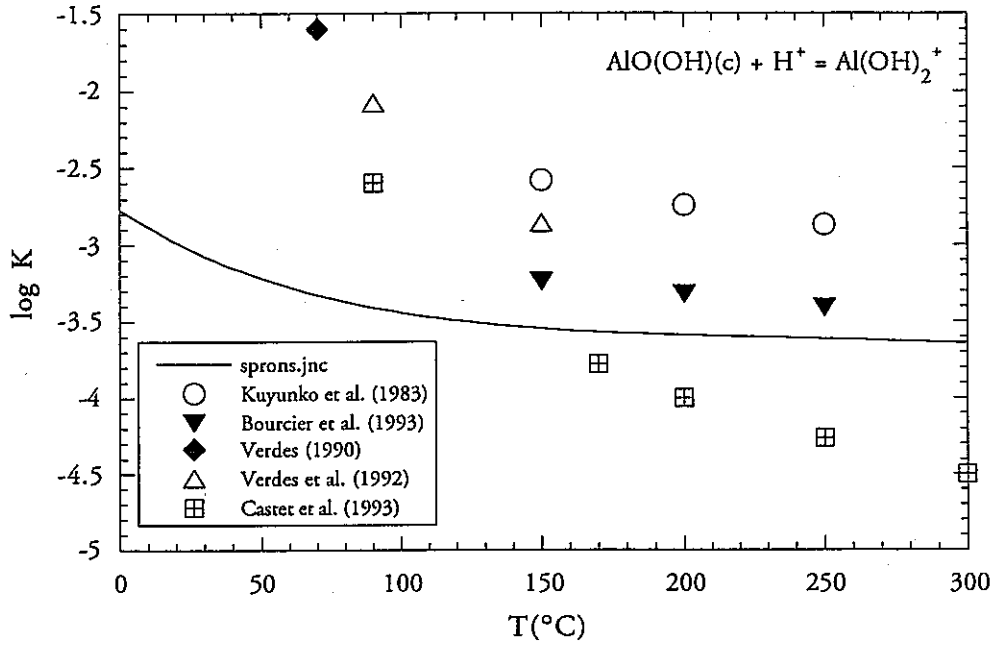


Fig. C.17: Logarithm of the equilibrium constant for the reaction boehmite + $H^+ \rightleftarrows Al(OH)_2^+$ between 0 and 300°C at *Psat*.

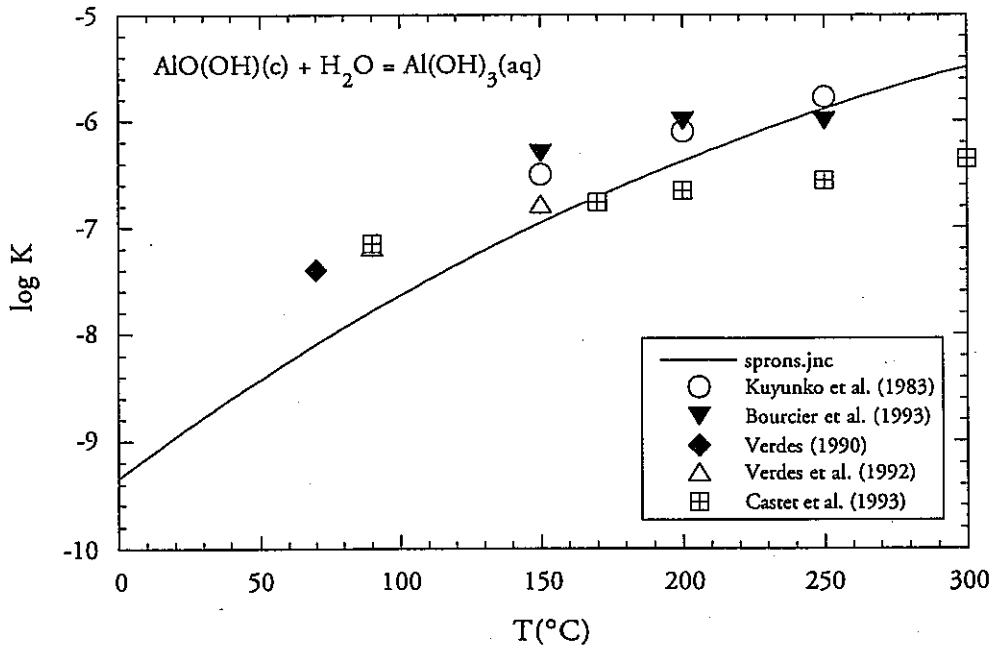


Fig. C.18: Logarithm of the equilibrium constant for the reaction boehmite + $H_2O(l) \rightleftarrows Al(OH)_3(aq)$ between 0 and 300°C at *Psat*.

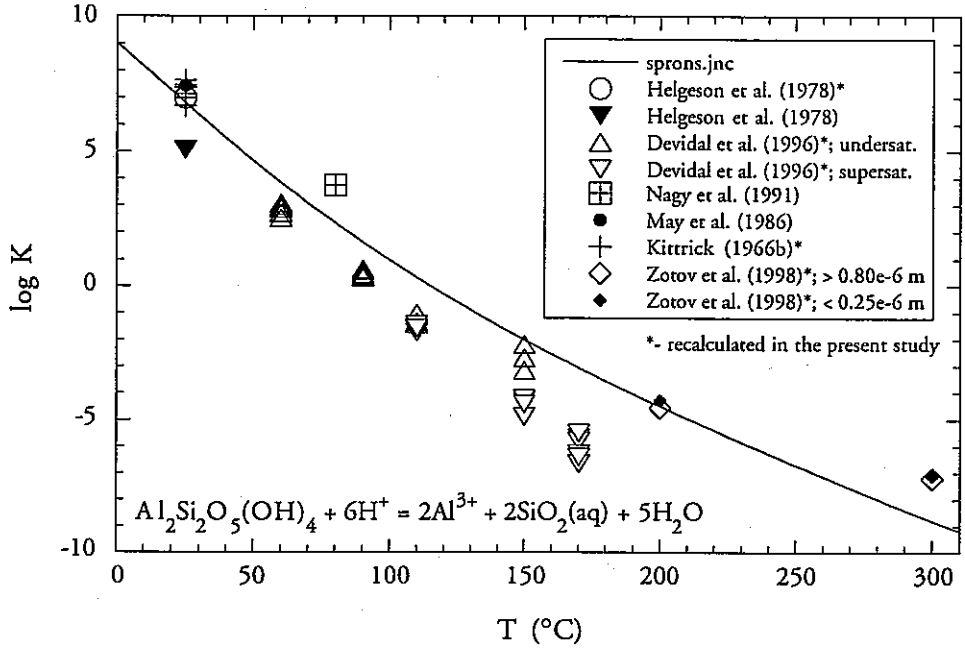


Fig. C.19: Logarithm of the equilibrium constant for the reaction kaolinite + $6H^+ \rightleftharpoons$ $2\,Al^{3+} + 2\,SiO_2(aq) + 5\,H_2O$ between 0 and 300°C at *Psat*.

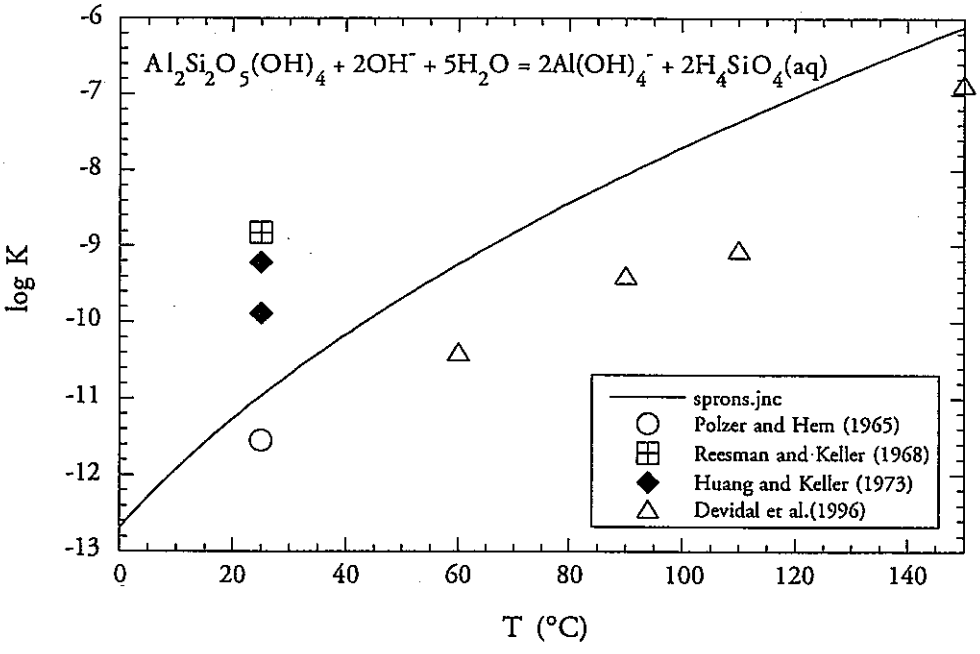


Fig. C.20: Logarithm of the equilibrium constant for the reaction kaolinite + $2\,OH^-$ + $5\,H_2O \rightleftharpoons 2\,Al(OH)_4^- + 2\,H_4SiO_4(aq)$ between 0 and 150°C at *Psat*. All experimental equilibrium constants evaluated by Devidal *et al.* (1996) based on their experimental results and results reported by Polzer and Hem (1965), Reesman and Keller (1968) and Huang and Keller (1973).

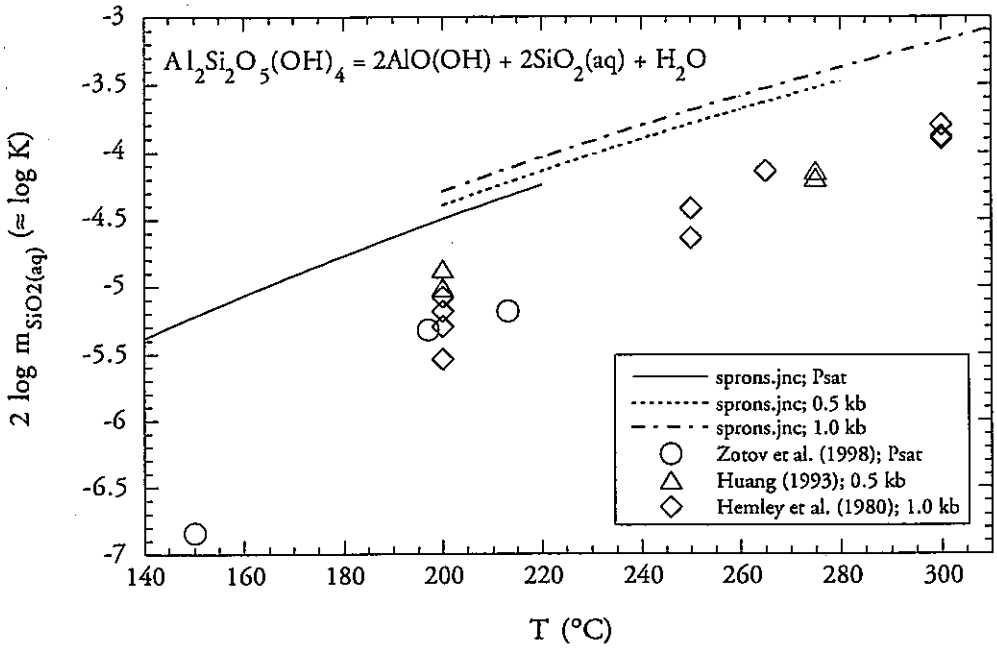


Fig. C.21: Logarithm of the equilibrium constant [≈ 2 log $m_{SiO2(aq)}$] for the reaction kaolinite ⇌ 2 boehmite + 2 SiO_2*(aq)* + H_2O between 140 and 300°C and pressures from *Psat* to 1 kb.

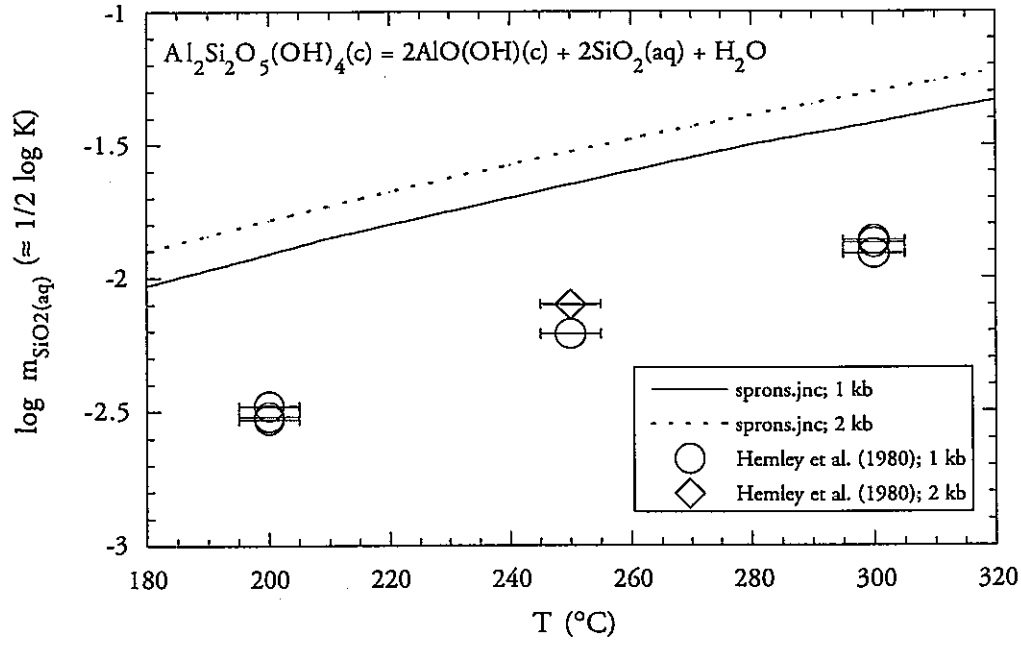


Fig. C.22: Plot of 1/2 log K [≈ log $m_{SiO2(aq)}$] for the reaction kaolinite ⇌ 2 diaspore + 2 SiO_2*(aq)* + H_2O between 180 and 320°C and pressures of 1 and 2 kb.

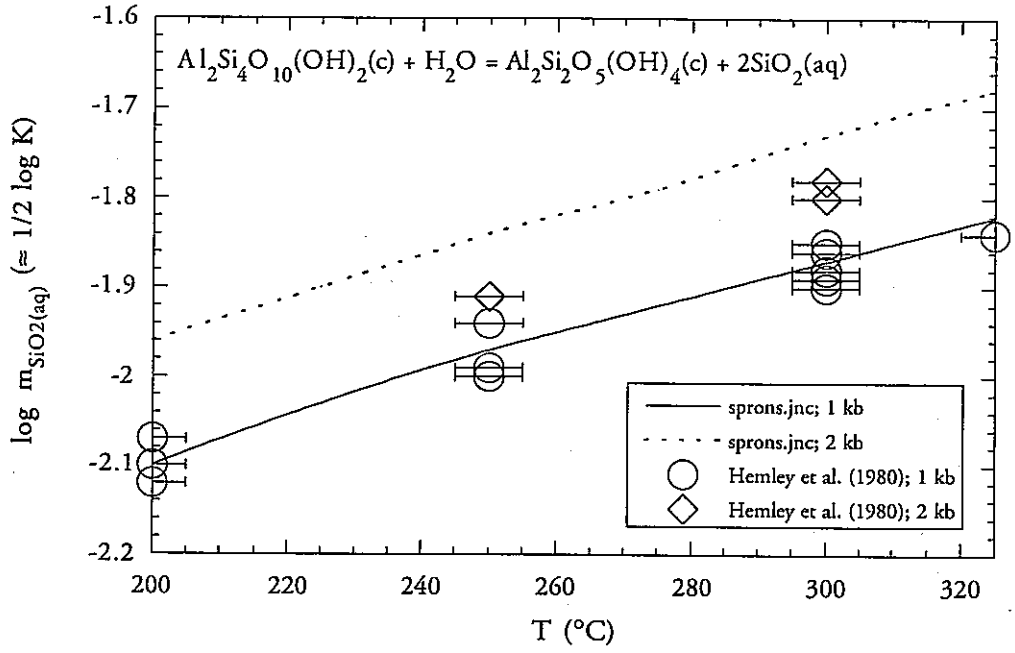


Fig. C.23: Plot of 1/2 log K [≈ log $m_{SiO2(aq)}$] for the reaction pyrophyllite + H_2O ⇌ kaolinite + 2 SiO_2*(aq)* between 200 and 320°C and pressures of 1 and 2 kb.

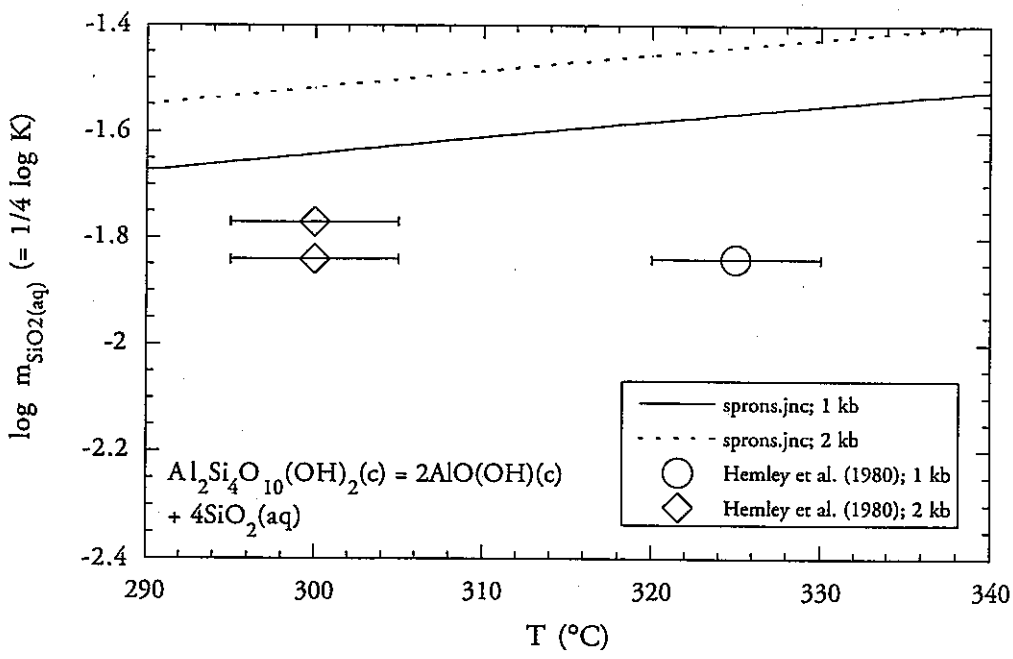


Fig. C.24: Plot of 1/4 log K [≈ log $m_{SiO2(aq)}$] for the reaction pyrophyllite ⇌ 2 diaspore + 4 SiO_2*(aq)* between 290 and 340°C and pressures of 1 and 2 kb.

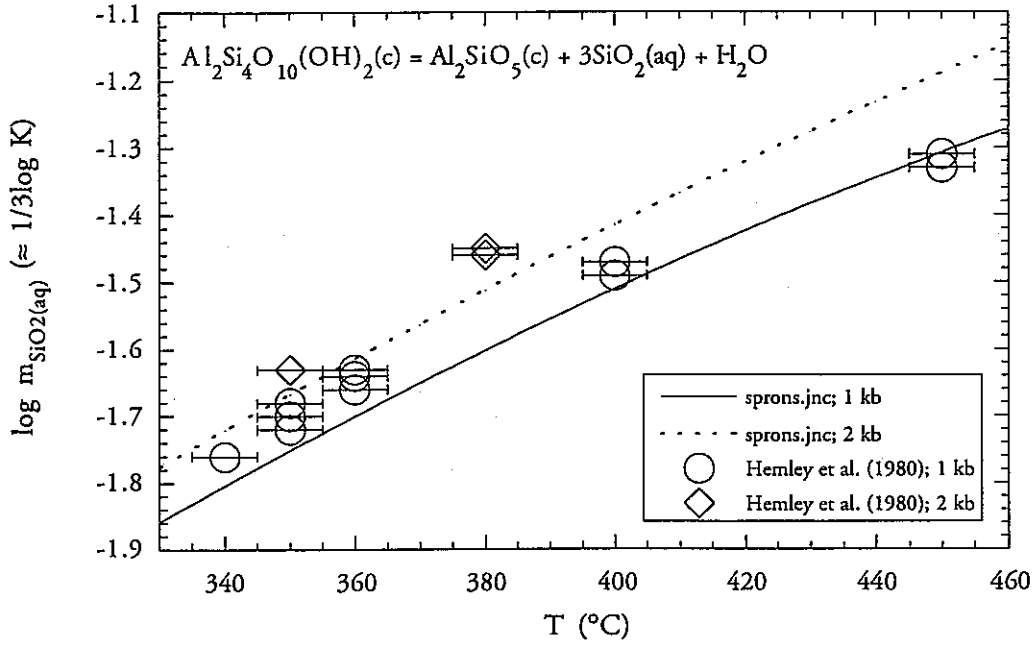


Fig. C.25: Plot of 1/3 log K [≈ log $m_{SiO2(aq)}$] for the reaction pyrophyllite ⇌ andalusite + 3 SiO_2*(aq)* + H_2O between 340 and 460°C and pressures of 1 and 2 kb.

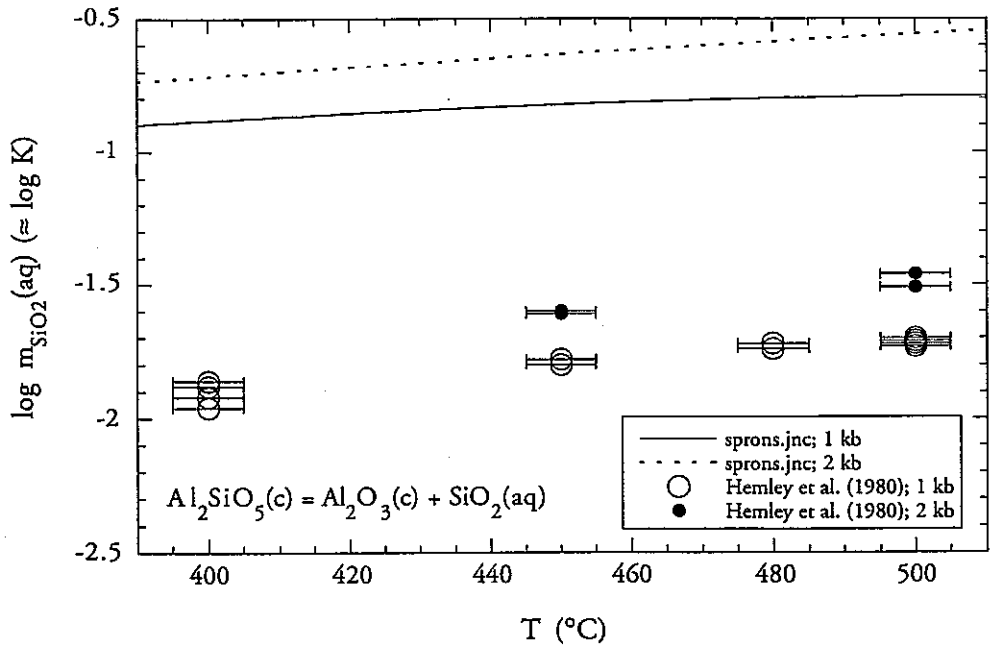


Fig. C.26: Logarithm of the equilibrium constant [≈ log $m_{SiO2(aq)}$] for the reaction andalusite ⇌ corundum + SiO_2*(aq)* between 390 and 510°C and pressures of 1 and 2 kb.

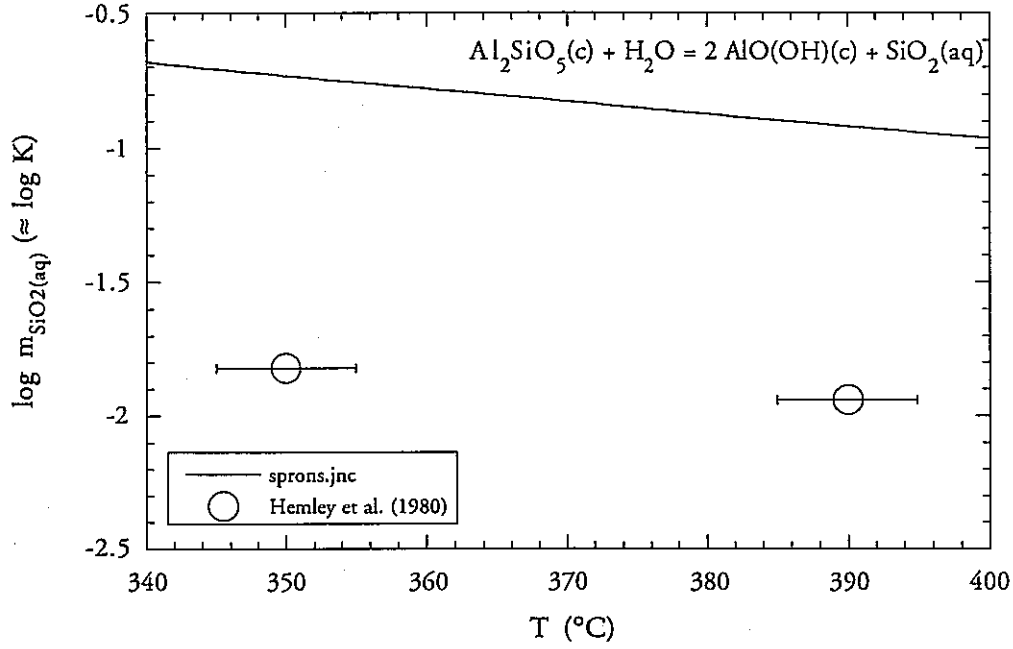


Fig. C.27: Logarithm of the equilibrium constant [≈ log $m_{SiO2(aq)}$] for the reaction andalusite + H_2O ⇌ diaspore + SiO_2*(aq)* between 340 and 400°C at 1 kb.

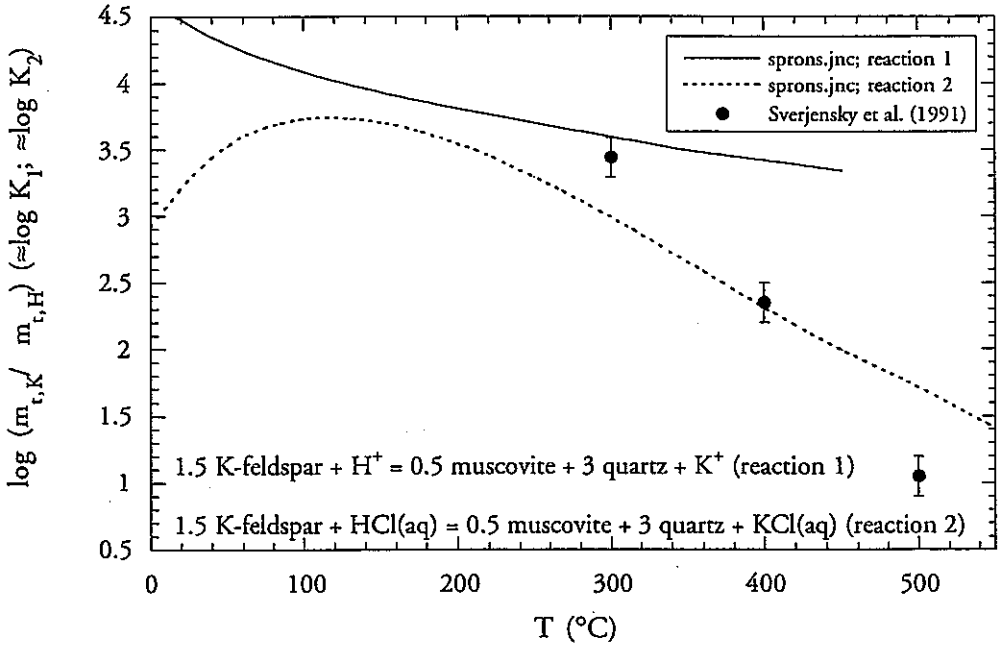


Fig. C.28: Logarithm of the equilibrium constant [≈ log ($m_{t,K}/m_{t,H}$)] for reactions in the system K_2O-Al_2O_3-SiO_2-HCl between 0 and 500°C at 0.5 kb.

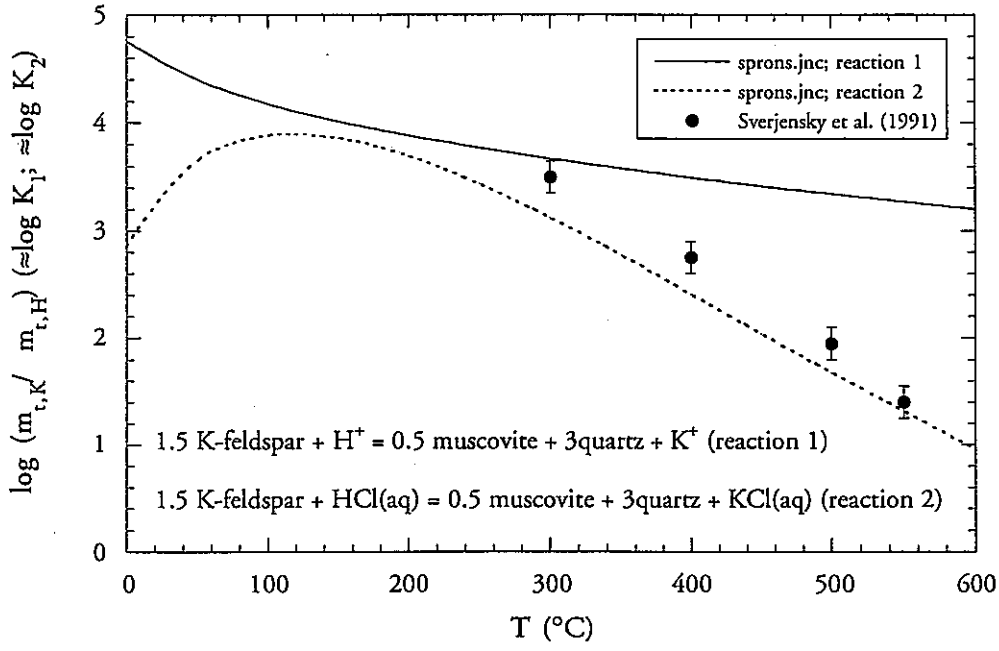


Fig. C.29: Logarithm of the equilibrium constant [≈ log ($m_{t,K}/m_{t,H}$)] for reactions in the system K_2O-Al_2O_3-SiO_2-HCl between 0 and 600°C at 1 kb.

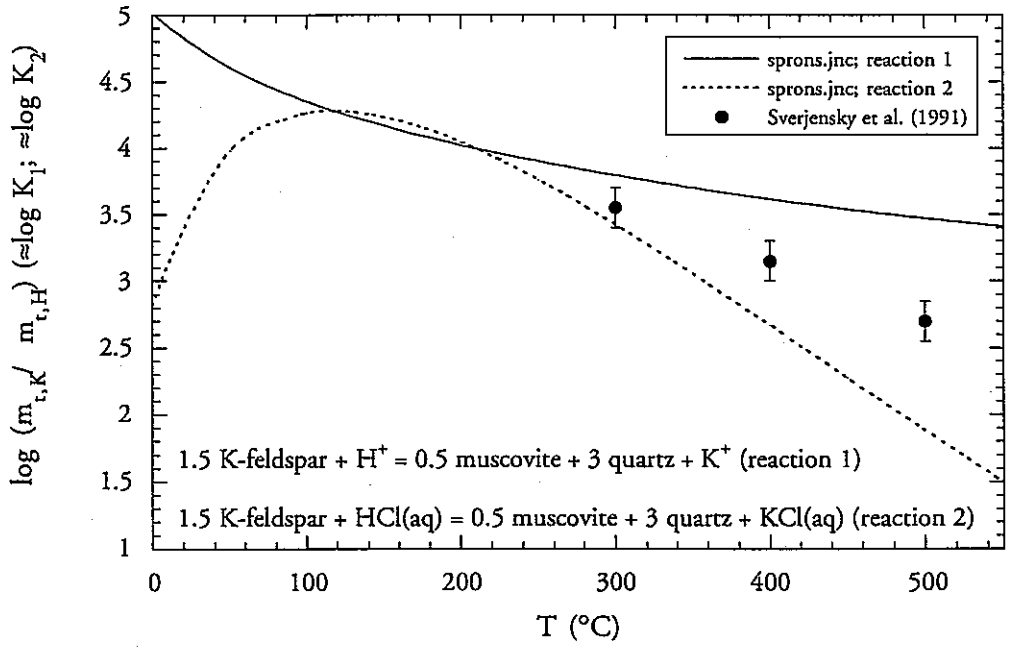


Fig. C.30: Logarithm of the equilibrium constant [≈ log ($m_{t,K}/m_{t,H}$)] for reactions in the system K_2O-Al_2O_3-SiO_2-HCl between 0 and 550°C at 2 kb.

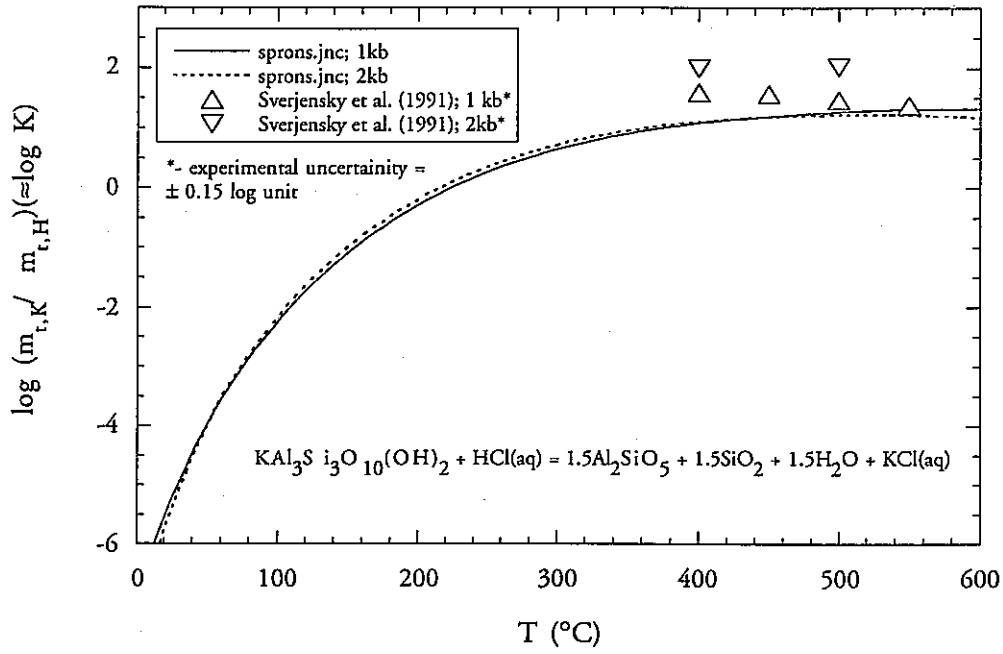


Fig. C.31: Logarithm of the equilibrium constant [≈ log ($m_{t,K}/m_{t,H}$)] for the reaction muscovite + HCl*(aq)* ⇌ 1.5 andalusite + 1.5 quartz + 1.5 H_2O + KCl*(aq)* between 0 and 600°C and pressures of 1 and 2 kb.

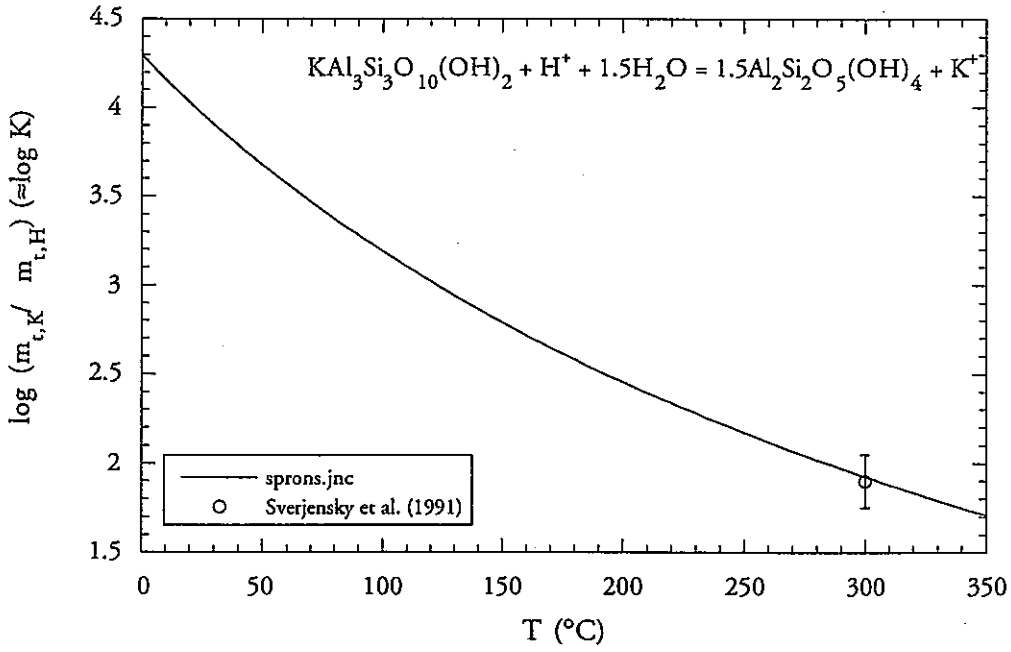


Fig. C.32: Logarithm of the equilibrium constant [≈ log ($m_{t,K}/m_{t,H}$)] for the reaction muscovite + H^+ + 1.5 H_2O ⇌ 1.5 kaolinite + K^+ between 0 and 350°C at 1 kb.

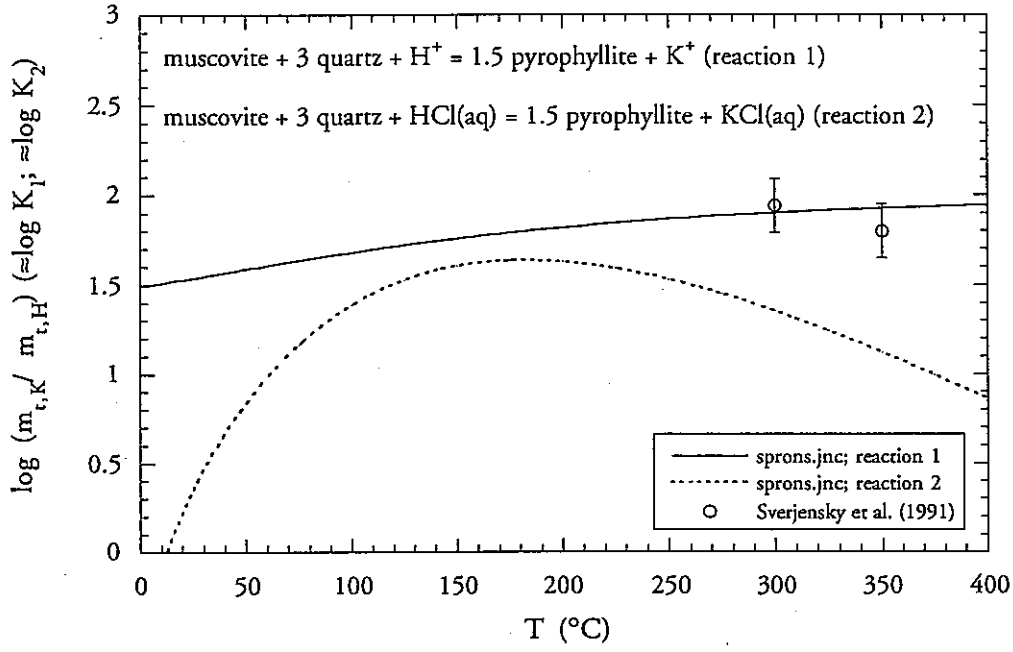


Fig. C.33: Logarithm of the equilibrium constant [≈ log ($m_{t,K}/m_{t,H}$)] for reactions in the system K_2O-Al_2O_3-SiO_2-HCl between 0 and 400°C at 1 kb.

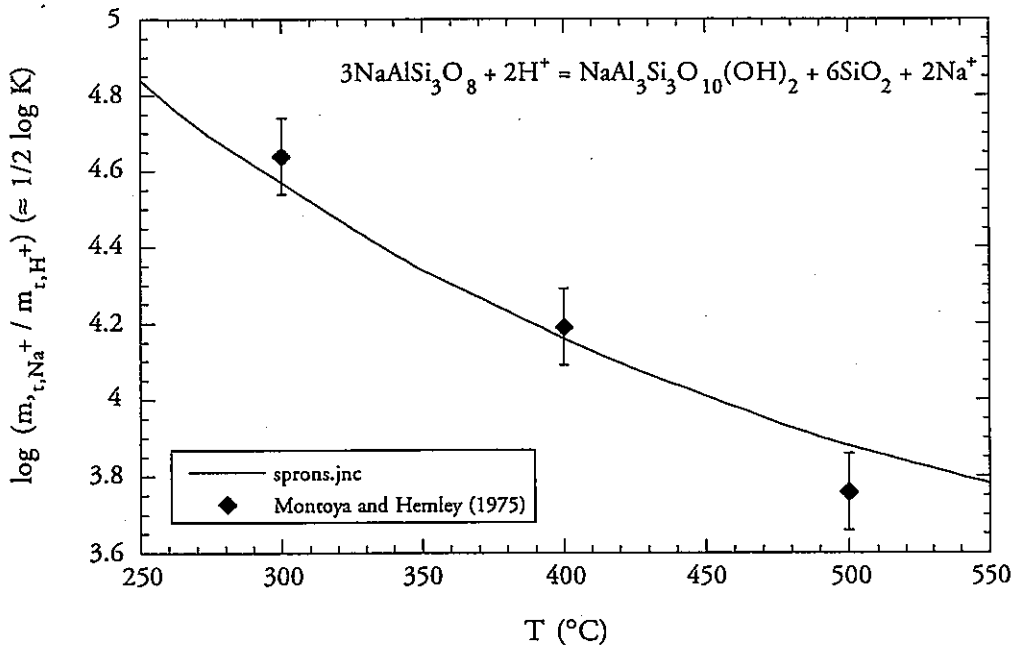


Fig. C.34: Logarithm of the equilibrium constant [≈ 2 (log $m_{t,Na}/m_{t,H}$)] for the reaction 3 albite + 2 H^+ ⇌ paragonite + 6 quartz + 2 Na^+ between 250 and 550°C at 1 kb.

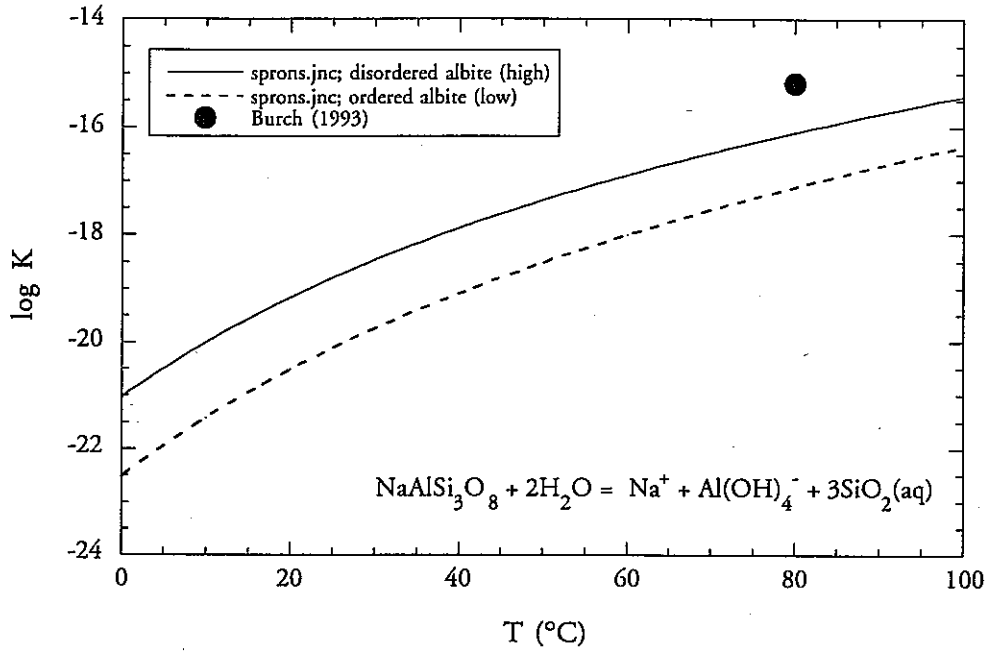


Fig. C.35: Logarithm of the equilibrium constant for the reaction albite + 2 H_2O ⇄ $Al(OH)_4^-$ + 3 SiO_2*(aq)* + Na^+ between 0 and 100°C at 1 bar.

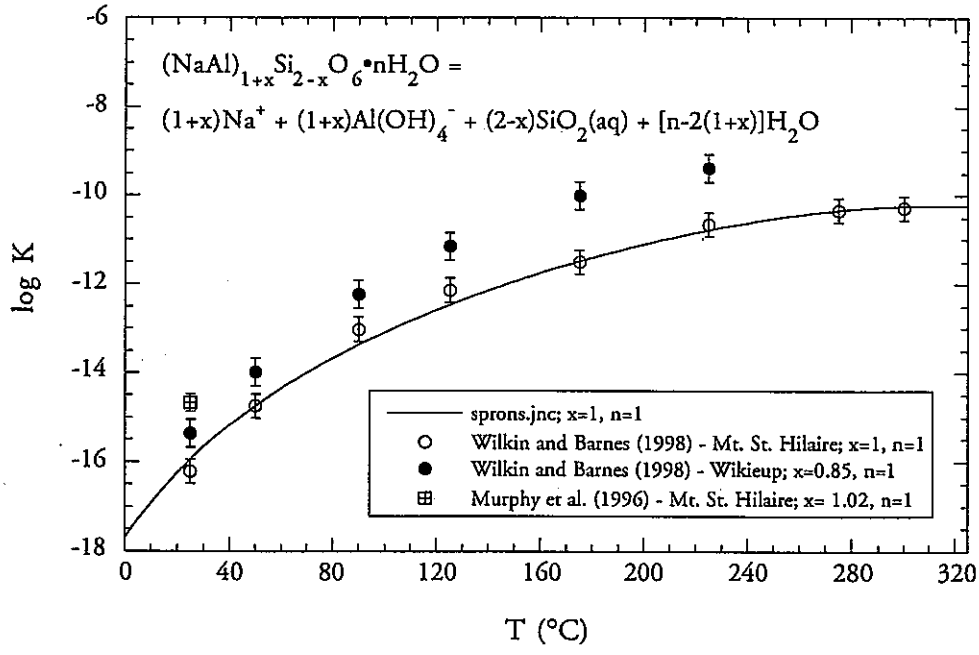


Fig. C.36: Logarithm of the equilibrium constant for the analcime hydrolysis reaction between 0 and 300°C at *Psat*.

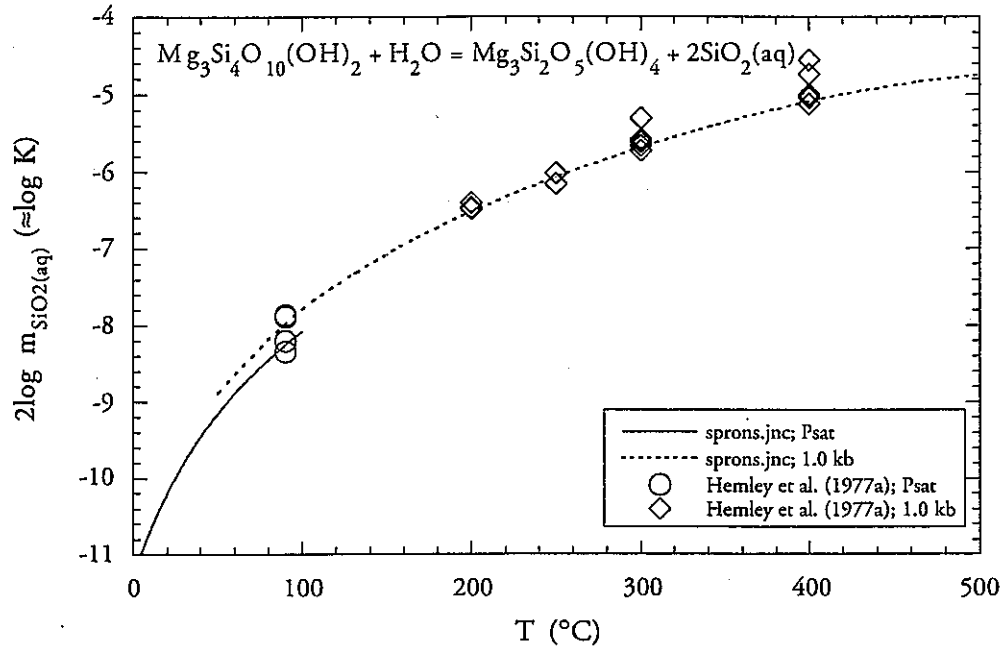


Fig. C.37: Logarithm of the equilibrium constant [≈ 2 log $m_{SiO2(aq)}$] for the reaction talc + H_2O ⇄ chrysotile + 2 SiO_2*(aq)* between 0 and 500°C at *Psat* and 1 kb.

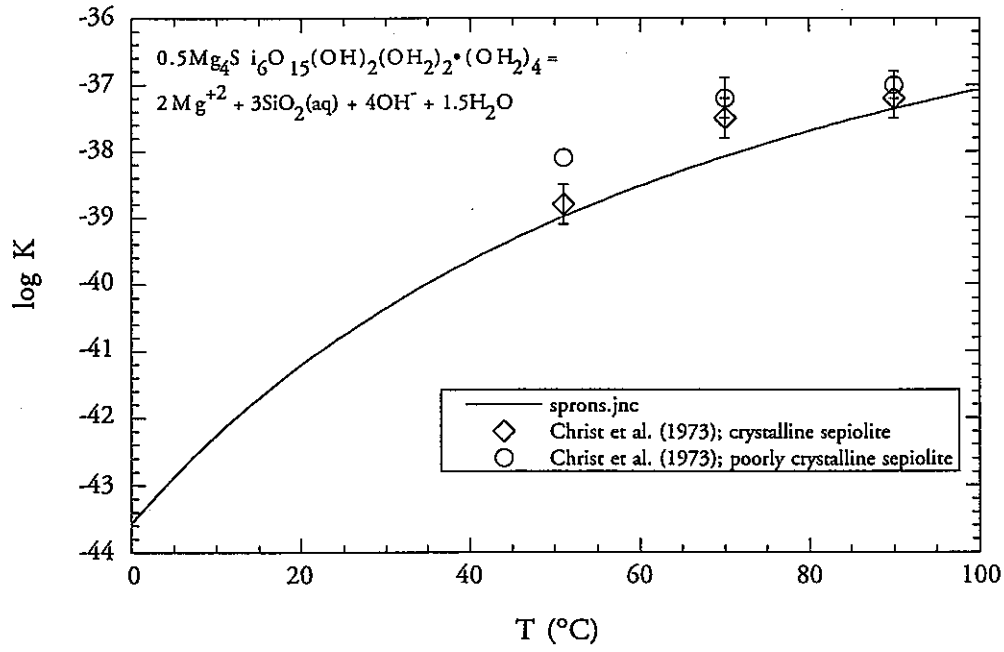


Fig. C.38: Logarithm of the equilibrium constant for the reaction sepiolite ⇄ 2 Mg^{2+} + 3 SiO_2*(aq)* + 4 OH^- + 1.5 H_2O between 0 and 100°C at 1 bar.

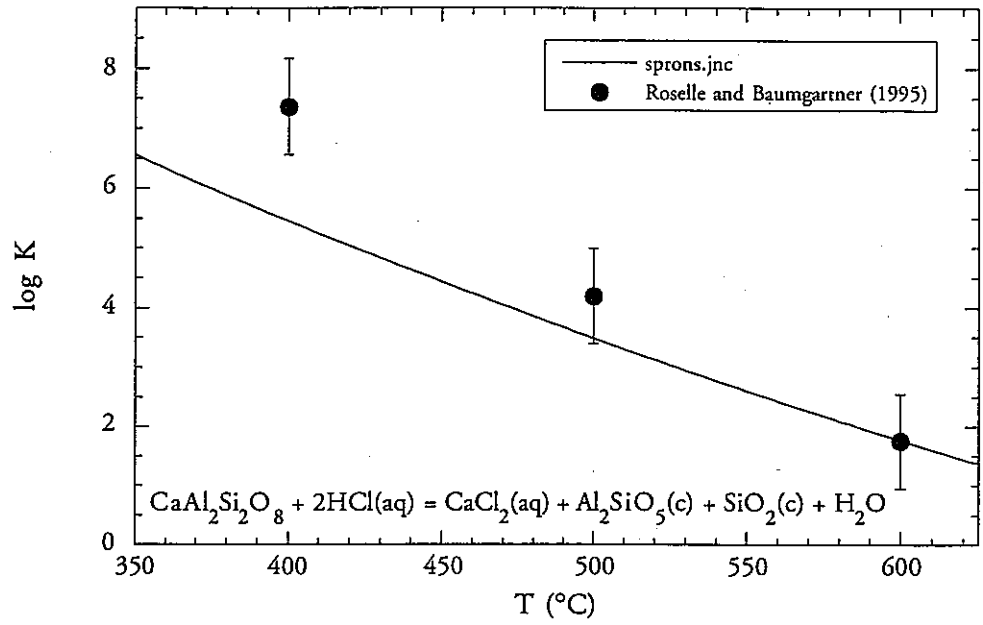


Fig. 39: Logarithm of the equilibrium constant for the reaction anorthite + 2 HCl*(aq)* ⇌ $CaCl_2$*(aq)* + andalusite + quartz + H_2O between 350 and 625°C at 2 kb.

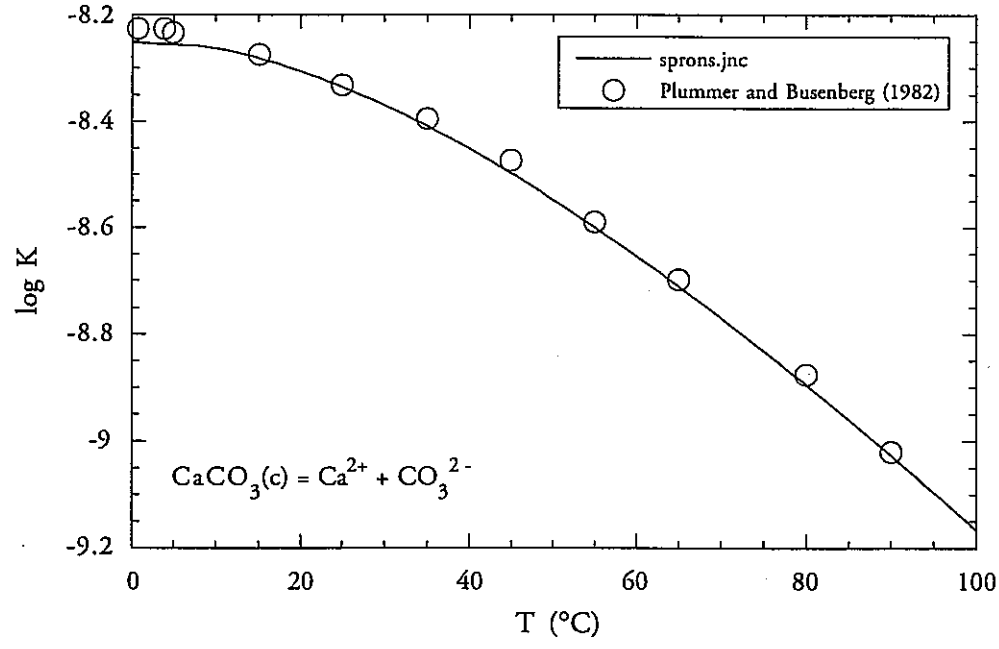


Fig C.40: Logarithm of the solubility product of aragonite between 0 and 100°C at 1 bar.

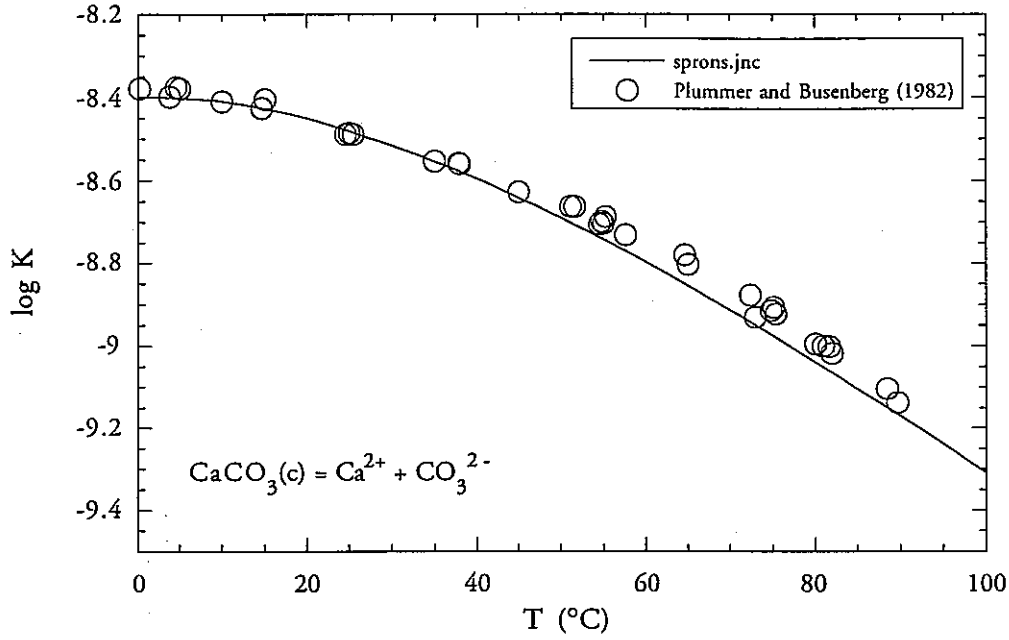


Fig C.41: Logarithm of the solubility product of calcite between 0 and 100°C at 1 bar.

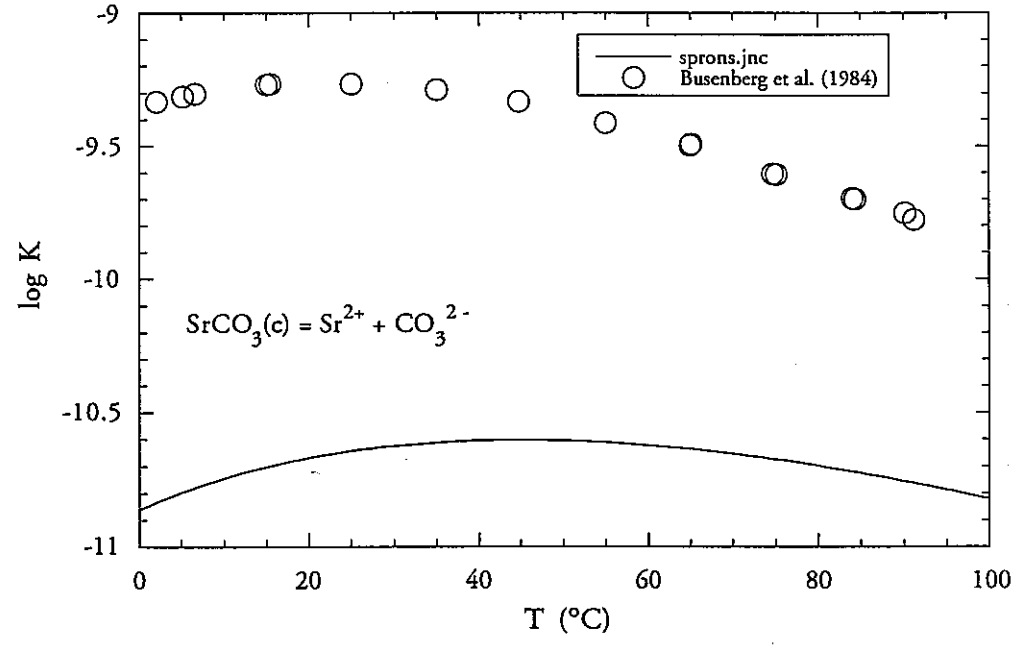


Fig C.42: Logarithm of the solubility product of strontianite between 0 and 100°C at 1 bar.

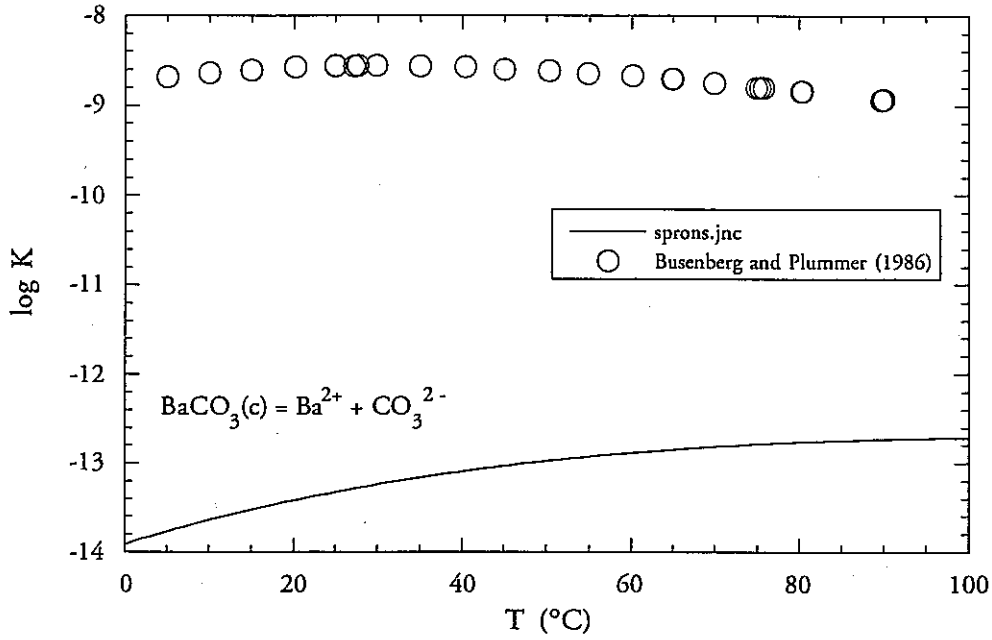


Fig C.43: Logarithm of the solubility product of witherite between 0 and 100°C at 1 bar.

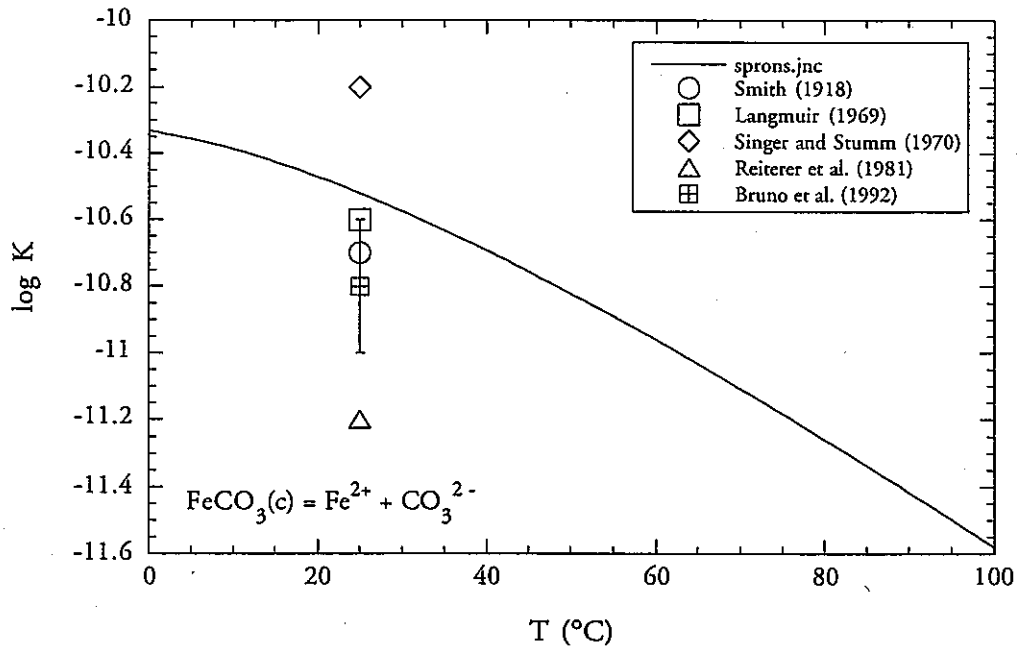


Fig C.44: Logarithm of the solubility product of siderite between 0 and 100°C at 1 bar.

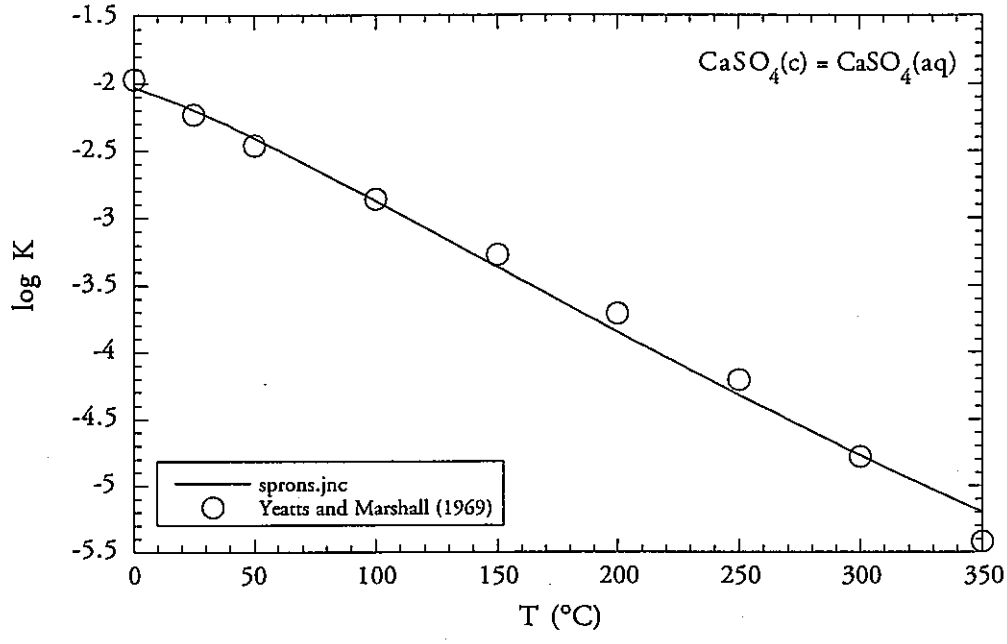


Fig C.45: Logarithm of the equilibrium constant for the reaction $CaSO_4$ (anhydrite) ⇌ $CaSO_4$*(aq)* between 0 and 350°C at *Psat*.

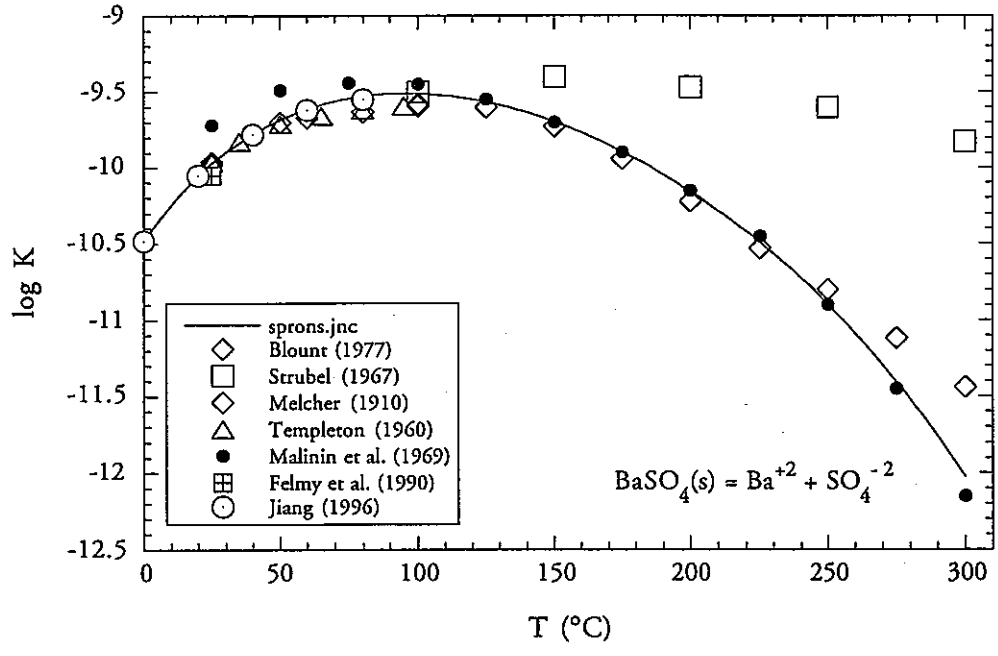


Fig C.46: Logarithm of the solubility product of barite between 0 and 300°C at *Psat*.

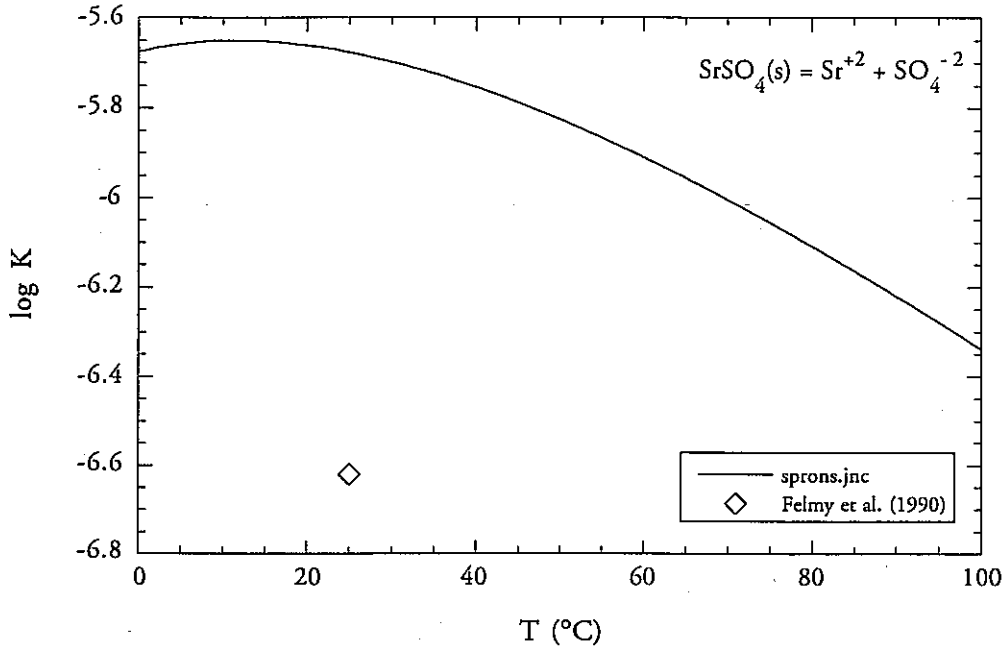


Fig C.47: Logarithm of the solubility product of celestite between 0 and 100°C at 1 bar.

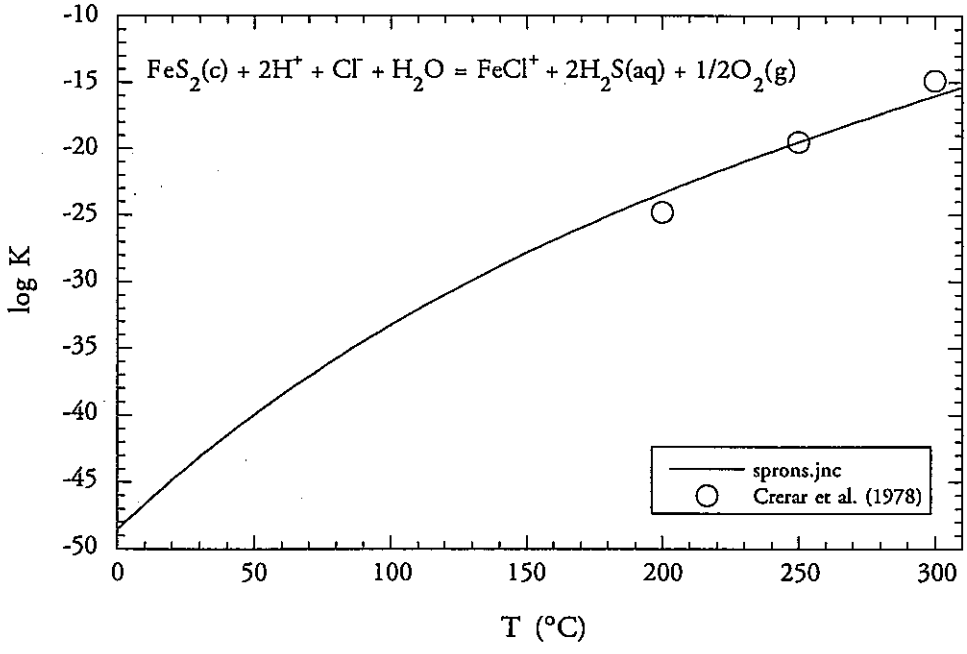


Fig C.48: Logarithm of the equilibrium constant for the reaction pyrite + 2 H^+ + Cl^- + H_2O ⇄ $FeCl^+$ + 2 $H_2S(aq)$ + 1/2 $O_2(g)$ between 0 and 300°C at *Psat*.

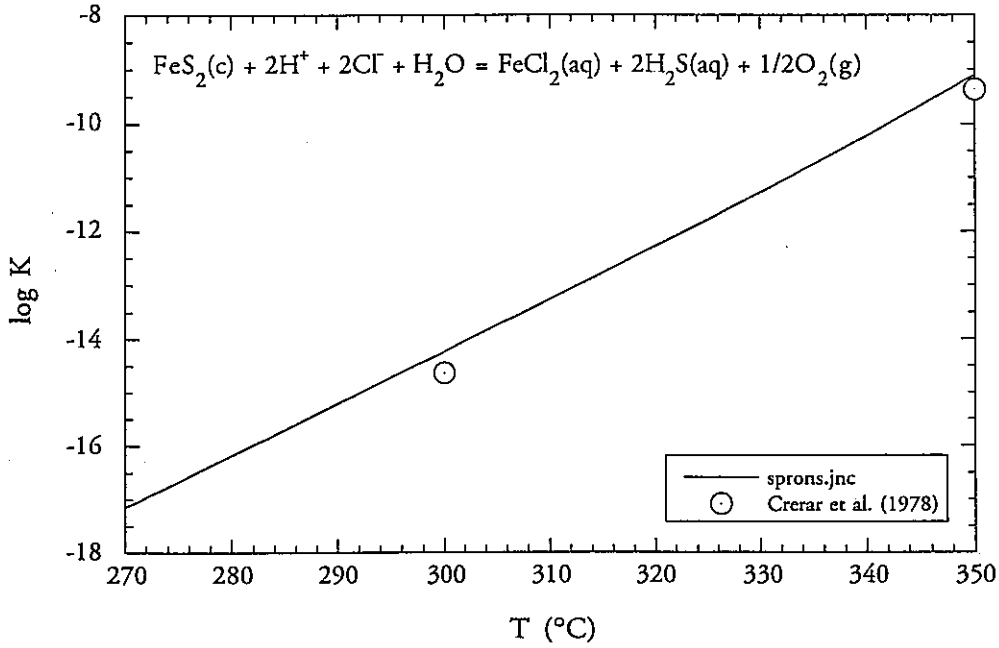


Fig C.49: Logarithm of the equilibrium constant for the reaction pyrite + 2 H^+ + 2 Cl^- + H_2O ⇌ $FeCl_2$*(aq)* + 2 H_2S*(aq)* + 1/2 O_2*(g)* between 270 and 350°C at *Psat*.

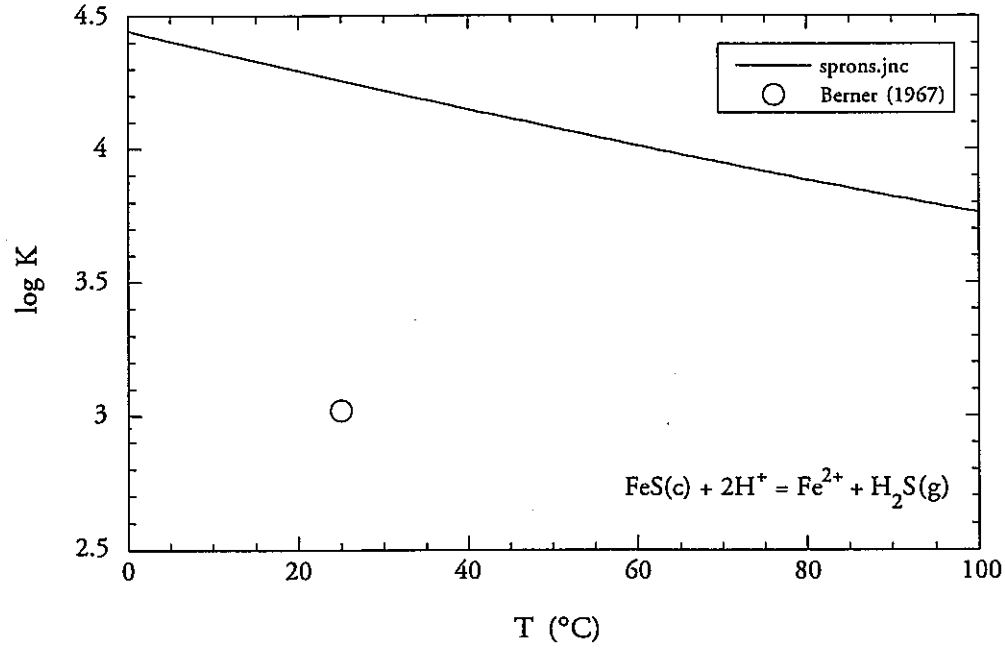


Fig C.50: Logarithm of the equilibrium constant for the reaction pyrrhotite + 2 H^+ ⇌ Fe^{2+} + H_2S*(aq)* between 0 and 100°C at 1 bar [calculated in the present study using log *K* = -21.9 at 25°C (Maronny, 1959) for the reaction H_2S*(g)* ⇌ 2 H^+ + S^{2-})].

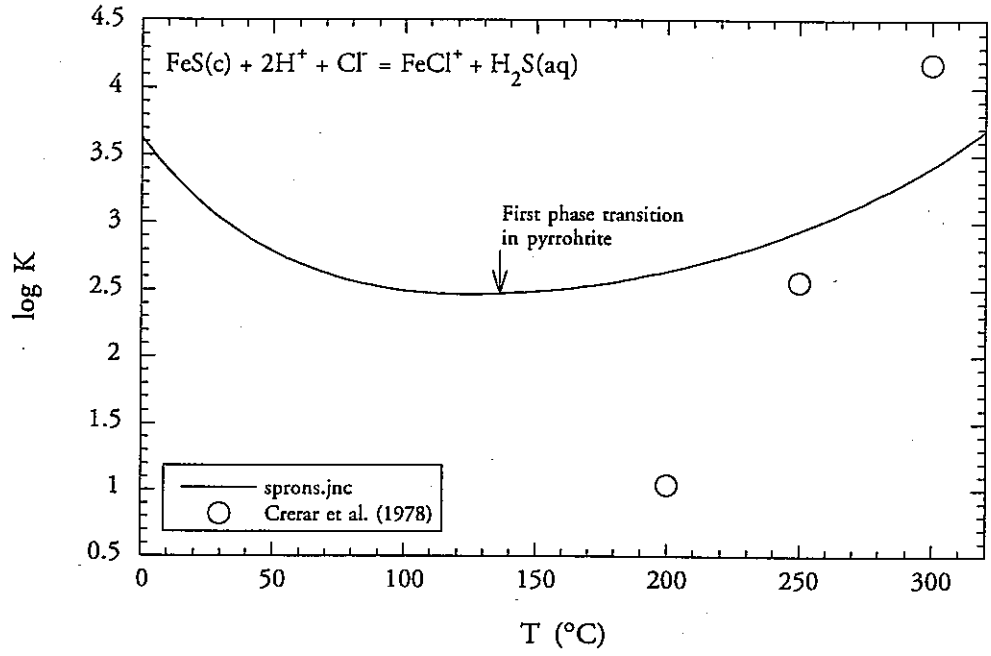


Fig C.51: Logarithm of the equilibrium constant for the reaction pyrrhotite + 2 H^+ + Cl^- ⇄ $FeCl^+$ + $H_2S(aq)$ between 0 and 300°C at *Psat*.

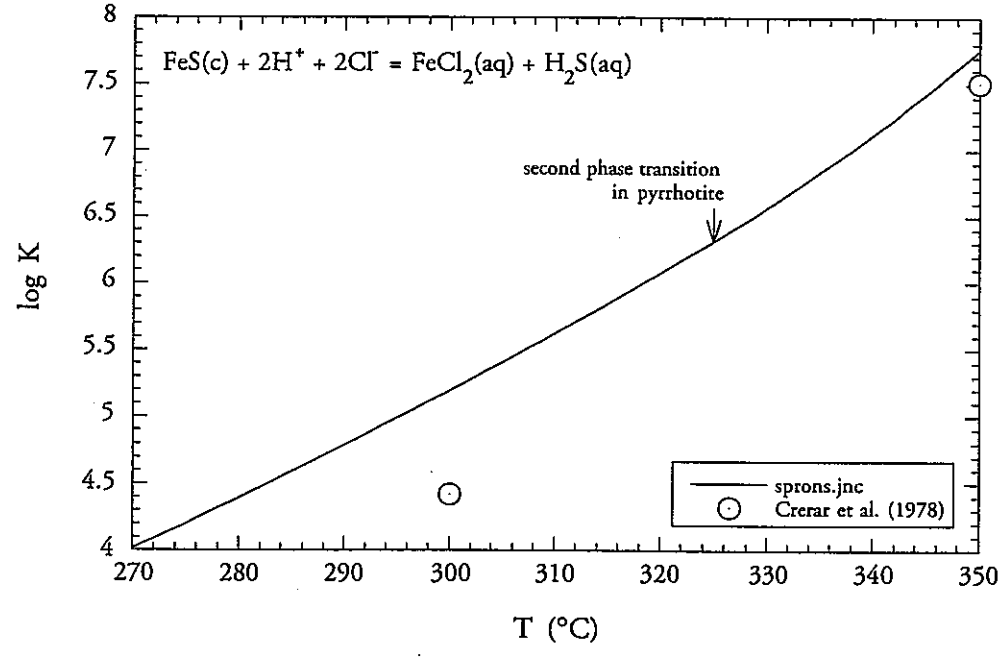


Fig C.52: Logarithm of the equilibrium constant for the reaction pyrrhotite + 2 H^+ + 2 Cl^- ⇄ $FeCl_2(aq)$ + $H_2S(aq)$ between 270 and 350°C at *Psat*.

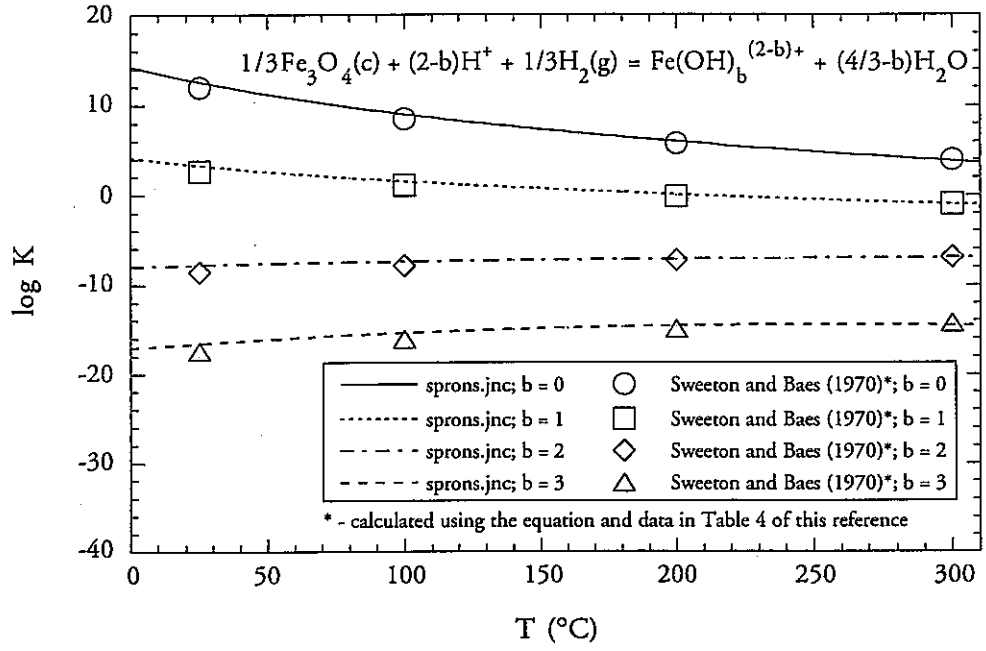


Fig C.53: Logarithm of the equilibrium constant for the reaction 1/3 magnetite + (2-b) H^+ + 1/3 $H_2(g)$ ⇄ $Fe(OH)_b^{(2-b)+}$ + (4/3-b) H_2O (b = 0, 1, 2, 3) between 0 and 300°C at *Psat*.

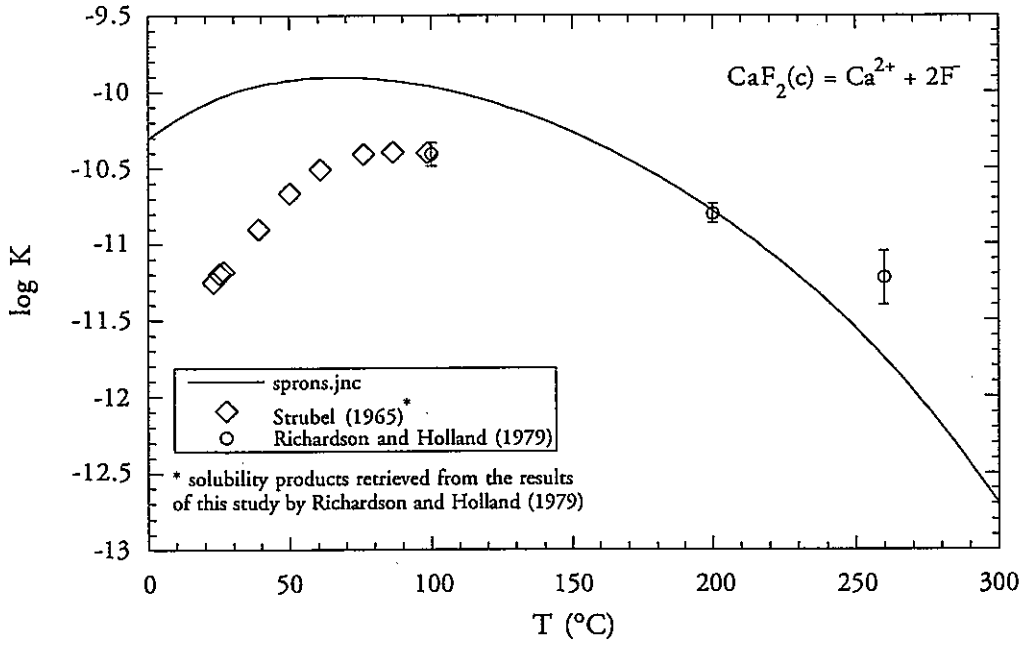


Fig C.54: Logarithm of the solubility product of fluorite between 0 and 300°C at *Psat*.

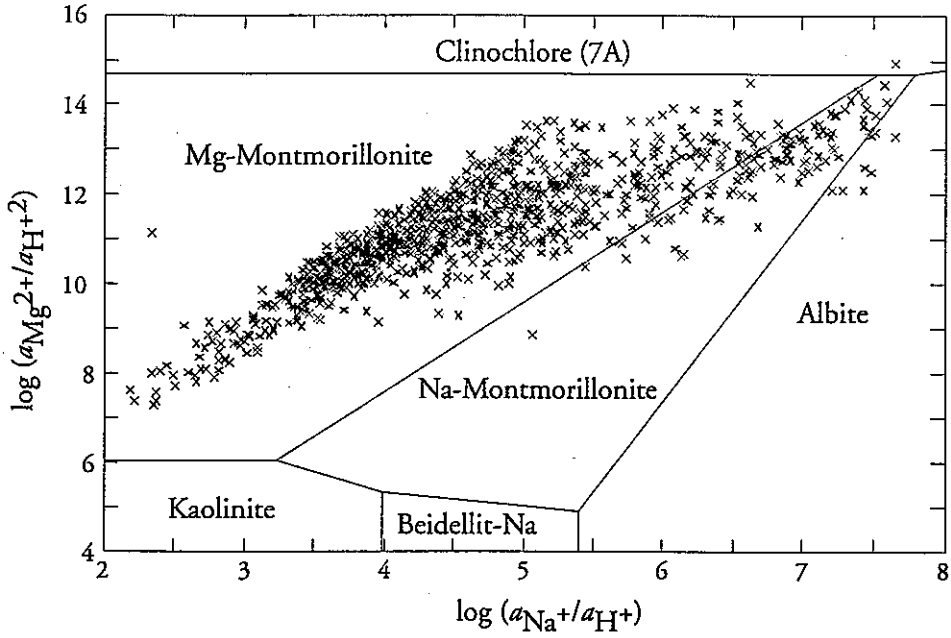


Fig. C.55: Stability relations among minerals and aqueous solutions in the system Na_2O-MgO-Al_2O_3-SiO_2-H_2O at 19°C and 1 bar. Symbols represent compositions of deep groundwaters in Japan (≈ 1000 samples).

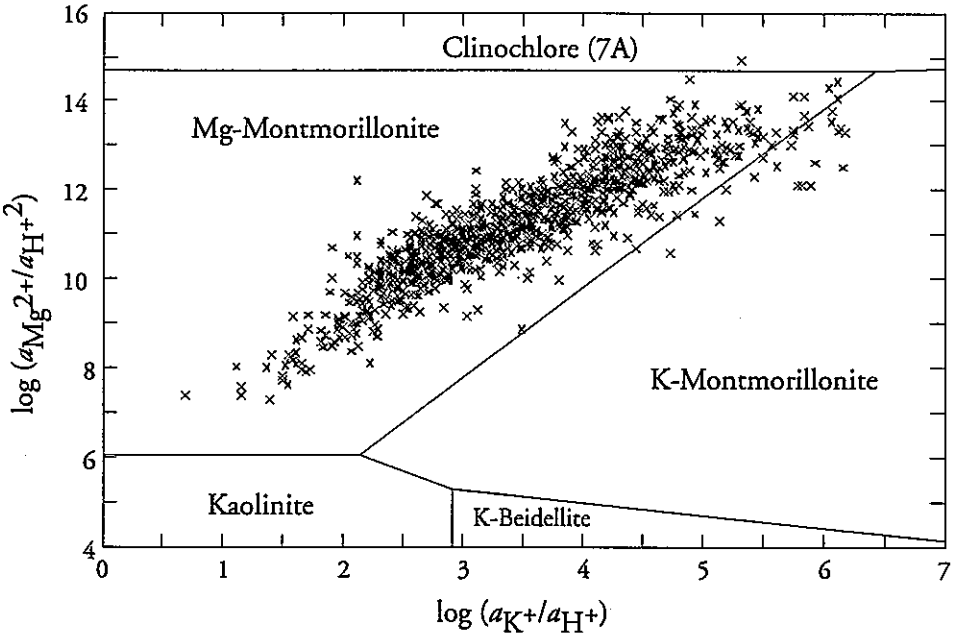


Fig. C.56: Stability relations among minerals and aqueous solutions in the system K_2O-MgO-Al_2O_3-SiO_2-H_2O at 19°C and 1 bar. Symbols represent compositions of deep groundwaters in Japan (≈ 1000 samples).

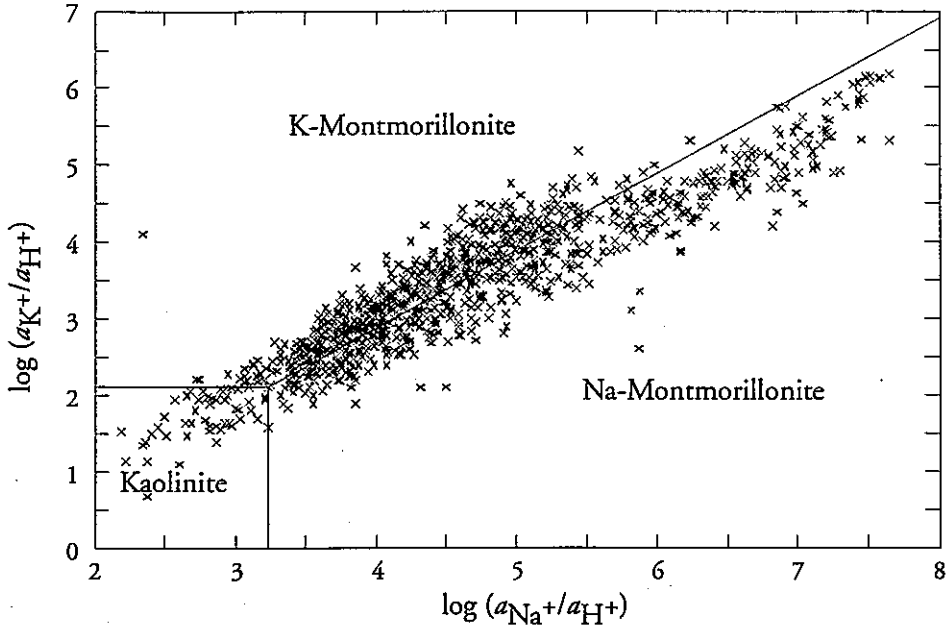


Fig. C.57: Stability relations among minerals and aqueous solutions in the system Na_2O- K_2O- MgO-Al_2O_3-SiO_2-H_2O at 19°C and 1 bar. Symbols represent compositions of deep groundwaters in Japan (≈ 1000 samples).

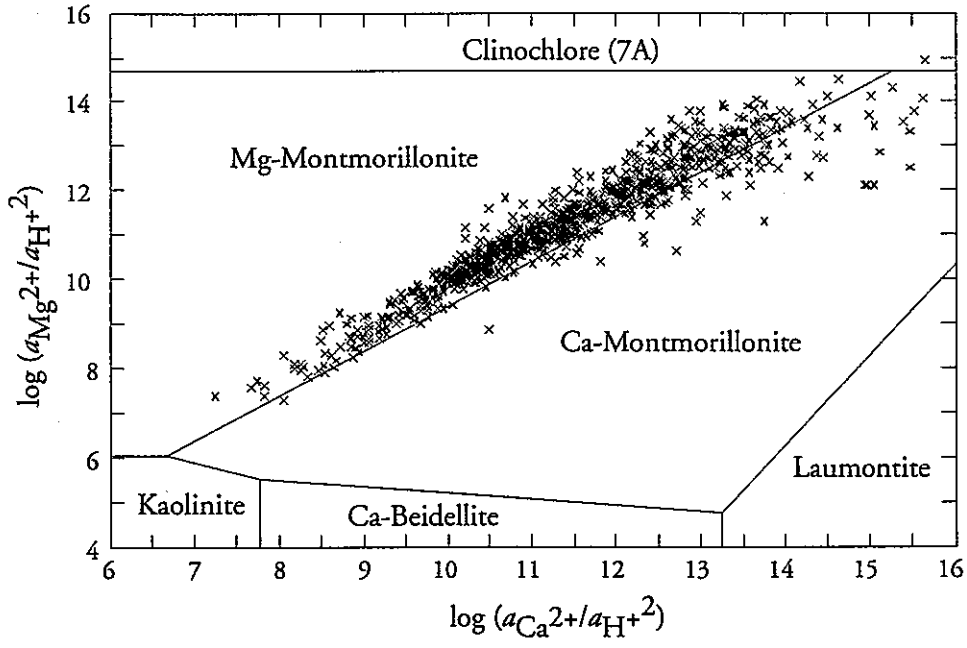


Fig. C.58: Stability relations among minerals and aqueous solutions in the system CaO-MgO-Al_2O_3-SiO_2-H_2O at 19°C and 1 bar. Symbols represent compositions of deep groundwaters in Japan (≈ 1000 samples).

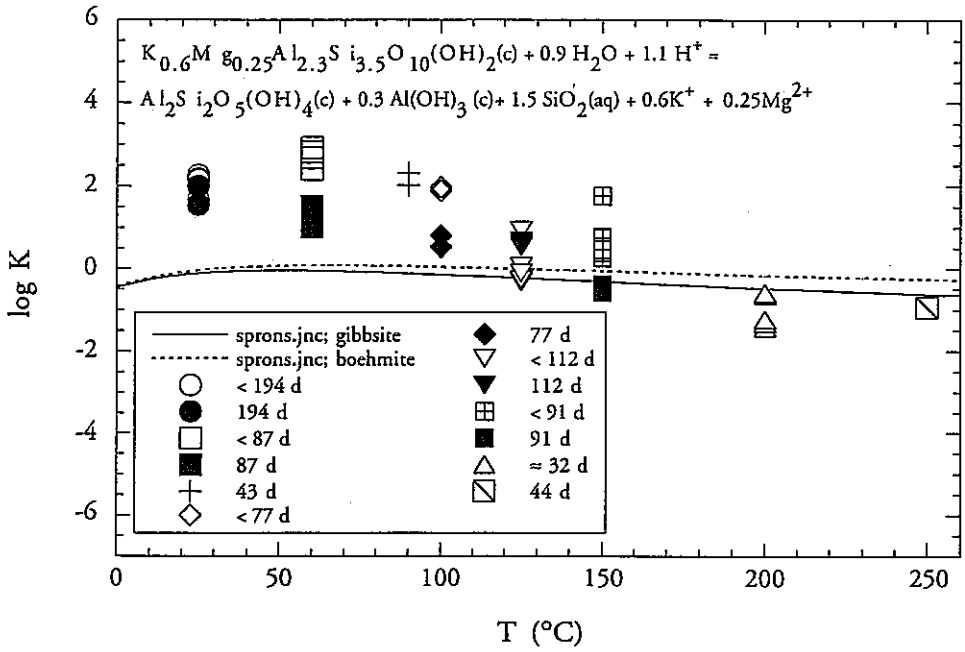


Fig C.59: Logarithm of the equilibrium constant for the reaction illite + 0.9 H_2O + 1.1 H^+ ⇌ kaolinite + gibbsite + 1.5 SiO_2*(aq)* + 0.6 K^+ + 0.25 Mg^{2+} between 0 and 250°C at *Psat* [experimental data from Aja *et al.* (1991b)].

Appendix D: Calculated and Experimental Equilibrium Constants of Aqueous Reactions as Functions of Pressure and Temperature

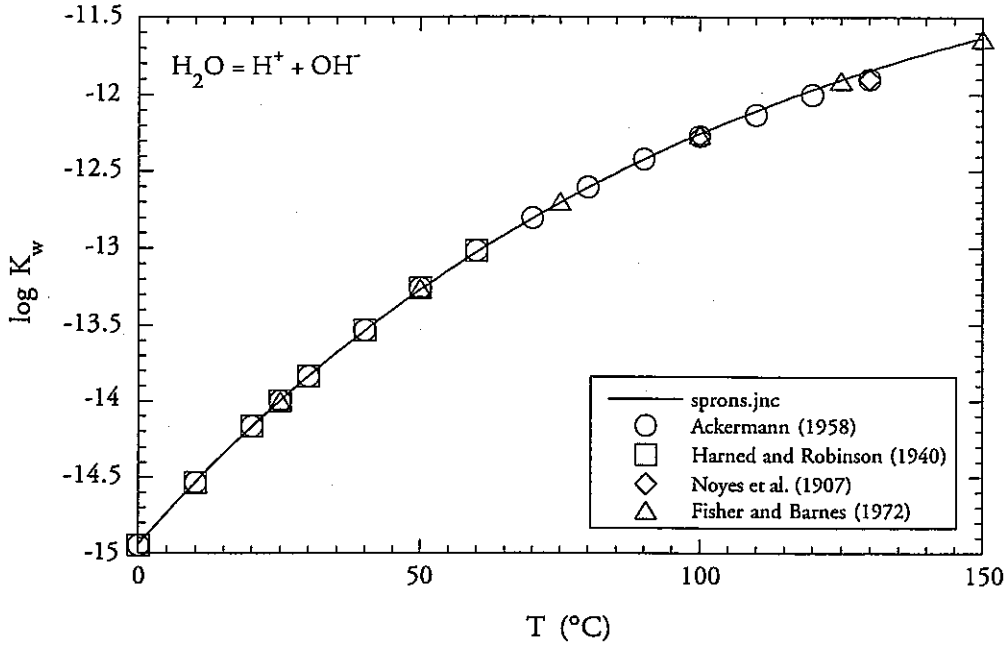


Fig. D.1: Logarithm of the equilibrium constant for the reaction $H_2O \rightleftharpoons H^+ + OH^-$ between 0 and 150°C at *Psat*.

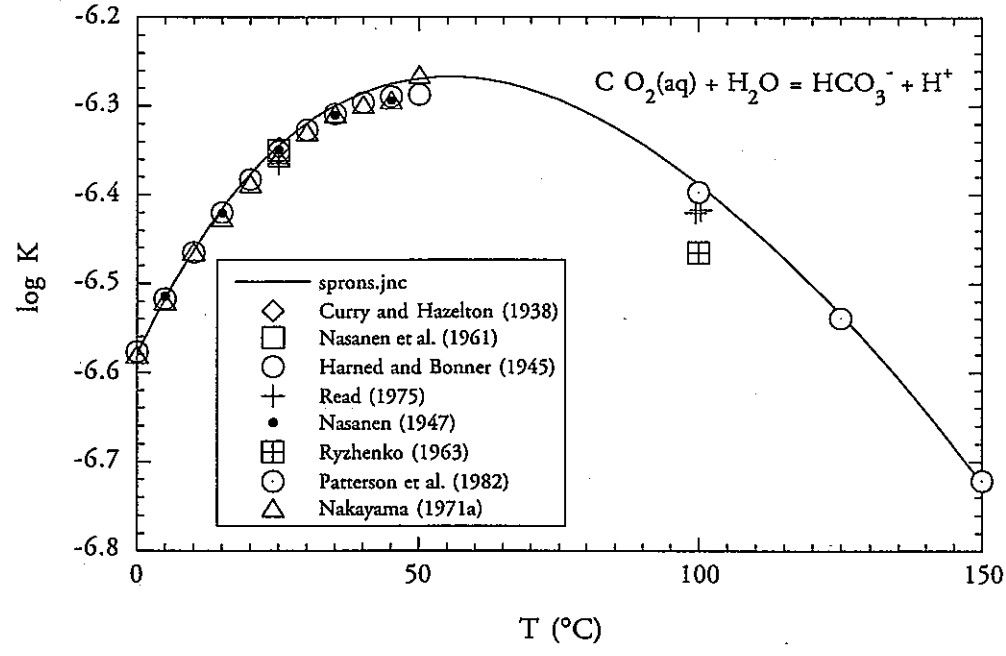


Fig. D.2: Logarithm of the equilibrium constant for the reaction $CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + H^+$ between 0 and 150°C at *Psat*.

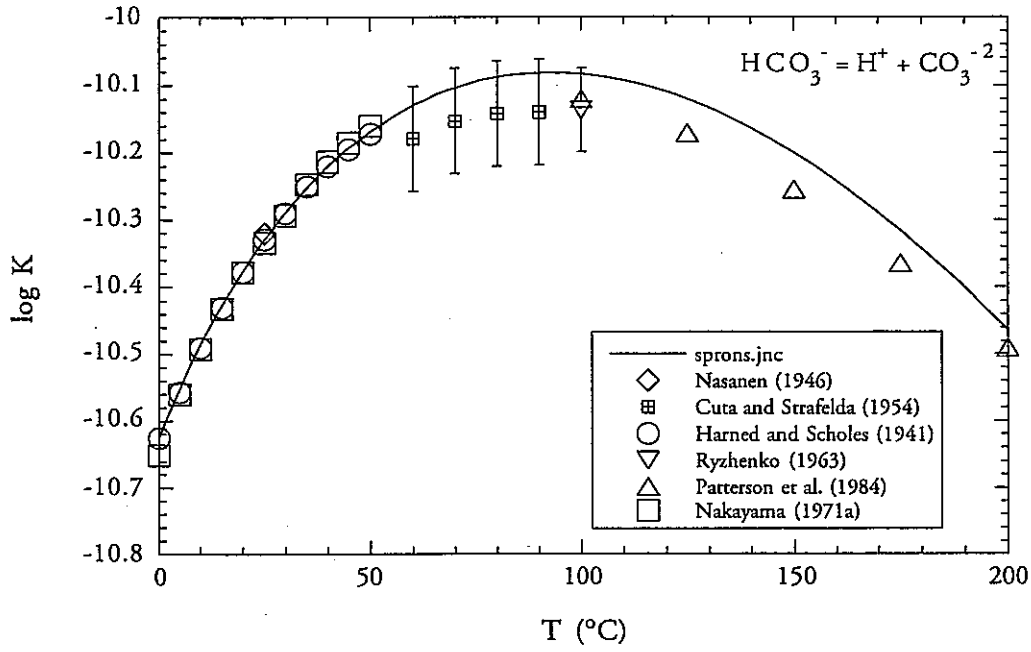


Fig. D.3: Logarithm of the equilibrium constant for the reaction HCO_3^- ⇌ H+ CO_3^{2-} between 0 and 200°C at *Psat*.

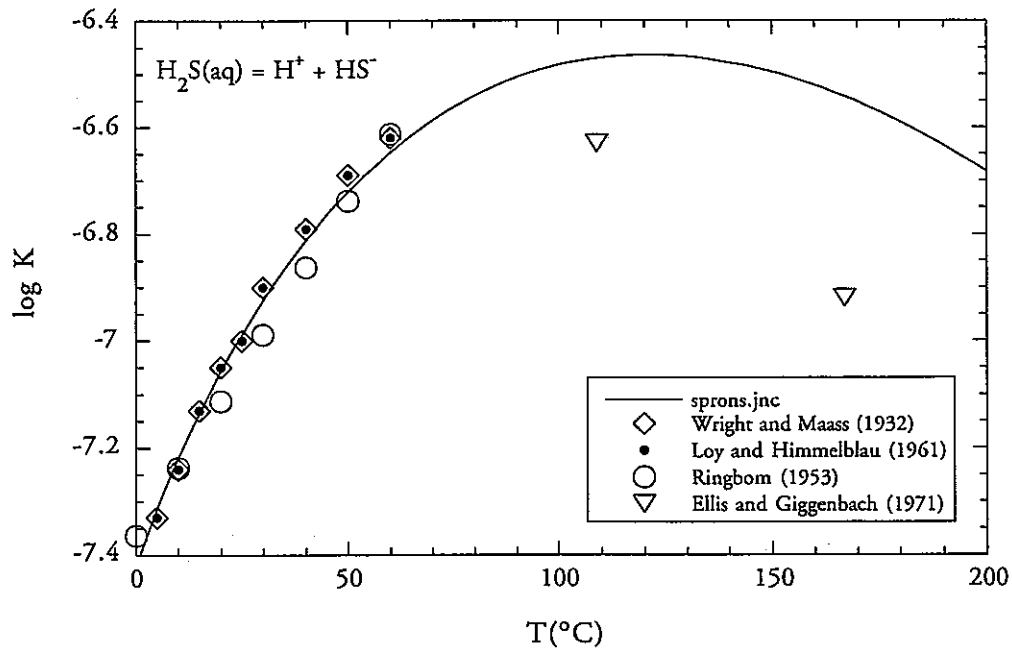


Fig. D.4: Logarithm of the equilibrium constant for the reaction $H_2S(aq)$ ⇌ H+ + HS- between 0 and 200°C at *Psat*.

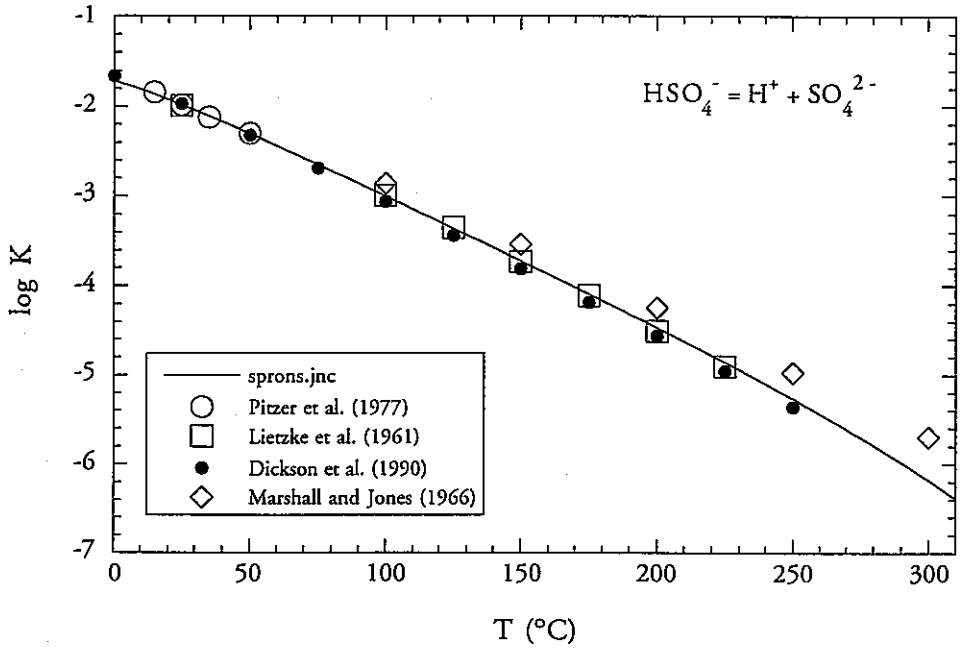


Fig. D.5: Logarithm of the equilibrium constant for the reaction $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$ between 0 and 300°C at *Psat*.

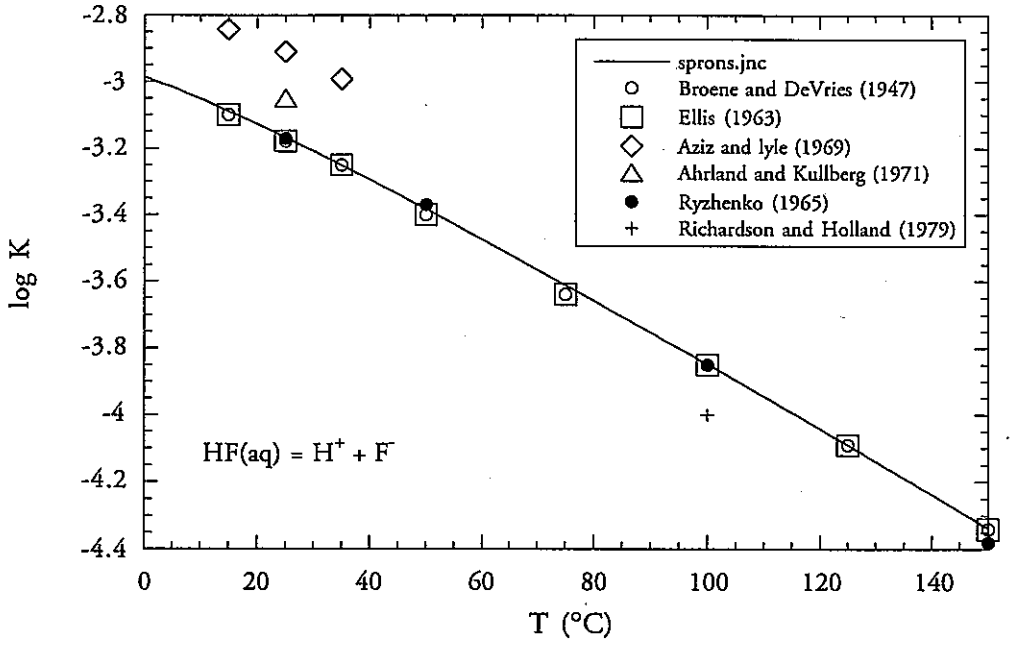


Fig. D.6: Logarithm of the equilibrium constant for the reaction $HF(aq) \rightleftarrows H^+ + F^-$ between 0 and 150°C at *Psat*.

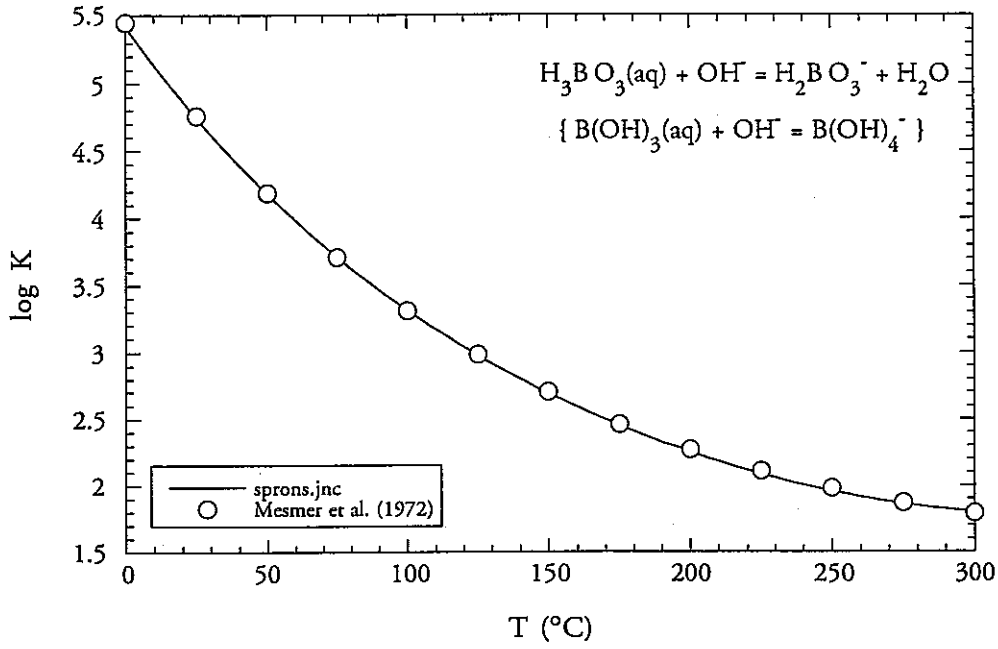


Fig. D.7: Logarithm of the equilibrium constant for the reaction H_3BO_3*(aq)* + OH^- ⇄ $H_2BO_3^-$ + H_2O between 0 and 300°C at *Psat.*

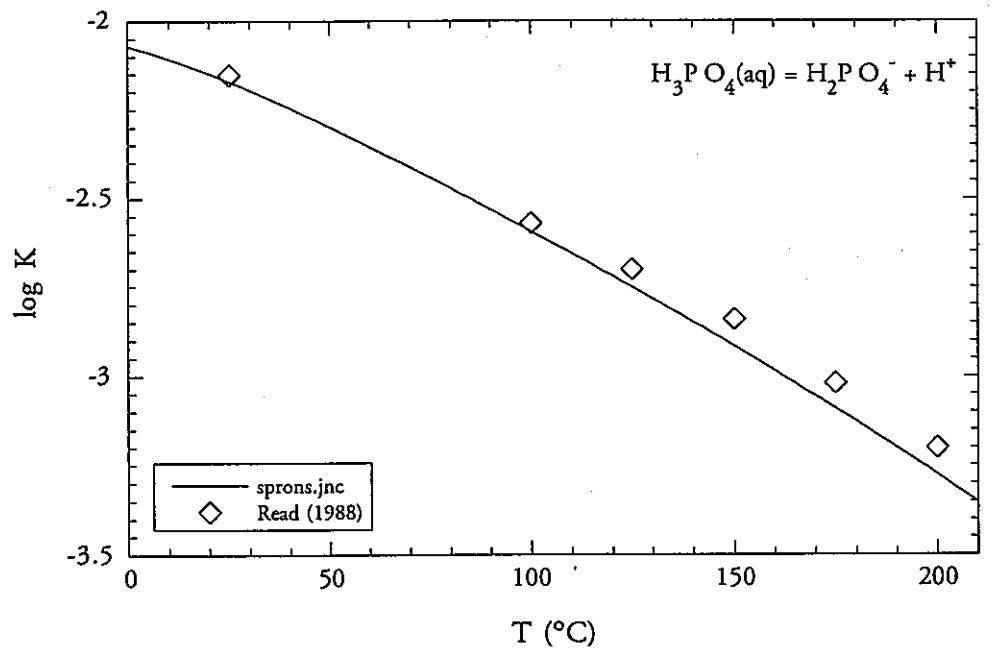


Fig. D.8: Logarithm of the equilibrium constant for the reaction H_3PO_4*(aq)* ⇄ $H_2PO_4^-$ + H^+ between 0 and 200°C at *Psat.*

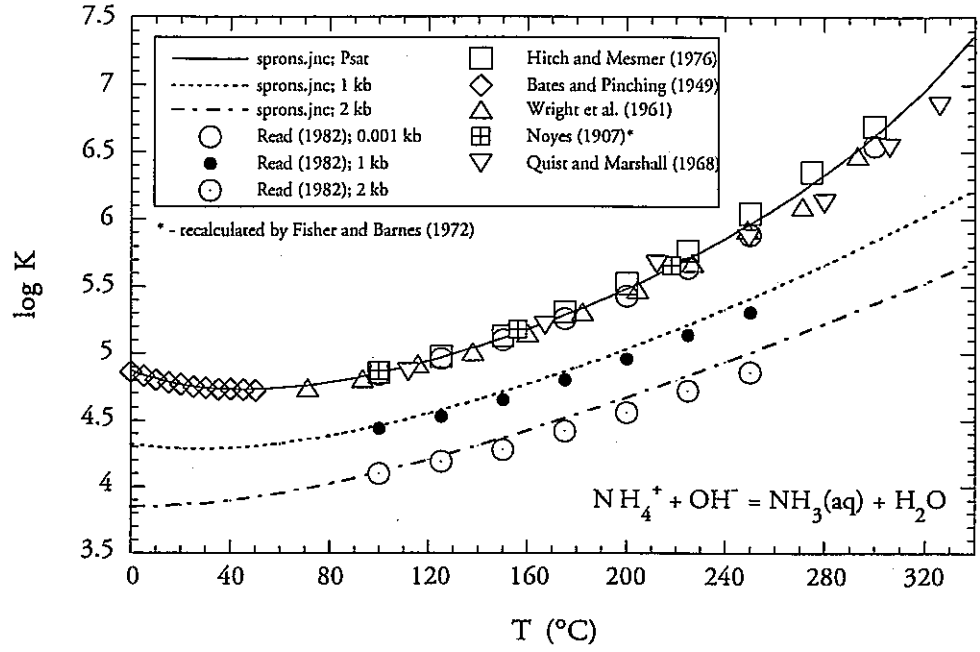


Fig. D.9: Logarithm of the equilibrium constant for the reaction $NH_4^+ + OH^- \rightleftharpoons NH_3(aq) + H_2O$ between 0 and 310°C and pressures from *Psat* to 2 kb.

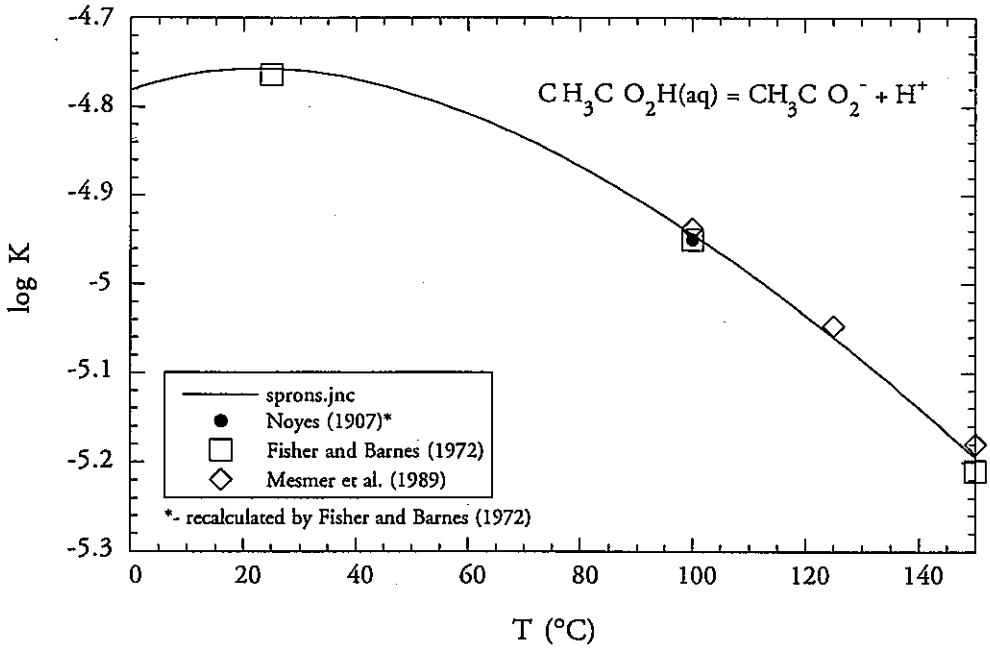


Fig. D.10: Logarithm of the equilibrium constant for the reaction $CH_3COOH \rightleftharpoons CH3COO^- + H^+$ between 0 and 150°C at *Psat*.

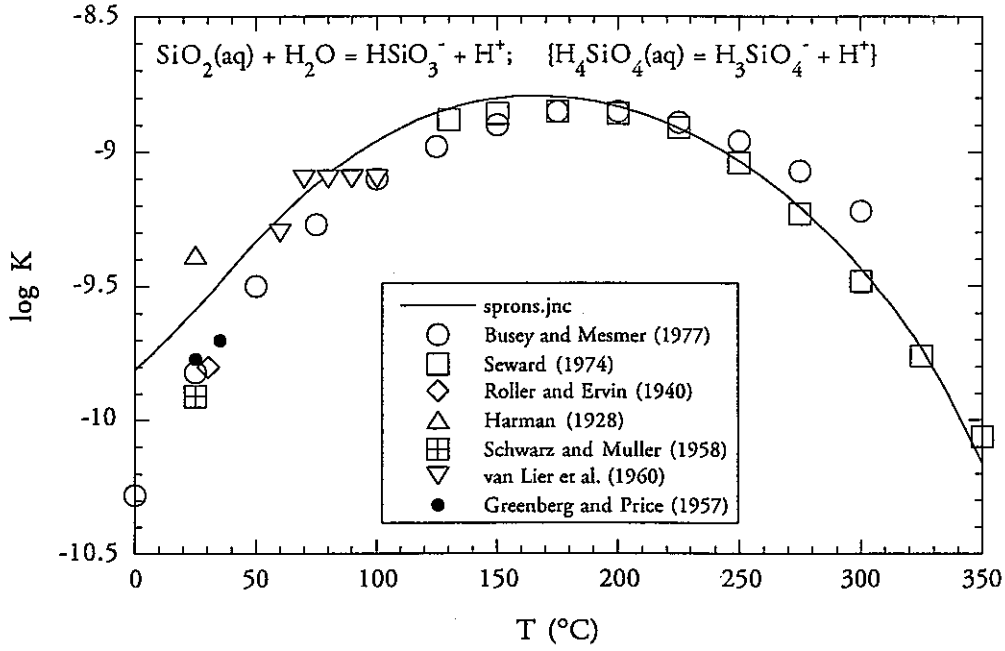


Fig. D.11: Logarithm of the equilibrium constant for the reaction H_4SiO_4*(aq)* ⇄ $H_3SiO_4^-$ + H^+ between 0 and 350°C at *Psat.*

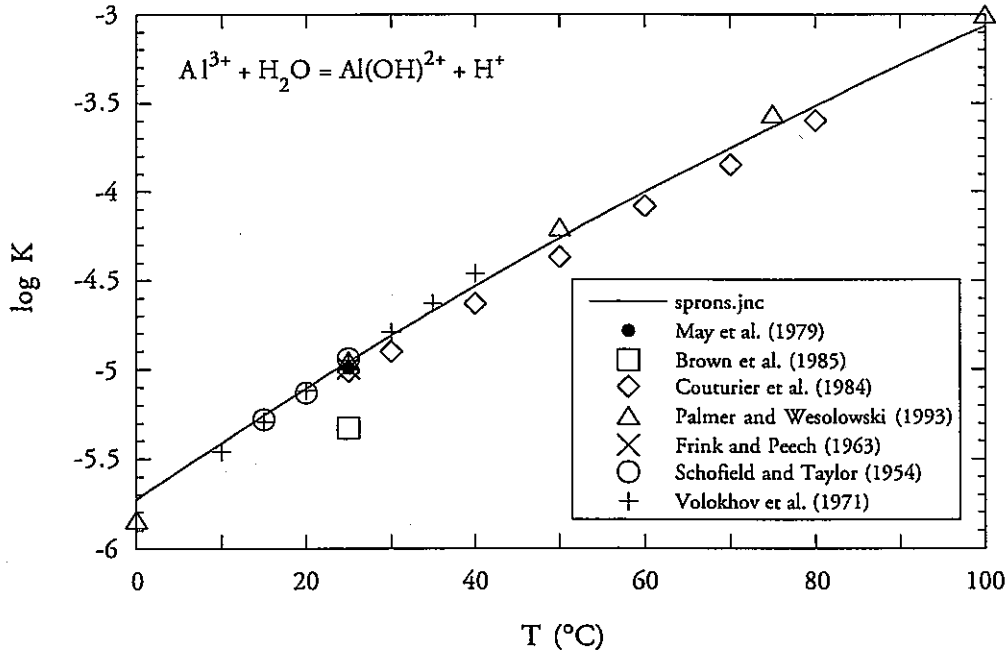


Fig. D.12: Logarithm of the equilibrium constant for the reaction Al^{3+} + H_2O ⇄ $AlOH^{2+}$ + H^+ between 0 and 100°C at 1 bar.

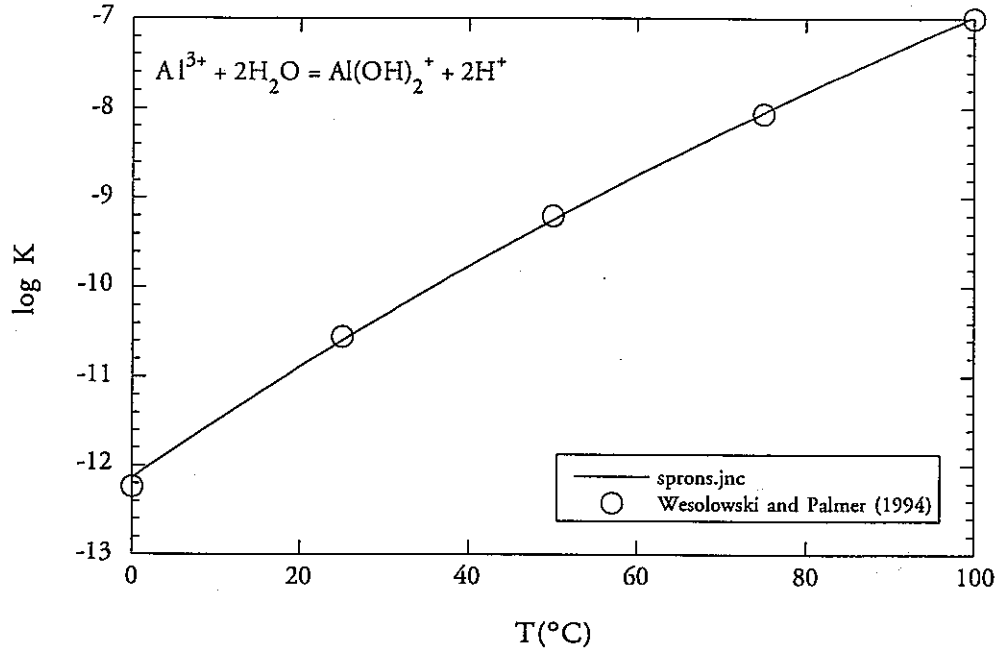


Fig. D.13: Logarithm of the equilibrium constant for the reaction $Al^{3+} + 2\ H_2O \rightleftharpoons Al(OH)_2^+ + 2\ H^+$ between 0 and 100°C at 1 bar.

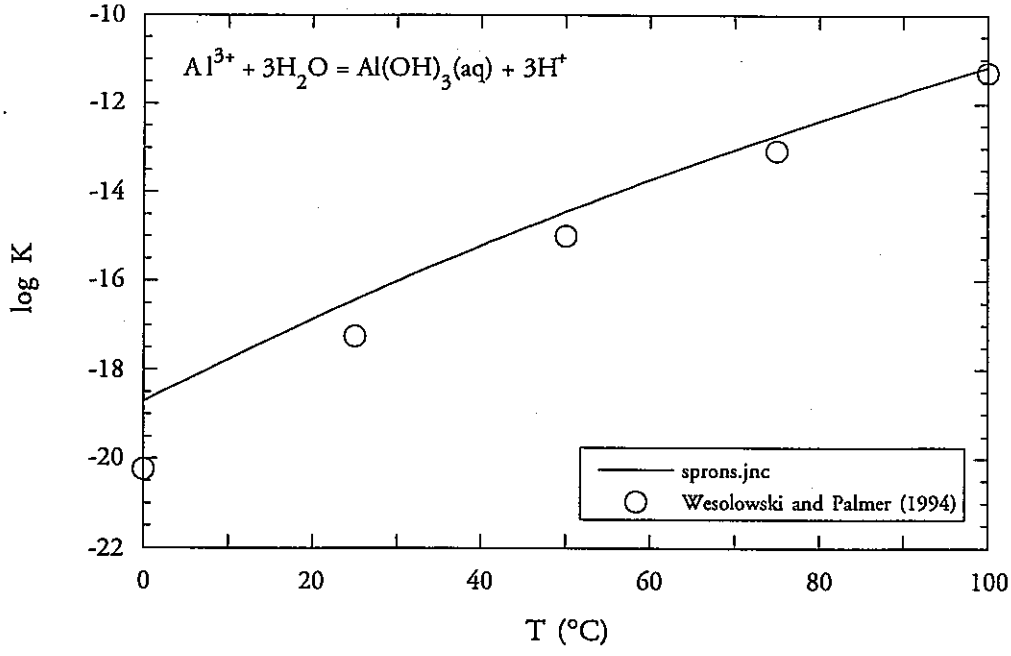


Fig. D.14: Logarithm of the equilibrium constant for the reaction $Al^{3+} + 3\ H_2O \rightleftharpoons Al(OH)_3(aq) + 3\ H^+$ between 0 and 100°C at 1 bar.

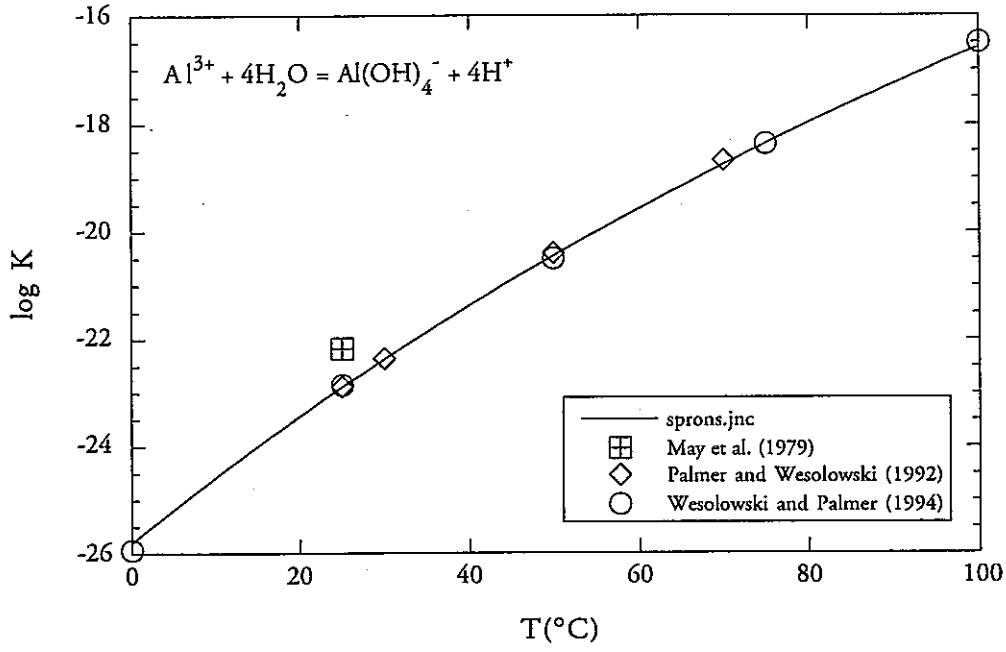


Fig. D.15: Logarithm of the equilibrium constant for the reaction $Al^{3+} + 4\ H_2O \rightleftarrows Al(OH)_4^- + 4\ H^+$ between 0 and 100°C at 1 bar.

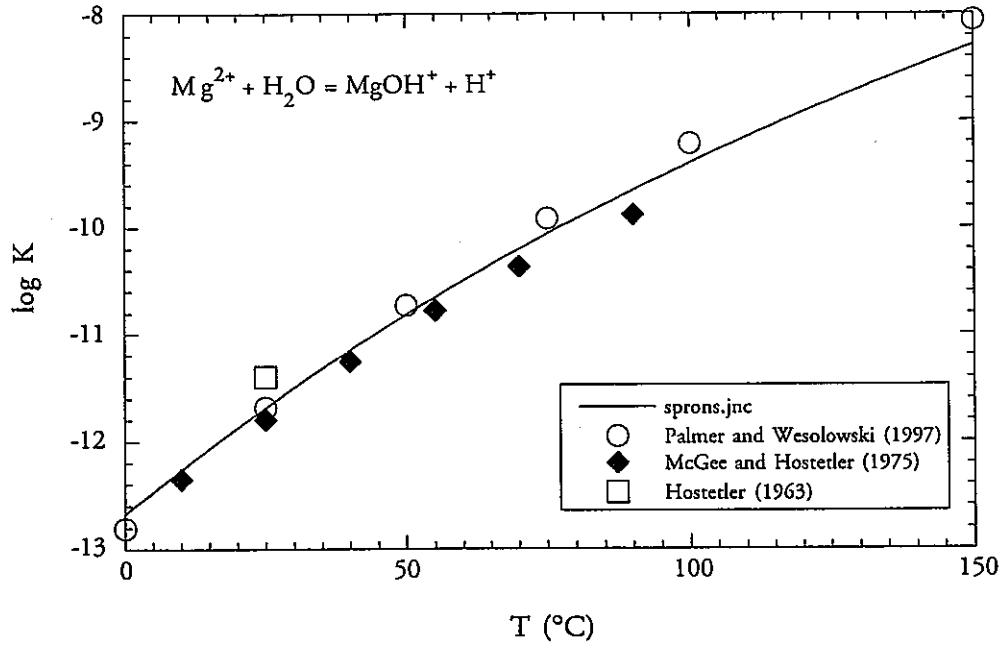


Fig. D.16: Logarithm of the equilibrium constant for the reaction $Mg^{2+} + H_2O \rightleftarrows MgOH^+ + H^+$ between 0 and 150°C at *Psat*.

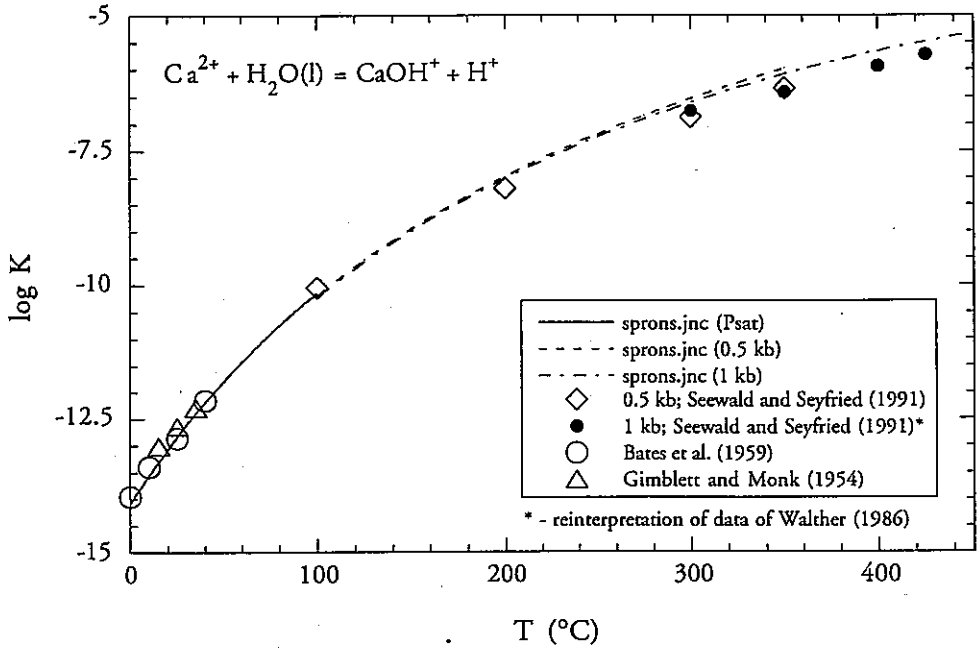


Fig. D.17: Logarithm of the equilibrium constant for the reaction $Ca^{2+} + H_2O \rightleftharpoons CaOH^+ + H^+$ between 0 and 450°C and pressures from *Psat* to 1 kb.

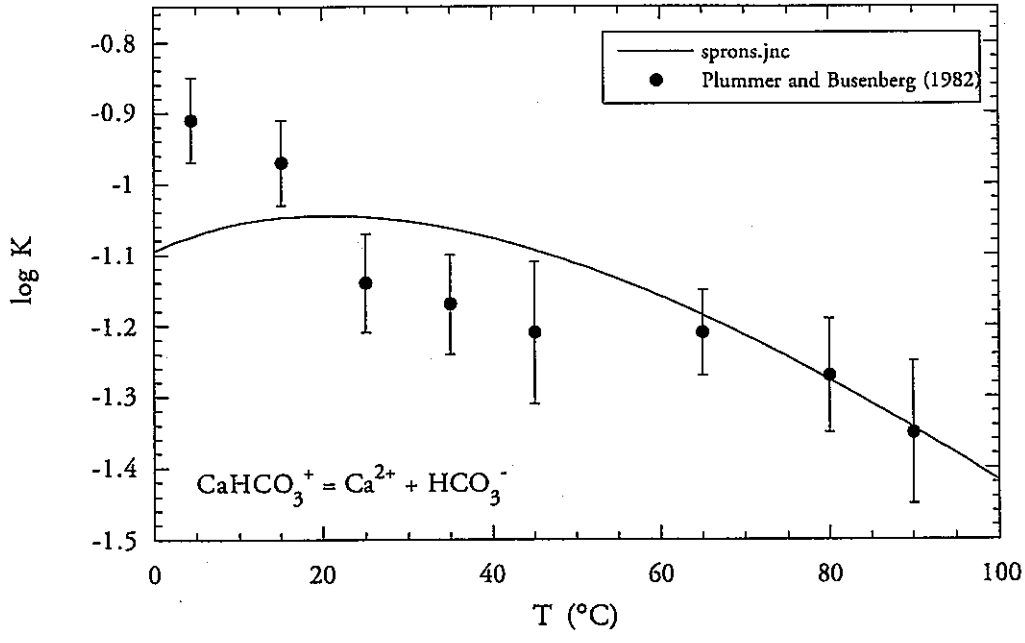


Fig. D.18: Logarithm of the equilibrium constant for the reaction $CaHCO_3^+ \rightleftharpoons Ca^{2+} + HCO_3^-$ between 0 and 100°C at 1 bar.

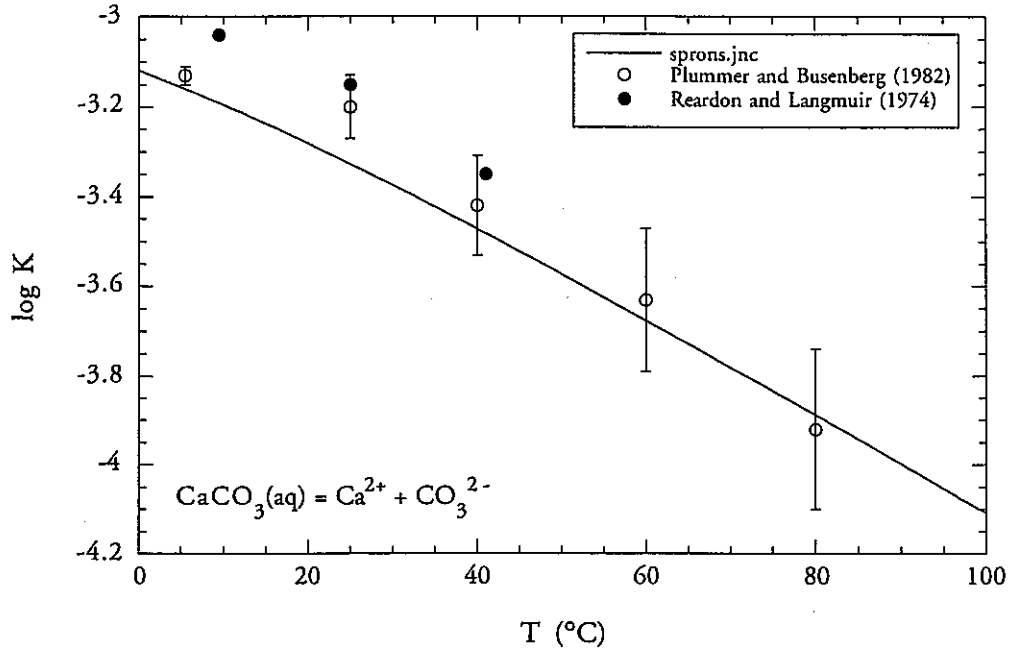


Fig. D.19: Logarithm of the equilibrium constant for the reaction $CaCO_3(aq) \rightleftarrows Ca^{2+} + CO_3^{2-}$ between 0 and 100°C at 1 bar.

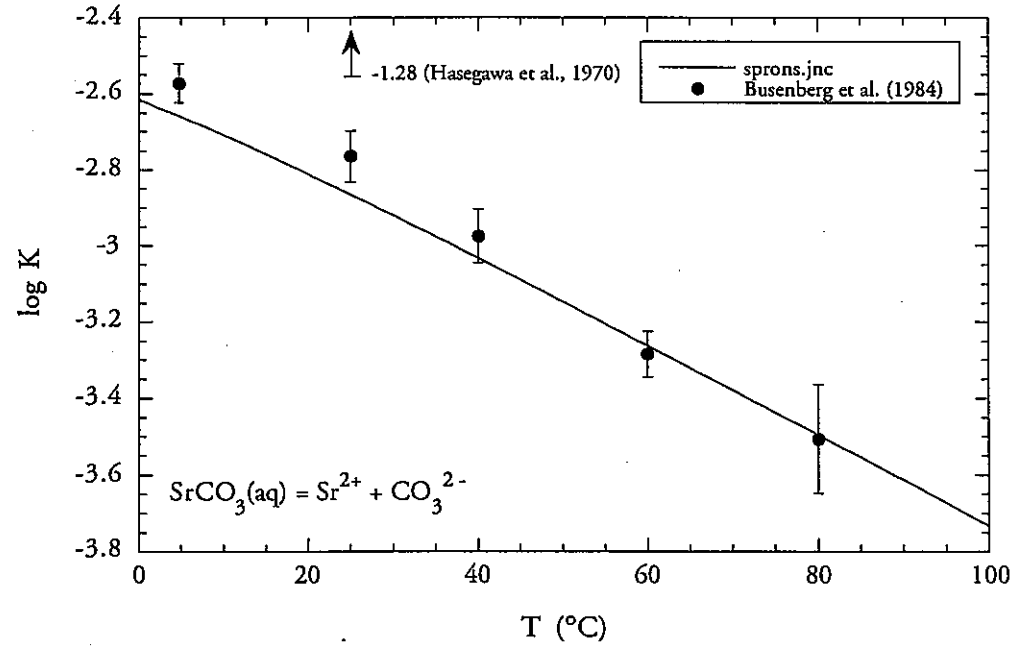


Fig. D.20: Logarithm of the equilibrium constant for the reaction $SrCO_3(aq) \rightleftarrows Sr^{2+} + CO_3^{2-}$ between 0 and 100°C at 1 bar.

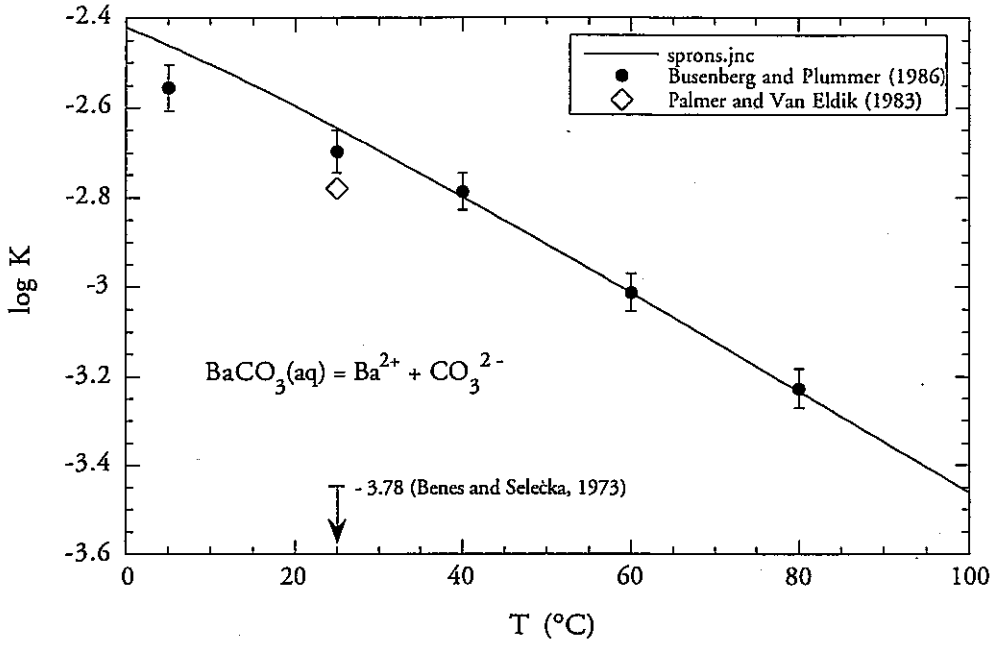


Fig. D.21: Logarithm of the equilibrium constant for the reaction $BaCO_3(aq) \rightleftharpoons Ba^{2+} + CO_3^{2-}$ between 0 and 100°C at 1 bar.

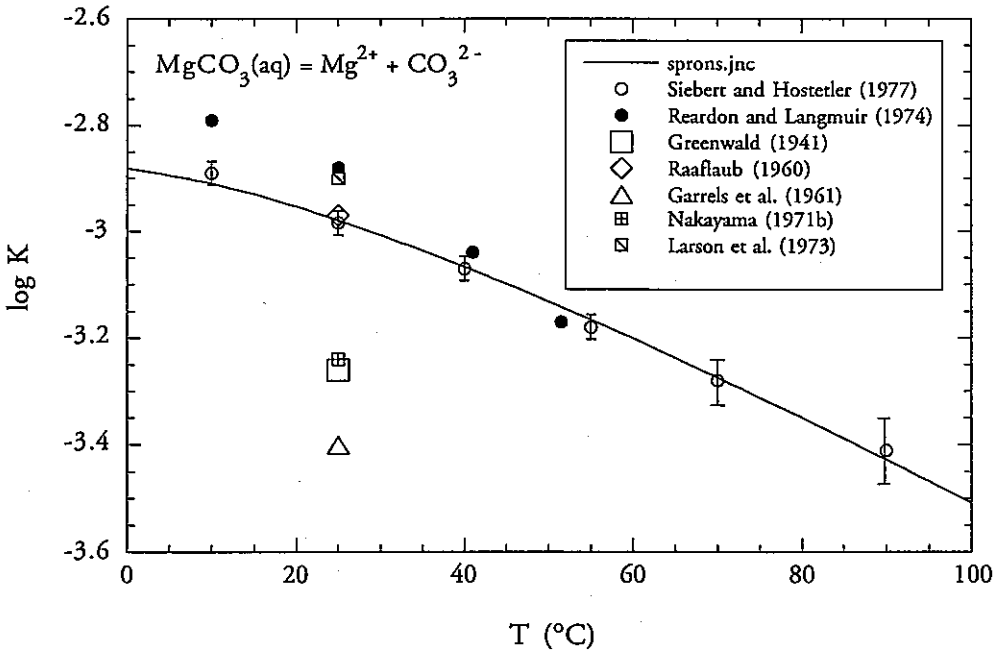


Fig. D.22: Logarithm of the equilibrium constant for the reaction $MgCO_3(aq) \rightleftharpoons Mg^{2+} + CO_3^{2-}$ between 0 and 100°C at 1 bar.

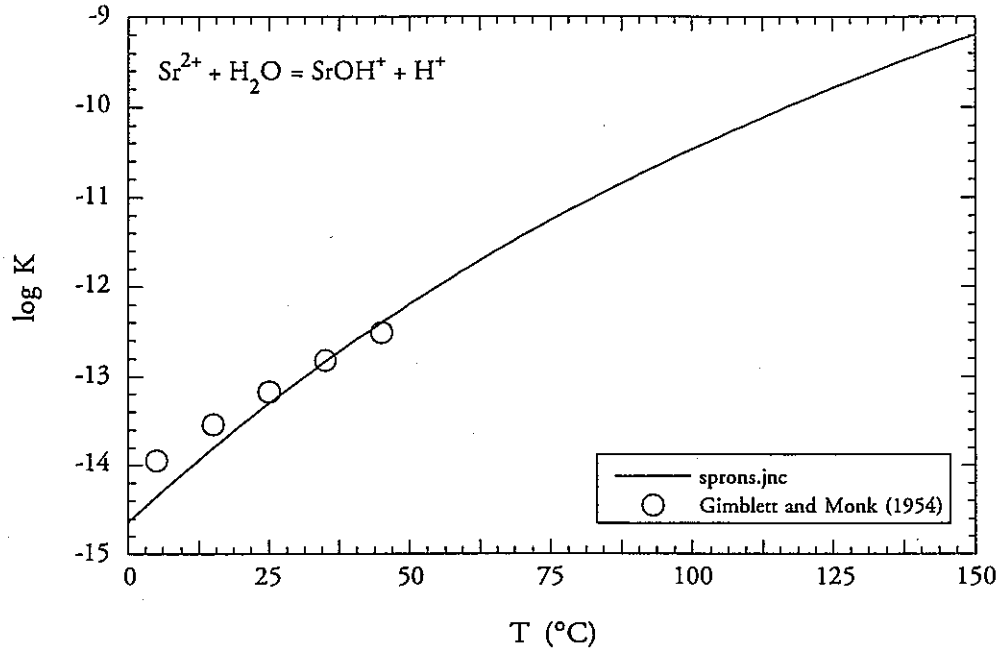


Fig. D.23: Logarithm of the equilibrium constant for the reaction $Sr^{2+} + H_2O \rightleftharpoons SrOH^+ + H^+$ between 0 and 150°C at *Psat*.

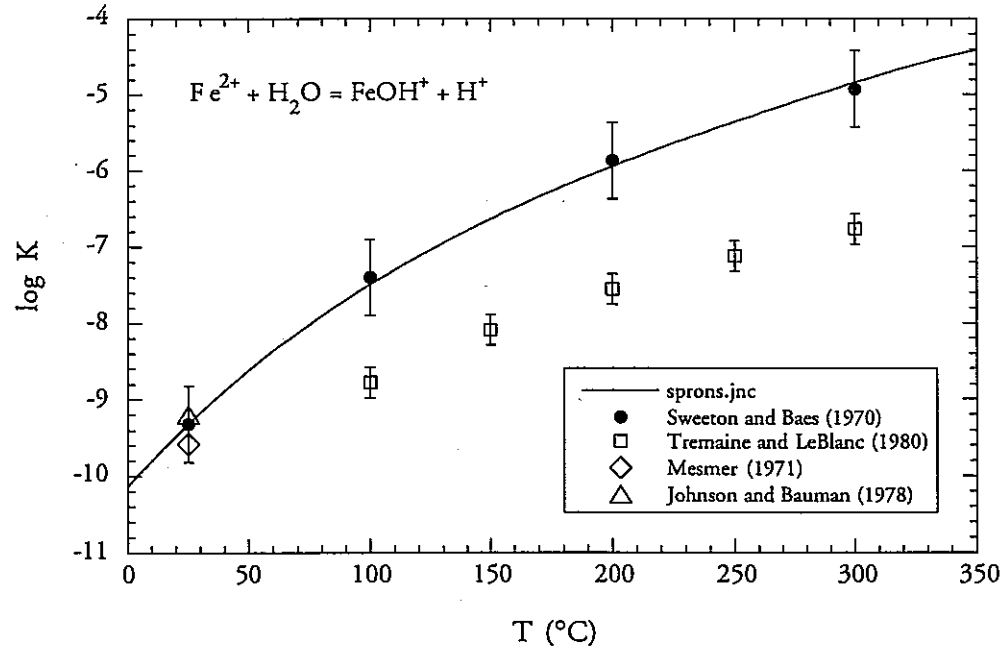


Fig. D.24: Logarithm of the equilibrium constant for the reaction $Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+$ between 0 and 350°C at *Psat*.

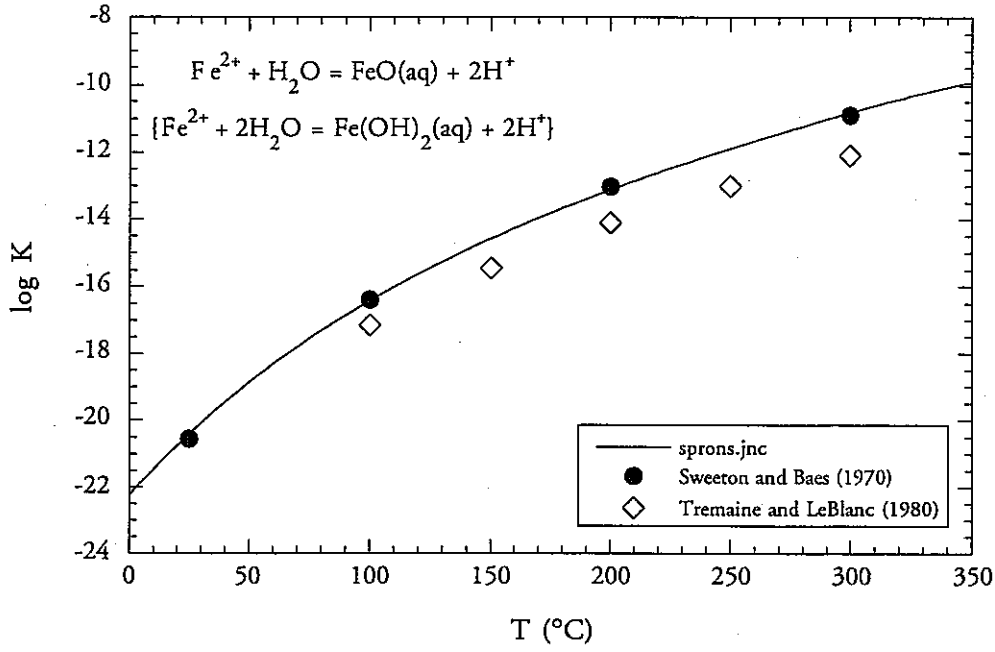


Fig. D.25: Logarithm of the equilibrium constant for the reaction $Fe^{2+} + 2H_2O \rightleftarrows Fe(OH)_2(aq) + 2H^+$ between 0 and 350°C at *Psat*.

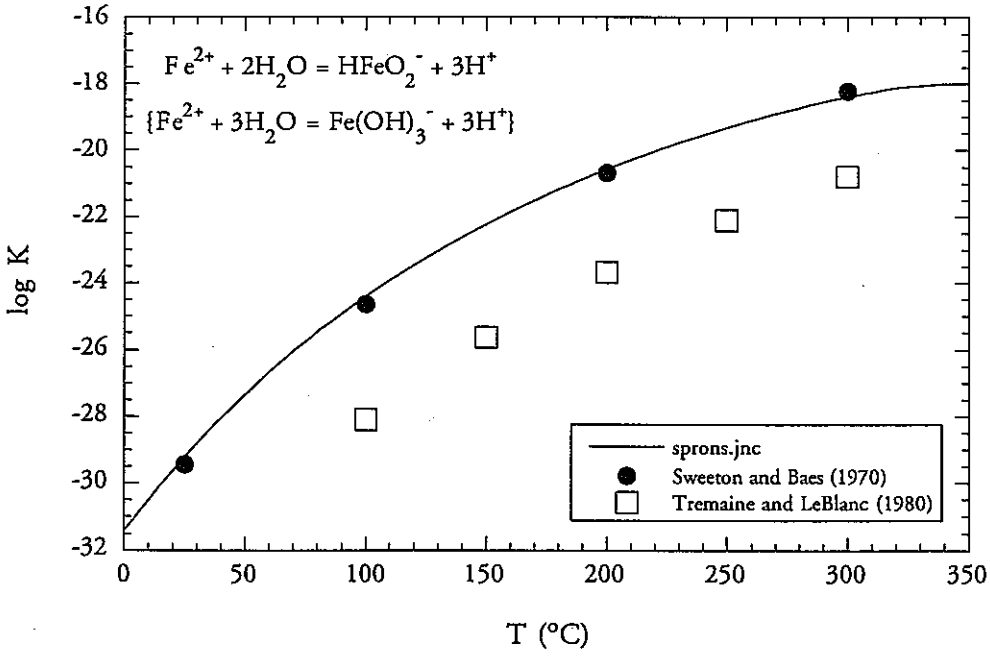


Fig. D.26: Logarithm of the equilibrium constant for the reaction $Fe^{2+} + 3\ H_2O \rightleftarrows Fe(OH)_3^- + 3\ H^+$ between 0 and 350°C at *Psat*.

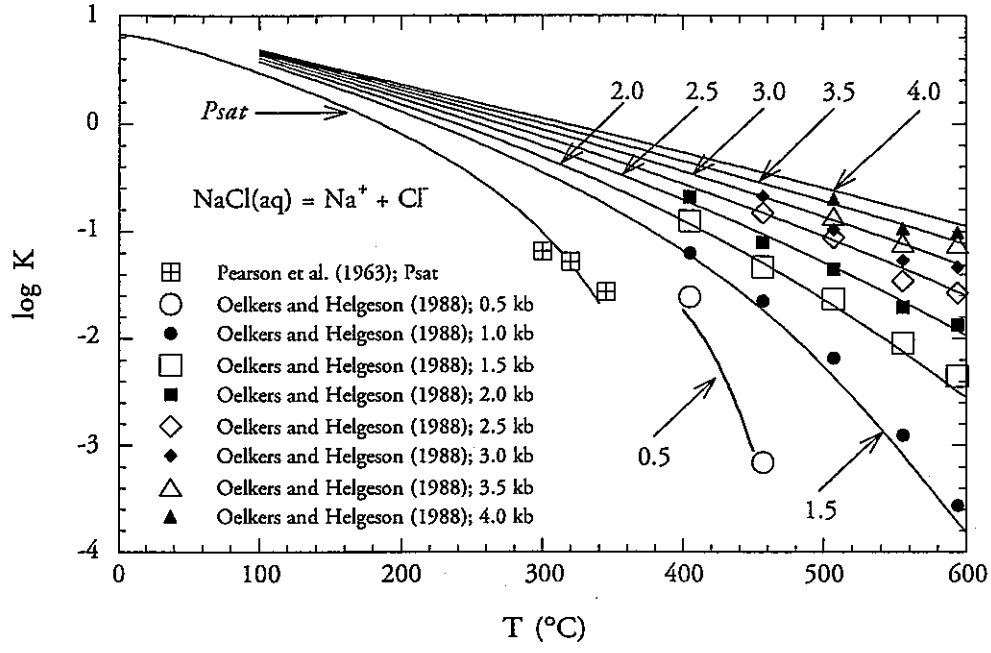


Fig. D.27: Logarithm of the equilibrium constant for the reaction NaCl*(aq)* ⇌ $Na^+ + Cl^-$ between 0 and 600°C and pressures from *Psat* to 4 kb.

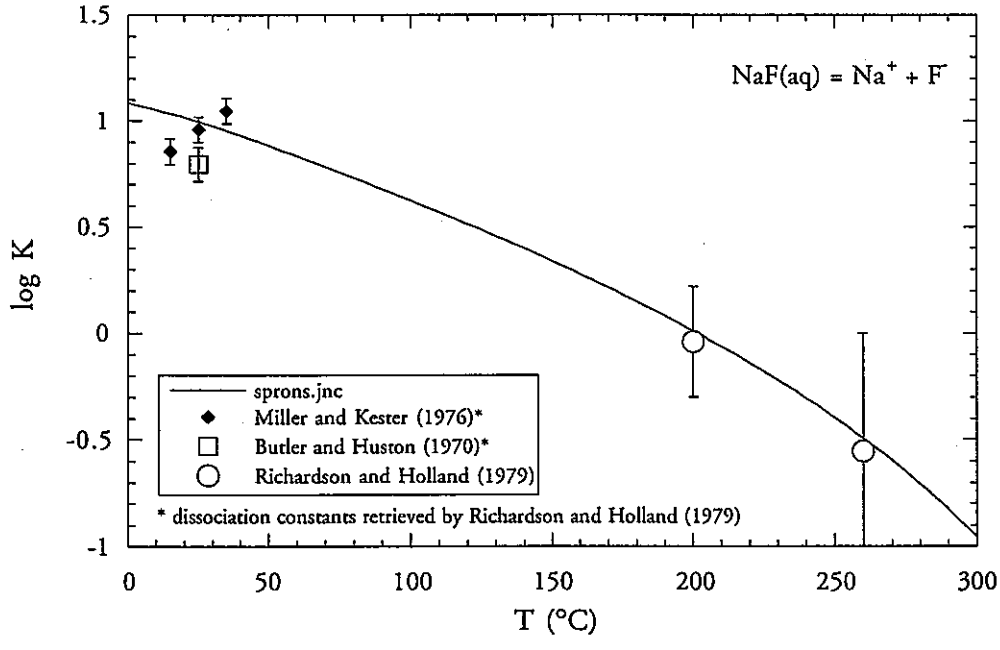


Fig. D.28: Logarithm of the equilibrium constant for the reaction NaF*(aq)* ⇌ $Na^+ + F^-$ between 0 and 300°C at *Psat*.

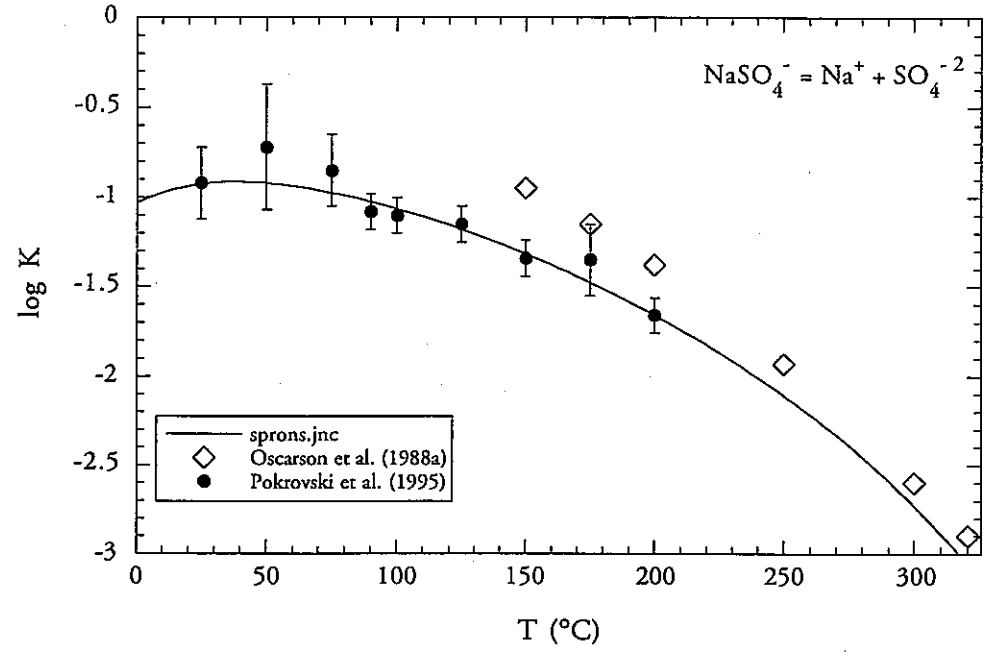


Fig. D.29: Logarithm of the equilibrium constant for the reaction $NaSO_4^- \rightleftarrows Na^+ + SO_4^{2-}$ between 0 and 330°C at *Psat*.

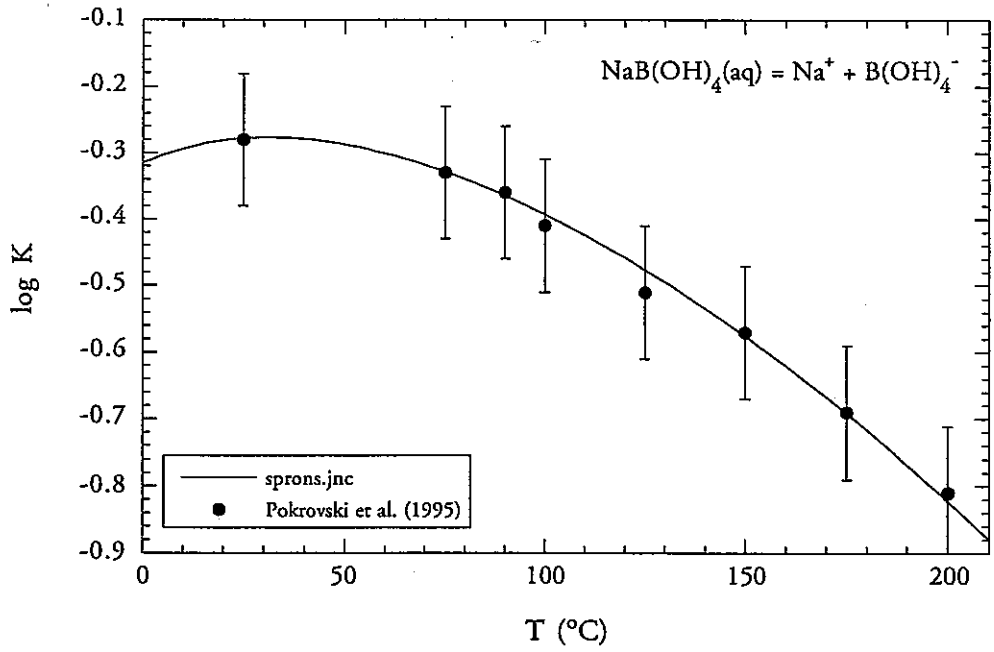


Fig. D.30: Logarithm of the equilibrium constant for the reaction $NaB(OH)_4(aq) \rightleftarrows Na^+ + B(OH)_4^-$ between 0 and 200°C at *Psat*.

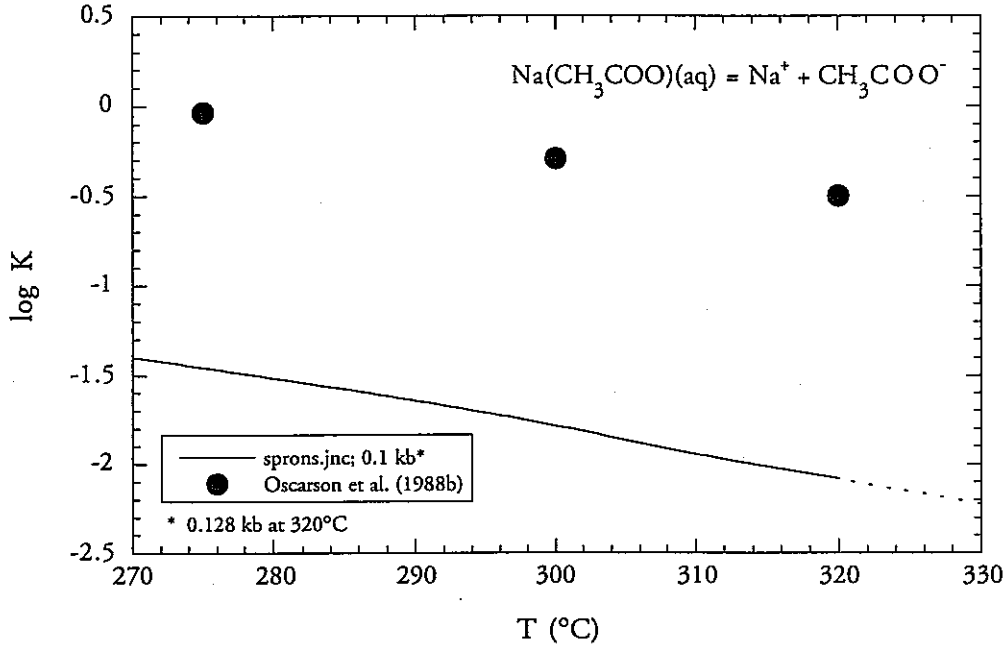


Fig. D.31: Logarithm of the equilibrium constant for the reaction $Na(CH_3COO)(aq) \rightleftharpoons Na^+ + CH_3COO^-$ between 270 and 320°C at *Psat.*

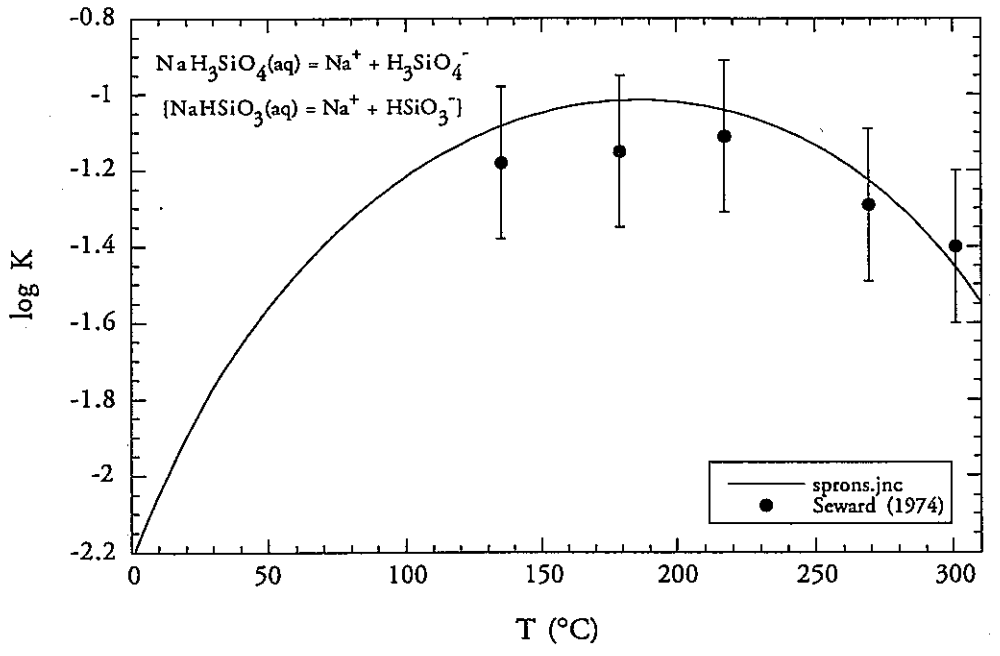


Fig. D.32: Logarithm of the equilibrium constant for the reaction $NaH_3SiO_4(aq) \rightleftharpoons Na^+ + H_3SiO_4^-$ between 0 and 300°C at *Psat.*

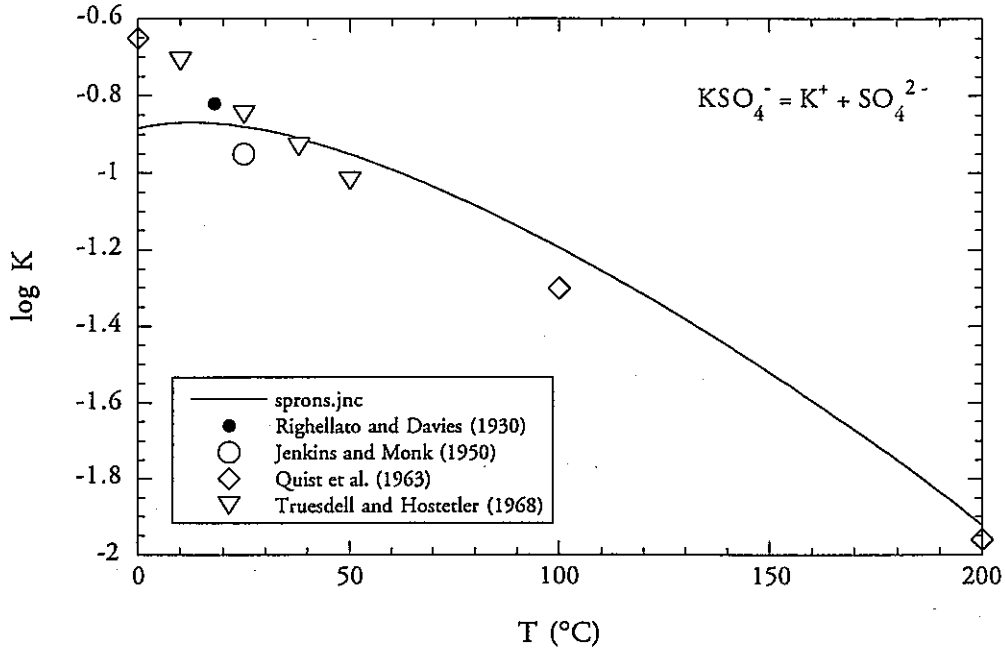


Fig. D.33: Logarithm of the equilibrium constant for the reaction $KSO_4^- \rightleftarrows K^+ + SO_4^{2-}$ between 0 and 200°C at *Psat*.

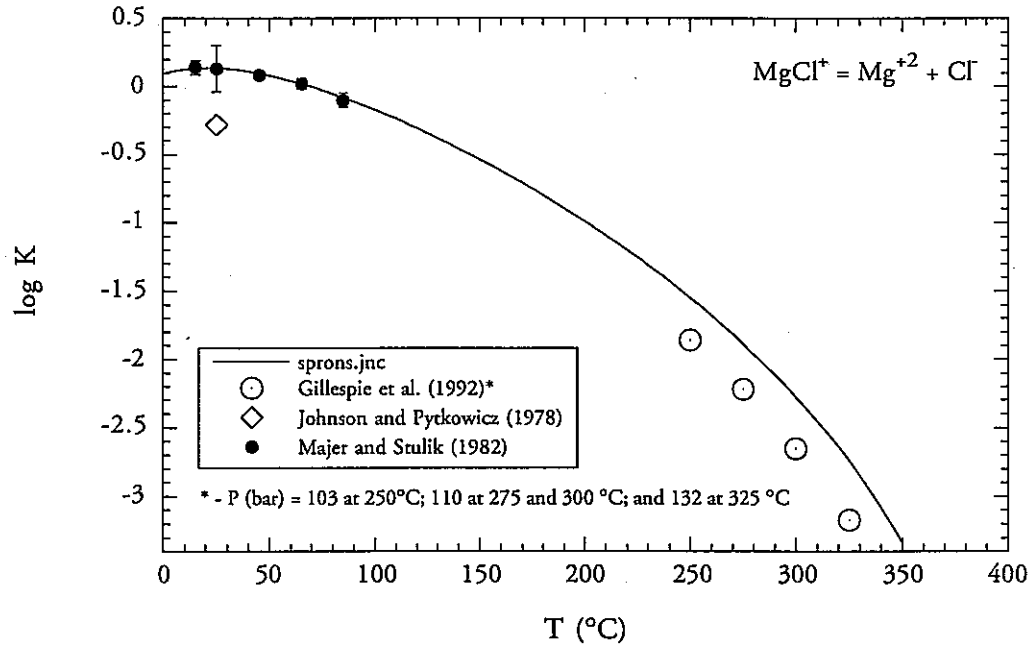


Fig. D.34: Logarithm of the equilibrium constant for the reaction $MgCl^+ \rightleftarrows Mg^{2+} + Cl^-$ between 0 and 350°C at *Psat*.

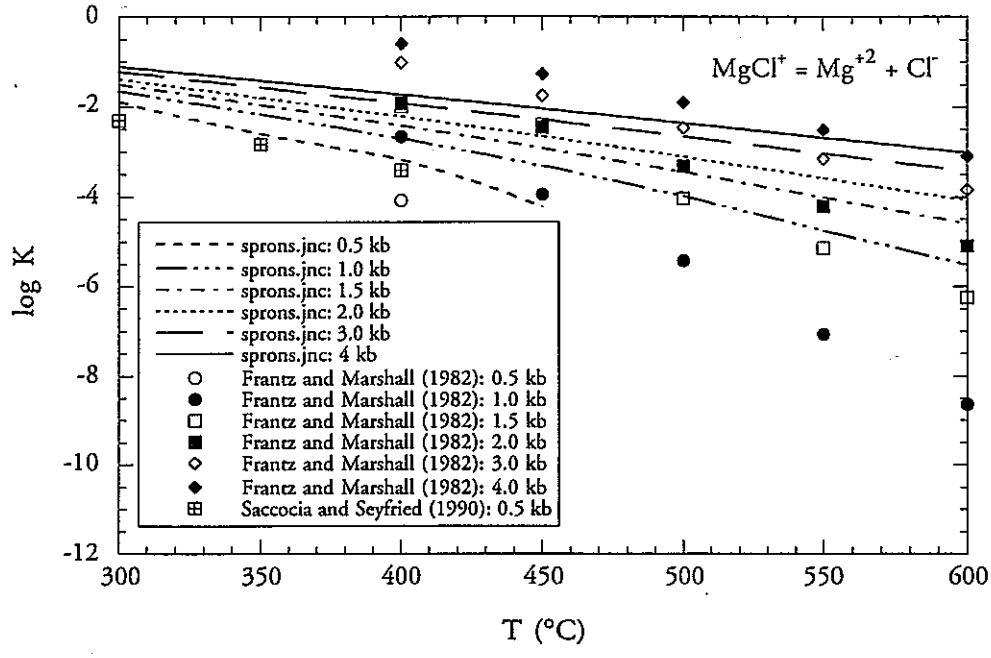


Fig. D.35: Logarithm of the equilibrium constant for the reaction $MgCl^+ \rightleftharpoons Mg^{2+} + Cl^-$ between 300 and 600°C and pressures from 0.5 to 4 kb.

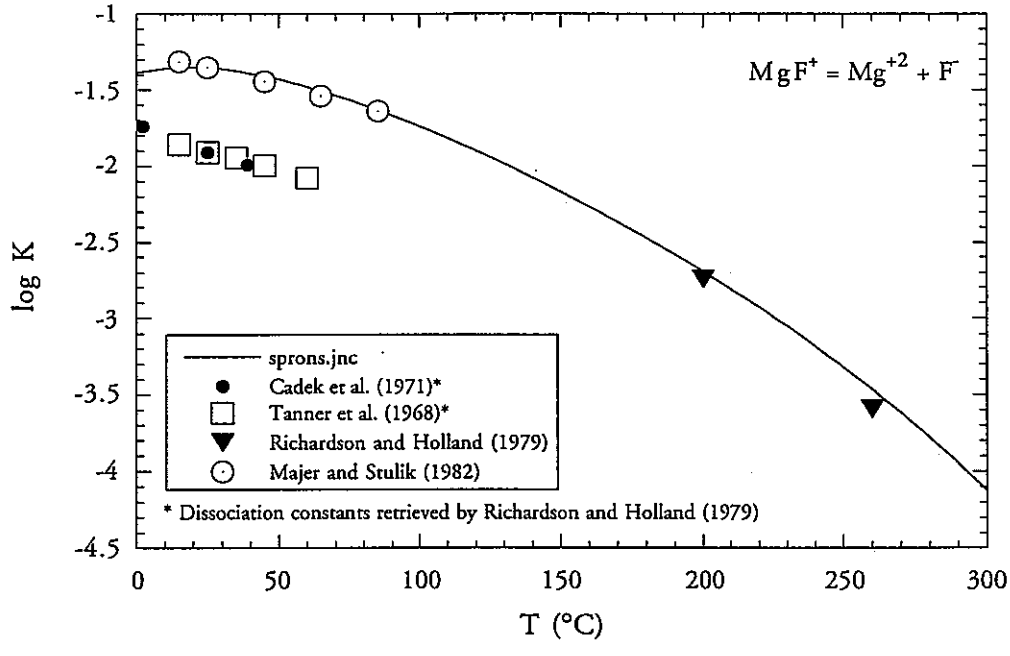


Fig. D.36: Logarithm of the equilibrium constant for the reaction $MgF^+ \rightleftharpoons Mg^{2+} + F^-$ between 0 and 300°C at *Psat*.

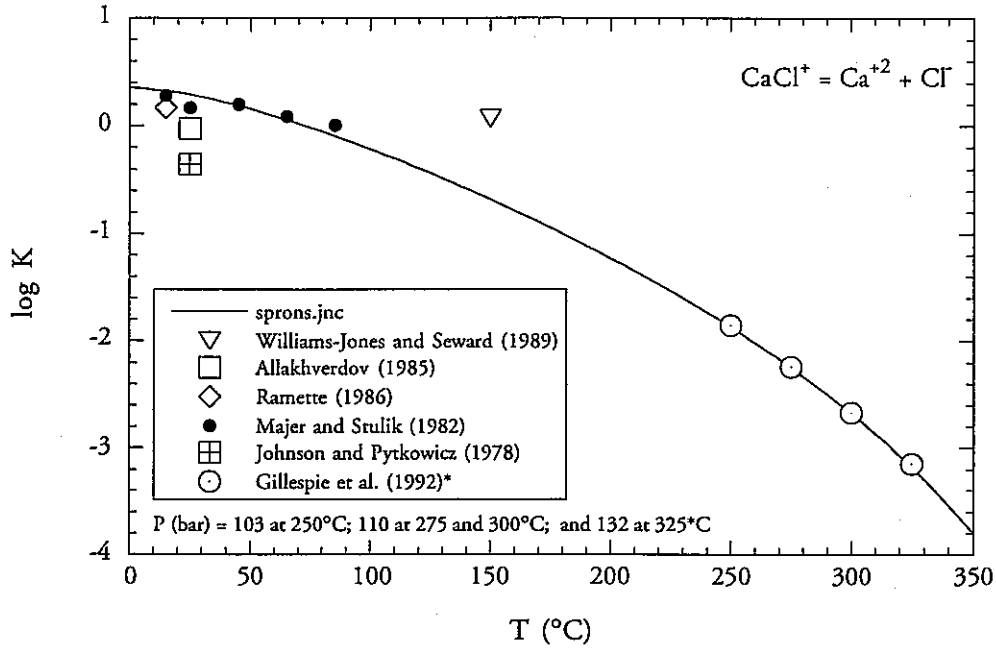


Fig. D.37: Logarithm of the equilibrium constant for the reaction $CaCl^{+} \rightleftarrows Ca^{2+} + Cl^{-}$ between 0 and 350°C at *Psat*.

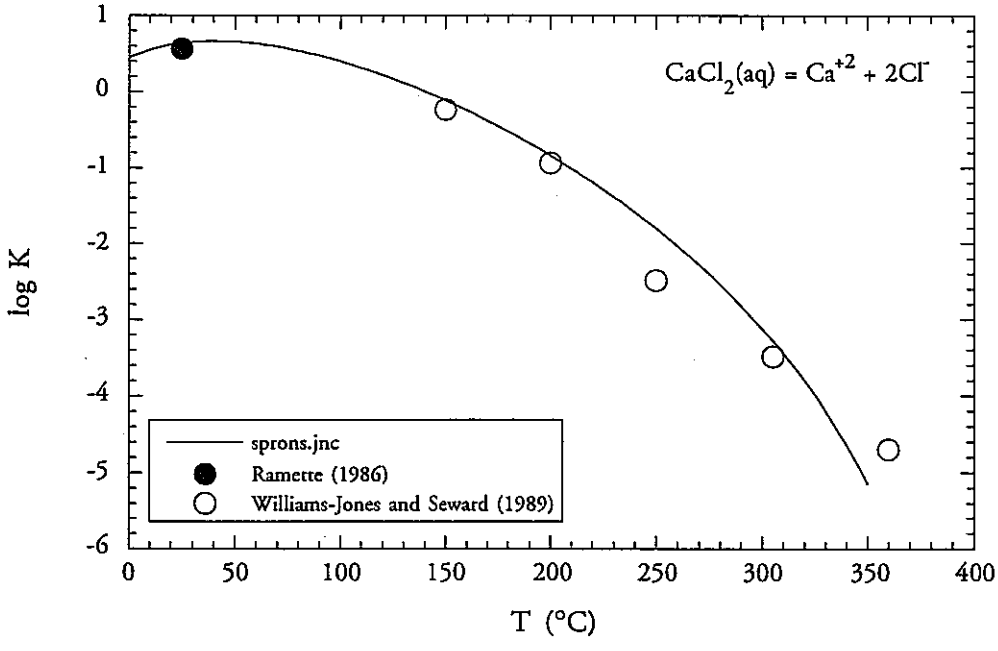


Fig. D.38: Logarithm of the equilibrium constant for the reaction $CaCl_2(aq) \rightleftarrows Ca^{2+} + 2\ Cl^{-}$ between 0 and 350°C at *Psat*.

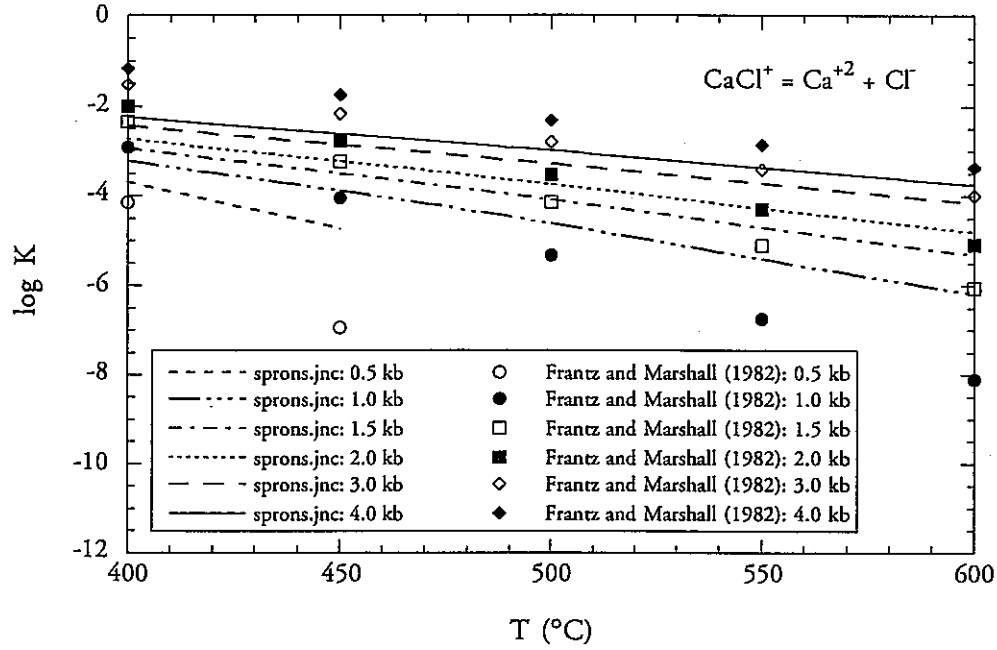


Fig. D.39: Logarithm of the equilibrium constant for the reaction $CaCl^+ \rightleftharpoons Ca^{2+} + Cl^-$ between 400 and 600°C and pressures from 0.5 to 4 kb.

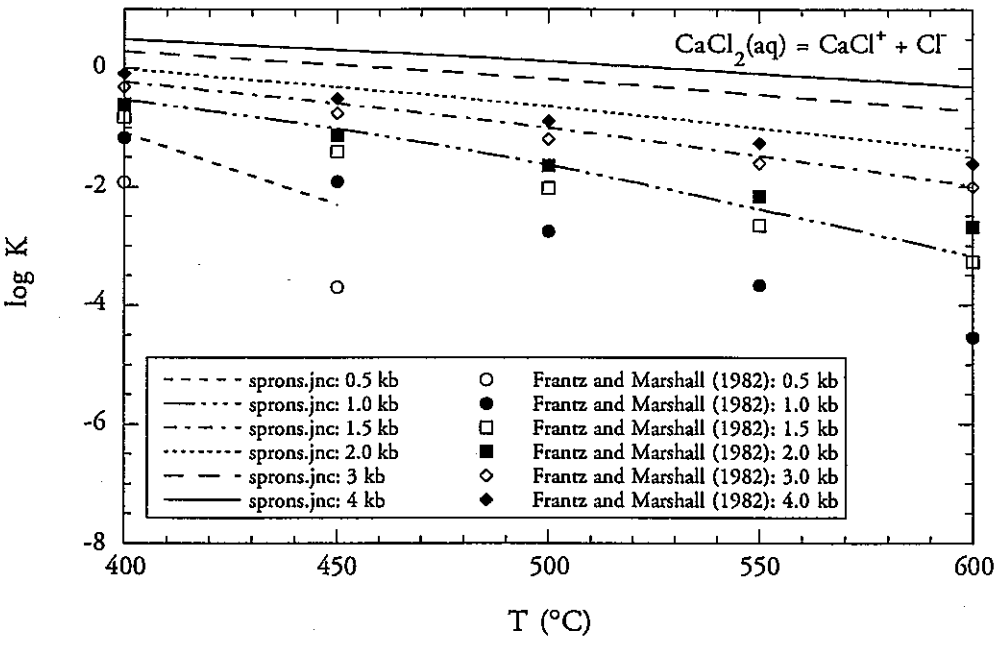


Fig. D.40: Logarithm of the equilibrium constant for the reaction $CaCl_2(aq) \rightleftharpoons CaCl^+ + Cl^-$ between 400 and 600°C and pressures from 0.5 to 4 kb.

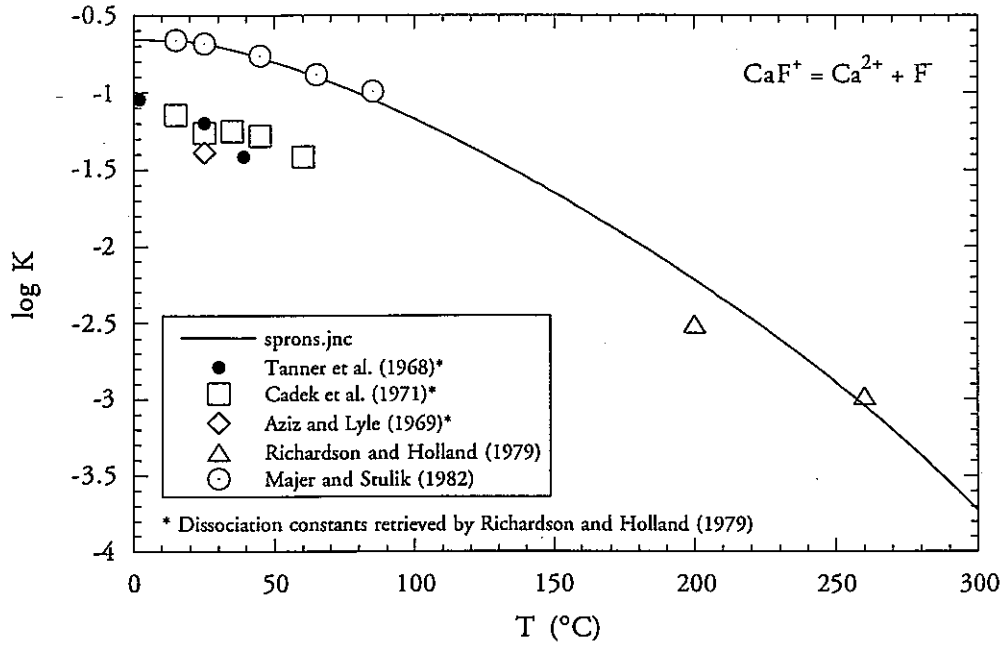


Fig. D.41: Logarithm of the equilibrium constant for the reaction $CaF^+ \rightleftarrows Ca^{2+} + F^-$ between 0 and 300°C at *Psat*.

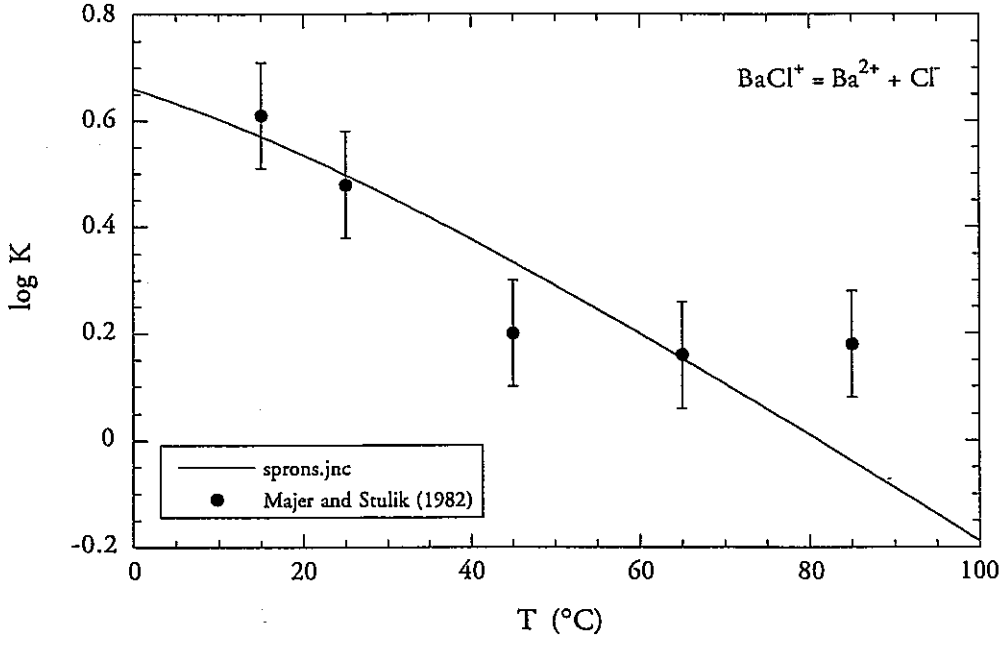


Fig. D.42: Logarithm of the equilibrium constant for the reaction $BaCl^+ \rightleftarrows Ba^{2+} + Cl^-$ between 0 and 100°C at 1 bar.

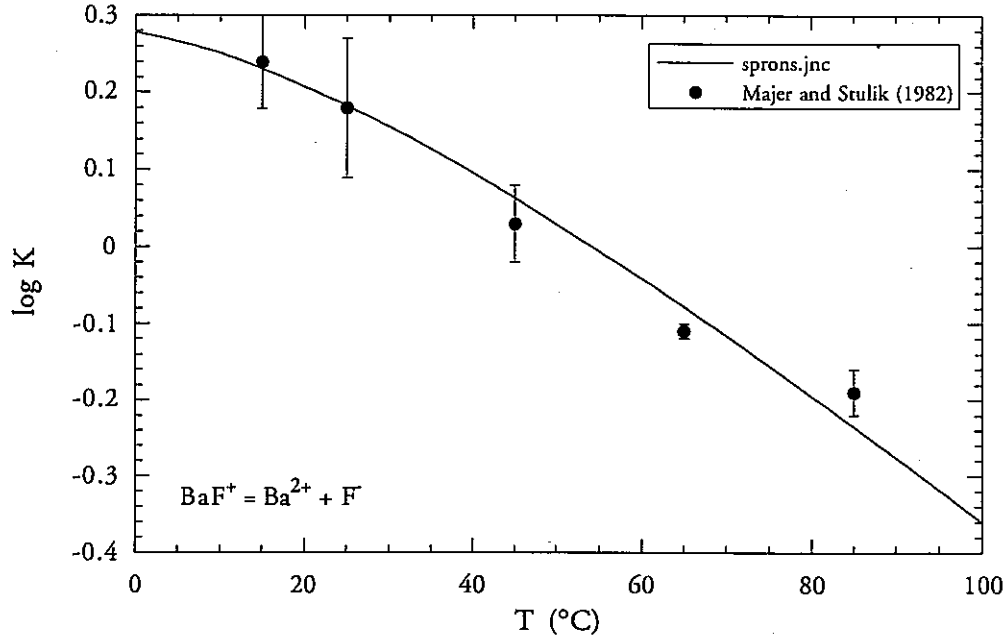


Fig. D.43: Logarithm of the equilibrium constant for the reaction $BaF^+ \rightleftharpoons Ba^{2+} + F^-$ between 0 and 100°C at 1 bar.

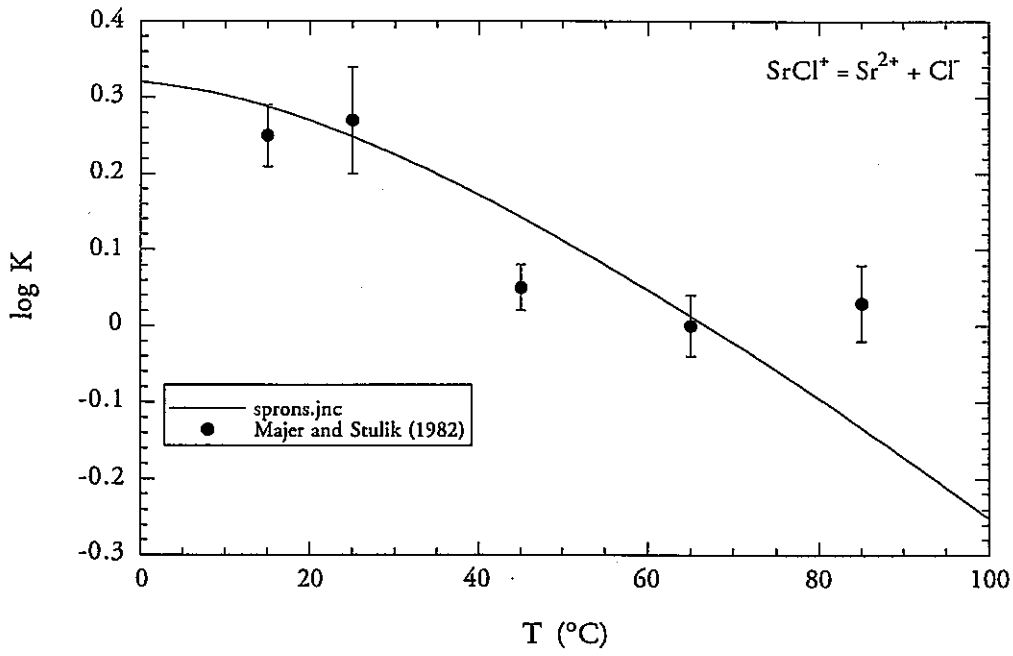


Fig. D.44: Logarithm of the equilibrium constant for the reaction $SrCl^+ \rightleftharpoons Sr^{2+} + Cl^-$ between 0 and 100°C at 1 bar.

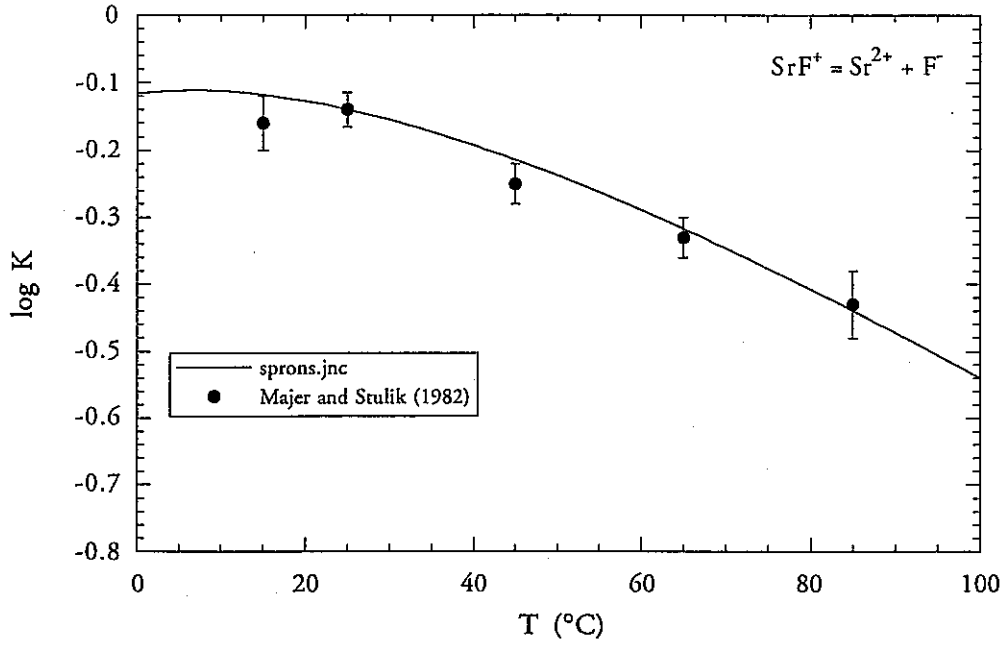


Fig. D.45: Logarithm of the equilibrium constant for the reaction $SrF^+ \rightleftharpoons Sr^{2+} + F^-$ between 0 and 100°C at 1 bar.

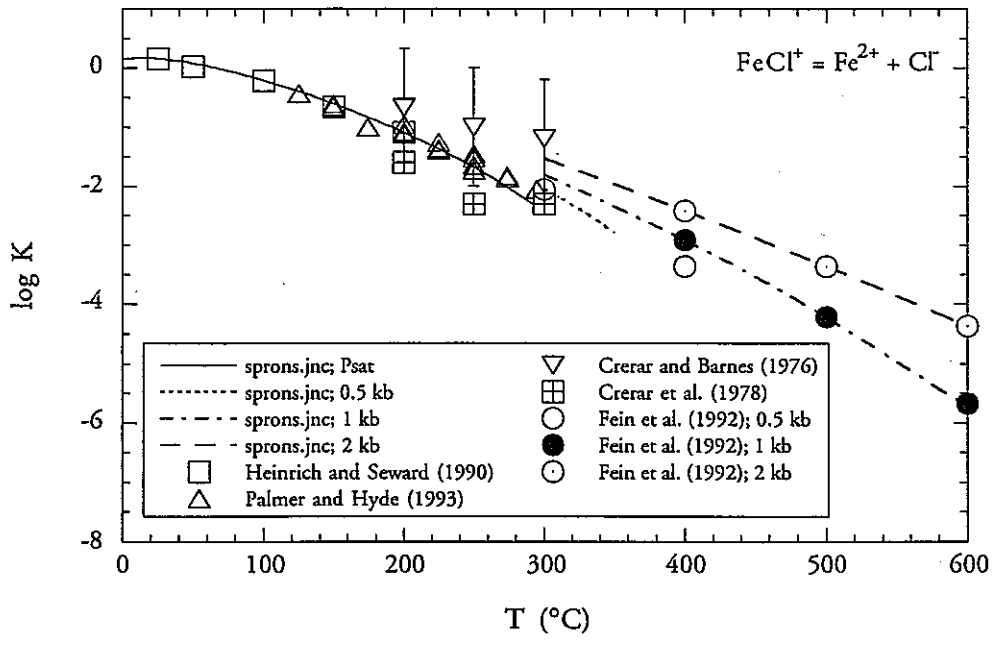


Fig. D.46: Logarithm of the equilibrium constant for the reaction $FeCl^+ \rightleftharpoons Fe^{2+} + Cl^-$ between 0 and 600°C and pressures from *Psat* to 2 kb.

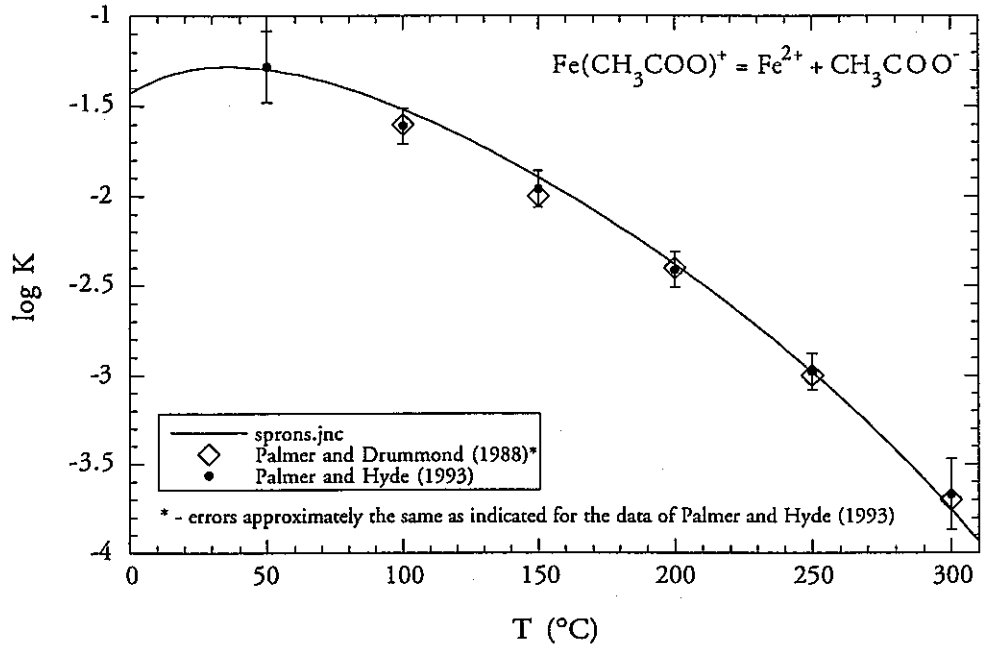


Fig. D.47: Logarithm of the equilibrium constant for the reaction $Fe(CH_3COO)^+ \rightleftharpoons Fe^{2+} + CH_3COO^-$ between 0 and 300°C at *Psat.*

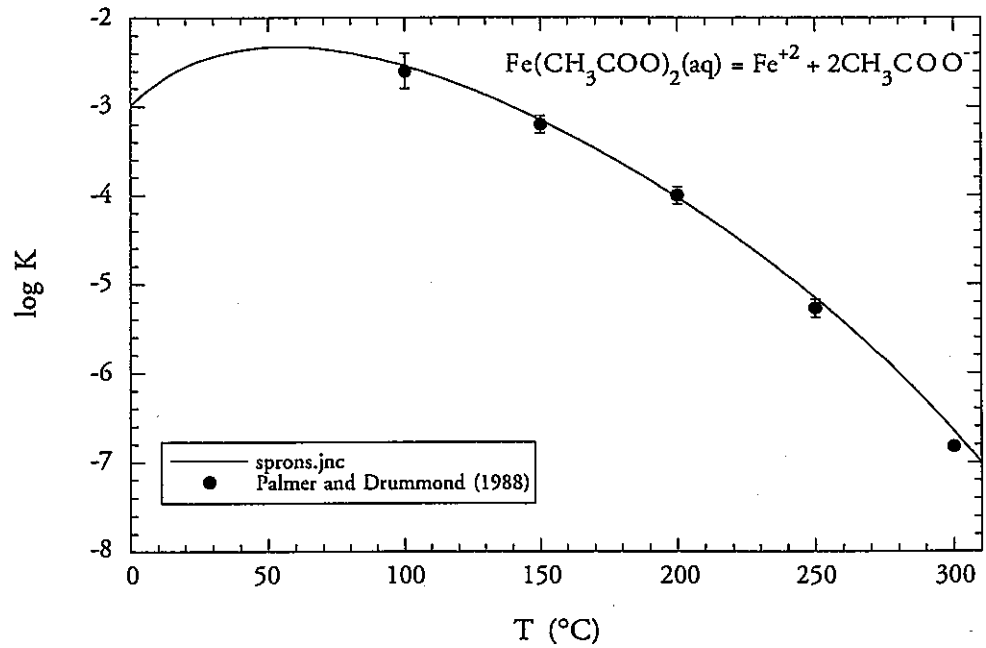


Fig. D.48: Logarithm of the equilibrium constant for the reaction $Fe(CH_3COO)_2(aq) \rightleftharpoons Fe^{2+} + 2\ CH3COO^-$ between 0 and 300°C at *Psat.*

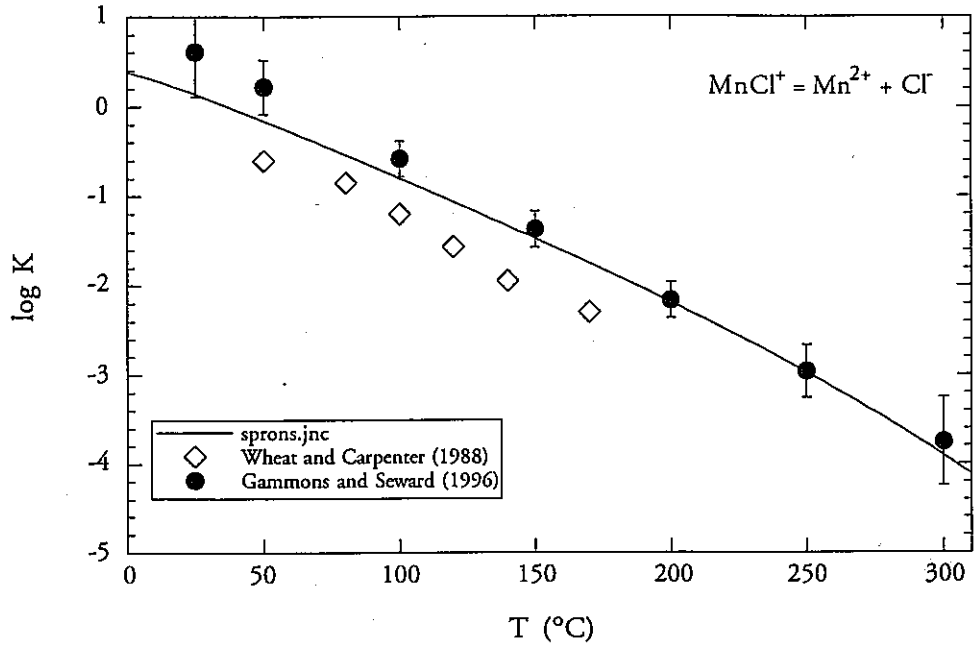


Fig. D.49: Logarithm of the equilibrium constant for the reaction $MnCl^+ \rightleftarrows Mn^{2+} + Cl^-$ between 0 and 300°C at *Psat*.

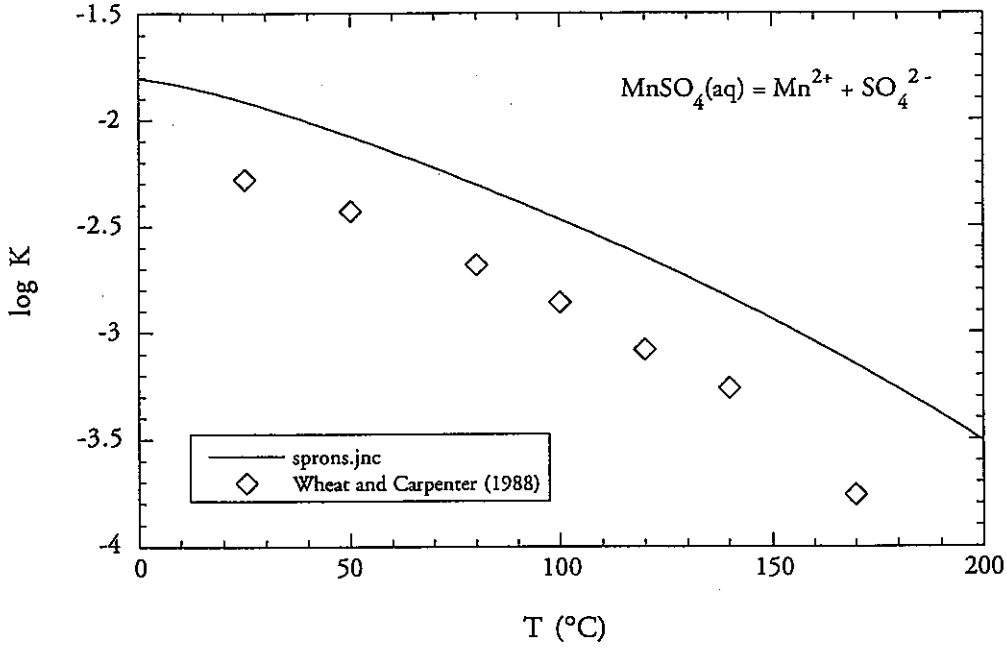


Fig. D.50: Logarithm of the equilibrium constant for the reaction $MnSO_4(aq) \rightleftarrows Mn^{2+} + SO_4^{2-}$ between 0 and 200°C at *Psat*.

Appendix E: Calculation Examples:

1- Apparent conventional partial molal Gibbs free energy of formation of $SiO_2(aq)$ at 100°C and 1 bar

2- Apparent molal Gibbs free energy of formation of quartz at 1 bar and the temperature of transition between α- and β-quartz

Introduction

To illustrate how equations in the SUPCRT model are evaluated as functions of temperature and pressure, we calculate the apparent conventional partial molal Gibbs free energy of formation of $SiO_2(aq)$ at 100°C and 1 bar, and the apparent molal Gibbs free energy of formation of quartz at 574.85°C and 1 bar representing P-T conditions at which α-quartz is converted to β-quartz (Helgeson et al., 1978).

1 Example #1: Calculation of $\Delta\bar{G}^{\circ}_{SiO_2(aq),\,1\,bar,\,100°C}$

The appropriate equation is (Section 4.1):

$$\Delta G^{\circ}_{P,T} \equiv \Delta G^{\circ}_{f} + (G^{\circ}_{P,T} - G^{\circ}_{P_r,T_r}), \qquad (4.1\_1)$$

where,

$$\bar{G}^{\circ}_{P,T} - \bar{G}^{\circ}_{P_r,T_r} = -\bar{S}^{\circ}_{P_r,T_r}(T - T_r) - c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(P - P_r) + a_2\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)$$
$$- c_2\left\{\left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right]\left[\frac{\Theta - T}{\Theta}\right] - \frac{T}{\Theta^2}\ln\left[\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right]\right\}$$
$$+ \left(\frac{1}{T-\Theta}\right)\left[a_3(P - P_r) + a_4\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right] + \omega\left(\frac{1}{\varepsilon} - 1\right) - \omega_{P_r,T_r}\left(\frac{1}{\varepsilon_{P_r,T_r}} - 1\right)$$
$$+ \omega_{P_r,T_r} Y_{P_r,T_r}(T - T_r), \qquad (4.2.2\_20)$$

and parameters are as defined in Sections 4.1 and 4.2.2. Evaluating the right-hand-side of the latter equation term-by-term using thermodynamic data for $SiO_2(aq)$ from Appendix A, and conventions in Table 5.1_3, gives:

first term;

$$-\bar{S}^{\circ}_{P_r,T_r}(T - T_r) = -18.0\ (\text{cal mol}^{-1}\text{K}^{-1})\,(373.15\ (\text{K}) - 298.15(\text{K})) = -1350\ (\text{cal mol}^{-1}),$$

second term;

$$-c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] =$$
$$-29.1\ (\text{cal mol}^{-1}\text{K}^{-1})\left[373.15(\text{K})\ln\left(\frac{373.15(\text{K})}{298.15(\text{K})}\right) - 373.15(\text{K}) + 298.15(\text{K})\right] =$$
$$-254.01\ (\text{cal mol}^{-1}),$$

third term;

$$a_1\left(P-P_r\right)=19.0(\text{cal mol}^{-1}\text{bar}^{-1})\left(1.013\ (\text{bar})-1(\text{bar})\right)=0.25(\text{cal mol}^{-1}),$$

fourth term;

$$a_2\ln\left[\frac{\Psi+P}{\Psi+P_r}\right]=170\ (\text{cal mol}^{-1})\ln\left[\frac{2600\ (\text{bar})\ +\ 1.013\ (\text{bar})}{2600\ (\text{bar})\ +\ 1.0\ (\text{bar})}\right]=8.5\text{x}10^{-4}(\text{cal mol}^{-1}),$$

(where Ψ is a pressure- and temperature-independent coefficient = 2600 bar, see Section 4.2.2.2)

fifth term;

$$-c_2\left\{\left[\left(\frac{1}{T-\Theta}\right)-\left(\frac{1}{T_r-\Theta}\right)\right]\left[\frac{\Theta-T}{\Theta}\right]-\frac{T}{\Theta^2}\ln\left[\frac{T_r\left(T-\Theta\right)}{T\left(T_r-\Theta\right)}\right]\right\}=$$

$$51.2\text{x}10^4(\text{cal K mol}^{-1})\left\{\left[\left(\frac{1}{373.15\ (\text{K})-228\ (\text{K})}\right)-\left(\frac{1}{298.15\ (\text{K})-228\ (\text{K})}\right)\right]\right\}$$

$$\left[\frac{228\ (\text{K})-373.15\ (\text{K})}{228\ (\text{K})}\right]-\frac{373.15\ (\text{K})}{228\ (\text{K})^2}\ln\left[\frac{298.15\ (\text{K})\left(373.15\ (\text{K})-228\ (\text{K})\right)}{373.15\ (\text{K})\left(298.15\ (\text{K})-228\ (\text{K})\right)}\right]=$$

563.2 (cal mol^{-1}),

(where Θ is a pressure- and temperature-independent coefficient = 228°K, see Section 4.2.2.2)

sixth term;

$$\left(\frac{1}{T-\Theta}\right)\left[a_3\left(P-P_r\right)+a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]=\left(\frac{1}{373.15\ (\text{K})-228\ (\text{K})}\right)$$

$$\text{x}\left[\begin{array}{c}20\ (\text{cal K mol}^{-1}\text{bar}^{-1})\ \left(1.013\ (\text{bar})-1.0\ (\text{bar})\right)\\ -2.7\text{x}10^4(\text{cal K mol}^{-1})\ln\left(\frac{2600\ (\text{bar})+1.013\ (\text{bar})}{2600\ (\text{bar})+\ 1.0\ (\text{bar})}\right)\end{array}\right]=$$

$9\text{x}10^{-4}$ (cal mol^{-1}),

seventh term;

$$\omega\left(\frac{1}{\varepsilon}-1\right)\ =\ 0.1291\text{x}10^5(\text{cal mol}^{-1})\left(\frac{1}{55.58}-1\right)=-12677.72\ (\text{cal mol}^{-1}),$$

[noting that $\omega = \omega_{Pr,Tr}$ at temperatures less than 448°K (Tanger and Helgeson, 1988), and that values of ε, the dielectric constant of $H_2O(l)$ (dimensionless) is taken from Weast (1979)]

eighth term;

$$-\omega_{Pr,Tr}\left(\frac{1}{\varepsilon_{Pr,Tr}}-1\right)= -0.1291\text{x}10^{5}\ (\text{cal mol}^{-1})\left(\frac{1}{78.36}-1\right)=12745.25\ (\text{cal mol}^{-1}),$$

and,

ninth term;

$$\omega_{Pr,Tr}Y_{Pr,Tr}(T-T_r) =$$

$$\left[0.1291\text{x}10^{5}(\text{cal mol}^{-1})\right]\left[-5.81\text{x}10^{-5}(\text{K}^{-1})\right](373.15\ (\text{K})-298.15(\text{K}))=$$

$$-56.25\ (\text{cal mol}^{-1}),$$

where the solvent born function, $Y_{Pr,\ Tr}$, at the reference pressure and temperature equals -5.81 x 10^{-5} K^{-1} (Tanger and Helgeson, 1988).

Adding the results calculated above for the nine terms on the right-hand-side of Eqn. (4.2.2_20) gives:

$$\bar{G}^{\circ}_{P,T}-\bar{G}^{\circ}_{Pr,Tr} = -1029\ \text{cal mol}^{-1}.$$

Substituting this value into Eqn. (4.1_1) with $\Delta G^{\circ}_{f,SiO2(aq)}$ from Appendix A gives the apparent partial molal Gibbs free energy of $SiO_2(aq)$ formation at 100°C and 1 bar:

$$\Delta\bar{G}^{\circ}_{P,T}=\Delta G^{\circ}_{f}+\left(G^{\circ}_{P,T}-G^{\circ}_{Pr,Tr}\right)= -199190\ (\text{cal mol}^{-1})-1029\ (\text{cal mol}^{-1})$$

$$= -200219\ \text{cal mol}^{-1}$$

This agrees closely with the value calculated using SUPCRT and SPRONS.JNC (-200229 cal mol-1). The minor discrepancy may be due to differences in precision between the two calculation approaches, and/or to differences in the dielectric constant of $H_2O(l)$ at 25 and 100°C as calculated in SUPCRT *vs.* the values reported by Weast (1979).

2 Example #2: Calculation of $\Delta G^{\circ}_{\text{quartz, 1 bar, 574.85°C}}$

The appropriate equation is (Section 4.1):

$$\Delta G^{\circ}_{P,T} \equiv \Delta G^{\circ}_{f} + (G^{\circ}_{P,T} - G^{\circ}_{Pr,Tr}), \qquad (4.1\_1)$$

where,

$$G^{\circ}_{P,T} - G^{\circ}_{P_r,T_r} = -S^{\circ}_{P_r,T_r}(T - T_r) + \sum_{i=1}^{1+\phi_T} a_i \left\{ T_{i+1} - T_i - T_{i+1} \ln\left(\frac{T_{i+1}}{T_i}\right) \right\}$$
$$+ \sum_{i=1}^{1+\phi_T} \left\{ \frac{(-c_i - b_i T_{i+1} T_i^2)(T_{i+1} - T_i)^2}{2 T_{i+1} T_i^2} \right\} + V^{\circ}_{P_r,T}(P - P_r)$$
$$- \sum_{i=1}^{\phi_P} \int_{P_{t,i,T}}^{P} \Delta V^{\circ}_{t,i}\, dP - \sum_{i=1}^{\phi_T} \frac{\Delta H^{\circ}_{t,i}}{T_{t,i}} (T - T_{t,i});$$

(4.2.1_6)

and parameters are as defined in Sections 4.1 and 4.2.1. The right-hand-side of the latter equation can be evaluated term-by-term using thermodynamic data for quartz from Appendix A, conventions specified in Table 5.1_2, and the constraints $T_i = T_r = 298.15$°K and $T_{i+1} = 848$°K (i.e., 574.85°C - the temperature of transition from α-quartz to β-quartz at 1 bar):

first term;

$$-S^{\circ}_{P_r,T_r}(T - T_r) = -9.88(\text{cal mol}^{-1}\text{K}^{-1})\,(848(\text{K}) - 298.15(\text{K})) = -5432.4\ (\text{cal mol}^{-1}),$$

second term;

$$a_1 \left\{ T_{i+1} - T_i - T_{i+1} \ln\left(\frac{T_{i+1}}{T_i}\right) \right\} =$$
$$11.22(\text{cal mol}^{-1}\text{K}^{-1}) \left\{ 848(\text{K}) - 298.15(\text{K}) - 848(\text{K}) \ln\left(\frac{848(\text{K})}{298.15(\text{K})}\right) \right\}$$
$$= -3776.1(\text{cal mol}^{-1}),$$

[noting that although $\phi_T = 1$ in this example, the second summation implicit in this term does not apply because T_{i+1} then equals T_i (i.e., 848°K)],

third term;

$$\left\{ \frac{(-c_i - b_i T_{i+1} T_i^2)(T_{i+1} - T_i)^2}{2 T_{i+1} T_i^2} \right\} =$$
$$\left\{ \frac{(2.7\text{x}10^5 - 8.2\text{x}10^{-3}\text{x}848(\text{K})\ \text{x}298.15(\text{K})^2)(848(\text{K}) - 298.15(\text{K}))^2}{2\ \text{x}\ 848(\text{K})\ \text{x}\ 298.15(\text{K})} \right\} =$$

$-698.1\ (\text{cal mol}^{-1})$,

[noting that units for c_i and b_i are cal K mol^{-1} and cal mol^{-1} K^{-2}, respectively, and that although $\phi_T = 1$, the second summation in this term does not apply because T_{i+1} then equals T_i (i.e., 848°K)],

fourth term;

$$V^{\circ}_{Pr,T}\left(P - P_r\right) = 0,$$

(because the pressure at the transition temperature in this example is equal to P_r)

fifth term;

$$-\sum_{i=1}^{\phi_P} \int_{P_{t,i}}^{P} \Delta V^{\circ}_{t,i} dP = 0,$$

(because the pressure at the transition temperature in this example is equal to P_r) , and

sixth term;

$$-\sum_{i=1}^{\phi_T} \frac{\Delta H^{\circ}_{t,i}}{T_{t,i}}\left(T - T_{T,i}\right) = 0$$

(because $T = T_{t,i}$).

Adding the results calculated above for the six terms on the right-hand-side of Eqn. (4.2.1_6) gives:

$$\bar{G}^{\circ}_{P,T} - \bar{G}^{\circ}_{Pr,Tr} = -9907 \text{ cal mol}^{-1}.$$

Substituting this value into Eqn. (4.1_1) with $\Delta G^{\circ}_{f,\,quartz}$ from Appendix A gives the apparent standard molal Gibbs free energy of formation quartz at 574.85°C and 1 bar:

$$\Delta \bar{G}^{\circ}_{P,T} = \Delta G^{\circ}_{f} + \left(G^{\circ}_{P,T} - G^{\circ}_{Pr,Tr}\right) = -204646 \text{ (cal mol}^{-1}) - 9907 \text{ (cal mol}^{-1})$$

$$= -214553 \text{ cal mol}^{-1},$$

which is in exact agreement with the value calculated using SPRONS.JNC and SUPCRT.