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# Thermodynamic Data Development Using the Solubility Method (Joint Research)

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The solubility method is one of the most powerful tools to obtain reliable thermodynamic data for 1) solubility products of discrete solids and double salts, 2) complexation constants for various ligands, 3) development of data in a wide range of pH values, 4) evaluation of data for metals that form very insoluble solids (e.g. tetravalent actinides), 5) determining solubility-controlling solids in different types of wastes and 6) elevated temperatures for redox sensitive systems. This document is focused on describing various aspects of obtaining thermodynamic data using the solubility method. This manuscript deals with various aspects of conducting solubility studies, including selecting the study topic, modeling to define important variables, selecting the range of variables and experimental parameters, anticipating results, general equipment requirements, conducting experiments, and interpreting experimental data.

Keywords: Solubility Method, Thermodynamic Data, Study Topic, Modeling, Variables, Experimental Parameter, Anticipating Results, Equipment Requirements, Interpreting Experimental Data

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# 溶解度法による熱力学データ整備 (共同研究)

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溶解度法は次のような熱力学データを信頼性高く求めるのに最も有力な方法の一つである。そ の熱力学データとは、1)個々の固相や複塩の溶解度積、2)種々の配位子の錯生成定数、3)広範囲な pH 域にわたるデータ、4) 極めて難溶性な固相(例えば、4価のアクチニド)を生成する金属の データ評価、5)様々な廃棄物中での溶解度制限固相の決定、6)酸化還元に鋭敏な系に対する温度上 昇である。本書は、溶解度法によってこのような熱力学データを取得する際の様々な特徴を記述 することに焦点をあてたものである。本書は、研究テーマの選定、重要な変数を定義するための モデル、変数や実験パラメータの範囲の選定、予測される結果、一般的な設備要求、実験の実施 および実験データの解釈、といった溶解度試験の実施における様々な特徴を記述している。

本報告書は、原子力機構とライ環境化学有限責任会社との共同研究(熱化学データ及び熱化学デ ータ解釈技術の整備(平成23年度国際共同研究))の一環として作成した熱力学データ整備のため のガイドラインである。

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#### 1 Introduction

There are many different methods for experimentally obtaining thermodynamic data (e.g., solubility, spectroscopy, ion exchange, potentiometry, isopiestic, calorimetry). Most of these methods have some inherent limitations. 1) Spectroscopic methods are not suitable to all species and generally require fairly high concentrations of the reactive species. 2) Solvent extraction is not suitable for all species because extractants for a wide variety of species are not available; it is generally suitable for extractions either in very acidic or in a very narrow range of pH values such that it is not possible to investigate reactions in the entire pH range that may be required (e.g., see [1] for discussion of Th-ISA literature data obtained by solvent extraction). 3) The solubility method is not well suited to solids that do not exhibit rapid precipitation/dissolution kinetics (e.g., crystalline tetravalent actinide dioxides at room temperatures), nor can solids with extremely high solubility be used to develop complexation constants for various ligands. Therefore to obtain reliable data, it is always best to use combinations of as many methods as needed.

The solubility method, aside from the limitation discussed above, it is one of the most powerful tools to obtain reliable thermodynamic data for 1) solubility products of discrete solids and double salts, 2) complexation constants for various ligands, 3) development of data in a wide range of pH values, 4) evaluation of data for metals that form very insoluble solids (e.g. tetravalent actinides) which make it difficult to use methods that require relatively high metal concentrations and/or if the ligand makes extremely strong complexes making it difficult to obtain reliable values for bare metal ion activities required for determining the complexation constants, 5) determining solubility-controlling solids in different types of wastes (e.g. radioactive waste glasses, contaminated soils; for successful application of this method to these types of problems see [2, 3], and 6) elevated temperatures for redox sensitive systems (e.g., see [4, 5]). This document is focused on describing various aspects of obtaining thermodynamic data using the solubility method. The examples, supporting citations, and the procedural details discussed in this document are all from the publications by Rai and coworkers. This does not mean that these are the only examples; several other authors present similar observations on different aspects of conducting solubility studies. However, for our convenience we chose to support the statements with examples from our published work. This manuscript deals with various aspects of conducting solubility studies, including selecting the study topic, modeling to define important variables, selecting the range of variables and experimental parameters, anticipating results, general equipment requirements, conducting experiments, and interpreting experimental data.

#### 2 Selection of study topic

The selection of elements for study should depend on their concentrations or perceived importance in waste disposal, environmental settings, and/or industrial processes. Once the element is selected, then it is important to conduct a critical review of the available thermodynamic data. Further studies are warranted only for those ligands that are expected to be present in significant concentrations or form strong complexes with the given element and if 1) no data are available for the given ligand, 2) the existing data

are limited (for example there may be only one value available which may need confirmation or the available data may just be estimated), 3) there is a wide variability in the reported values for complexation constants of a given ligand which cannot be reconciled through critical reviews and remodeling those experimental studies which are well executed, 4) it can be ascertained that the methodology used for obtaining the data is fraught with problems and that an improved methodology can be used to obtain reliable values, and 5) no data are available for applications to high temperatures and/or concentrated salt solutions (e.g. brines) if these conditions are expected to be important in the system.

#### **3** Preliminary modeling to difine important variables

In several situations preliminary modeling can help define the ranges in values of different variables or help define the compositions of starting solutions to obtain desired fixed values of different variables (e.g., pH), especially in relatively concentrated solutions that are otherwise difficult to accurately define. The existing or estimated thermodynamic data (even though it may not be reliable and may need verification) can be used to calculate the solubility of a desired solid phase at a range in concentrations of the desired ligand. Based on these calculations, a range in ligand concentrations in a given range of pH values where these calculations show significant increase in concentration can be incorporated into the experimental design. As an example, using the Np(IV)-carbonate data available in1985, Rai et al. [6] calculated that the Np(IV) concentrations will be  $> 0.01 \text{ mol.kg}^{-1}$  at pH values  $\ge 12$  in the presence of 0.01 mol.kg<sup>-1</sup> carbonate. To check the accuracy of these predictions, they investigated the solubility of NpO<sub>2</sub>(am) in this alkaline region in the presence of 0.01 mol.kg<sup>-1</sup> carbonate. These results showed that the actual observed Np(IV) concentrations in all pH values were very low and at or near the detection limit of Np (~10<sup>-8</sup> mol.kg<sup>-1</sup>), thereby confirming that the available data for Np(IV)-carbonate complexes were This initial study then formed the bases for extensive studies on determining not reliable. An(IV)-carbonate complexes [7-12].

In some cases it may be desired to conduct the solubility studies at a fixed pH value in a wide range in ligand concentrations where the ligand is also sensitive to changes in pH. In these cases it is a priori impossible to set the acid and ligand concentration to obtain a fixed pH value without the aid of preliminary modeling. As an example, Rai et al. [13] wanted to conduct studies at a fixed pH value of 2.5 in phosphate solutions ranging in concentrations from low (0.0128 mol.kg<sup>-1</sup>) to as high as 1.00 mol.kg<sup>-1</sup>. Because phosphate can have multiple species (H<sub>3</sub>PO<sub>4</sub>(aq), H<sub>2</sub>PO<sub>4</sub><sup>-2</sup>, HPO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>) that change with changes in pH and the ionic strength of the solutions, it is difficult to obtain reliable fixed pH values a priori without thermodynamic modeling. In this case we [13] took advantage of the Pitzer model to calculate pairs of HCl and NaH<sub>2</sub>PO<sub>4</sub> concentrations that would provide a fixed pH value of 2.5 (Table 1). The pH measurements of equilibrated solutions thus prepared agreed closely with the calculated values (Table 1), showing the usefulness of this calculation method.

- 4 Selection of range of variables and experimental parameters
- 4.1 Selecting a range in ligand concentrations

Many solids are hydroxides or oxides and many reactions contain  $H^+/OH^-$  as a part of the equation. Therefore, pH or pOH is a master variable for many studies. Although the normal environmental range in pH values of most waters is rather narrow (4-9, [14]), it is often desirable to conduct studies in very acidic to highly alkaline conditions so that the general governing reactions can be ascertained with a greater degree of certainty. In addition, many oxides and hydroxides (e.g. Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, tetravalent actinide hydroxides) are fairly insoluble (solubilities at or near the detection limit) in the intermediate environmental range of pH values, so it is absolutely essential for pH values beyond this region to be incorporated in the study plan to have any degree of success in defining the solubility-controlling reactions.

Solubility studies must be conducted as a function of the ligand concentration associated with the solid (e.g., X in the case of solid MX) and/or as a function of another ligand concentration for which the complexation constant values for the metal (e.g., M in the case of solid MX) are required. In cases where the metal ion hydrolyzes, the solid is oxide or hydroxide, or the ligand species changes as a function of pH, studies must also involve solubility as a function of pH in addition to as a function of the ligand concentration. If the metal or the ligand is redox sensitive then studies as a function of Eh or at fixed Eh values will be required. Several factors determine the range of variables to be selected, and to illustrate these factors a few specific examples are given.

In studies conducted as a function of pH, the range in pH values and/or the number of pH data points to be selected in a certain pH region can be based on two different criteria: 1) thermodynamic modeling, if such data are available, or 2) an exploratory set with a few points but a large range in pH values and then setting up sets with a large number of data points in the important pH regions where the metal concentrations show different dependencies as a function of pH. For example, in the SnO<sub>2</sub>(c) solubility study [15], it was known that SnO<sub>2</sub>(c) is extremely insoluble and that to obtain meaningful data a large number of data points would be required in the very acidic region, although the precise location of this region was not known. We set a large number of data points in the pH region of 0 through 3.5 and a relatively few points in the pH region of about 3.5 to 14.3 (Fig 1). It turned out that we very well covered the low pH region (0 -1.5) where the solubility of SnO<sub>2</sub>(c) decreases with the increase in pH and reaches the detection limit at pH values of about 1.5. A barely adequate number of data points were available in the pH region >~8 where the solubility either increases with the increase in pH due to the dominance of SnO<sub>6</sub><sup>2-</sup> species or is constant as a result of formation of a double salt (Na<sub>2</sub>Sn(OH)<sub>6</sub>). The information about the possible solubility-controlling reactions in this pH region (>~8) could then be used to start additional solubility studies to fully explore these dominant reactions.

The following examples illustrate a procedure for the selection of variables when the metal ion (e.g.,

Fe(III) and Pu(IV)) and the ligand (e.g., ethylenediaminetetraacetic acid, EDTA)) are both affected by changes in pH. EDTA can bind with up to six protons [16], thereby producing seven species (H<sub>6</sub>EDTA<sup>2+</sup>. H<sub>5</sub>EDTA<sup>+</sup>, H<sub>4</sub>EDTA(aq), H<sub>3</sub>EDTA<sup>-</sup>, H<sub>2</sub>EDTA<sup>2-</sup>, HEDTA<sup>3-</sup>, EDTA<sup>4-</sup>) with different EDTA species dominant in different pH regions. It is a priori (without any knowledge of this system) difficult to decipher complexation constants of these different EDTA species with Fe(III) or Pu(IV). An experimental approach to deciphering these effects should involve conducting a preliminary set of solubility experiments with Fe(III) or Pu(IV) solids with at least two fixed EDTA concentrations as a function of a large range in pH values. Such an experiment with Fe(OH)<sub>3</sub>(2-line ferrihydrite) (Fig. 2) and its interpretation [17] showed that only two Fe(III)-EDTA complexes (FeEDTA<sup>-</sup> and Fe(OH)EDTA<sup>2-</sup> are important in the pH region  $>\sim 2$ ; only EDTA<sup>4-</sup> was found to be responsible for complexation with Fe<sup>3+</sup>, and none of the other EDTA species (such as H<sub>3</sub>EDTA<sup>-</sup>, H<sub>2</sub>EDTA<sup>2-</sup>, HEDTA<sup>3-</sup>) showed any significant complexation. Based on these data one should then set up additional solubility experiments at fixed pH values [selected pH values should represent regions of dominance for the Fe(III)-EDTA complexes; in this example the pH region of dominance for FeEDTA<sup>-</sup> is approximately 2 to 6 and it is approximately 6 to 12 for the Fe(OH)EDTA<sup>2-</sup> species] as a function of EDTA to provide definitive values for complexation constants for these various species. In a similar way the studies conducted with PuO<sub>2</sub>(am) at a fixed EDTA concentration (0.0001 mol.kg<sup>-1</sup>) and as a large range in pH values [17] showed that the dominant Pu(IV)-EDTA species in different pH regions are: Pu(OH)EDTA<sup>-</sup> (pH <~5.5), Pu(OH)<sub>2</sub>EDTA<sup>2-</sup> (pH ~5.5 - 9.5), and  $Pu(OH)_3EDTA^{3-}$  (pH >~9.5) (Fig. 3). As was the case with Fe(III)-EDTA complexes, only the EDTA<sup>4-</sup> forms complexes with Pu(IV) and the complexes of other EDTA species (such as H<sub>3</sub>EDTA<sup>-</sup>, H<sub>2</sub>EDTA<sup>2-</sup>, HEDTA<sup>3-</sup>), if they form, are unimportant. Based on these data one should then set up additional solubility experiments at fixed pH values [selected pH values should represent regions of dominance for the Pu(IV)-EDTA complexes] as a function of EDTA to provide definitive values for complexation constants for these various species.

#### 4.2 Selecting and characterizing solid phase

Several different criteria are used in selecting an appropriate solid phase for study. 1) The solid phase whose solubility product is unknown or uncertain and needs confirmation. 2) The solid phase whose solubility product is known and has reasonably low solubility and which is desirable to use for determining complexation constants of the metal ion of the solid phase with an another ligand. 3) The solid phase whose solubility can be approached from both the oversaturation and undersaturation directions (solid phases may be crystalline or amorphous and pure phases or solid solutions). If the solubility can not be approached from both the over- and under-saturation directions at normal atmospheric conditions then experimental protocol must be changed (e.g., conducting experiments at higher temperatures) to accommodate this requirement<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup> It should be mentioned that those crystalline (e.g.  $CaCO_3(c)$ ,  $CaSO_4(c)$ ,  $BaSO_4(c)$ ,  $Th(SO_4)_2.9H_2O(c)$ ) and amorphous pure or solid solutions that can readily precipitate from the aqueous phase at room temperature are

Many different techniques either alone or in combination (e.g., x-ray diffraction, SEM, TEM, spectrophotometric and chemical analyses) can be used to characterize the solid phase. No attempt will be made here to describe these techniques except to emphasize that the solid phases must be thoroughly characterized using the best methods available at the start and end of the solubility studies to make sure that the nature of equilibrating solid phase is known. The characterization must cover different ranges in which the observed solubility changes as a function of a given variable.

Care must be taken in selecting the amount of the solid phase to be used in studies. It should be large enough that 1) it will exceed the maximum amount that may dissolve under a given set of conditions, 2) after the amount dissolved, there should be sufficient left for solid phase characterization, and 3) in some cases the solid phase may act as an adsorbent for the ligand being studied (e.g.,  $Fe(OH)_3(am)$  for EDTA); in those cases it is necessary to scale the solid phase to a smaller amount to minimize the impact on the ligand concentration and to make certain that the concentration of the ligand will not be significantly impacted due to adsorption by the solid phase.

#### 4.3 Selection of redox agents for controlling oxidation states

Several actinides (U, Np, and Pu) and other elements important in nuclear waste disposal (e.g., Tc and Se) exhibit multiple oxidation states in the environmental range of pH and Eh values. Therefore experimental evaluations involving these different oxidation states require that these specific oxidation states are stable throughout the duration of experiments. One of the best ways to assure this is through the use of appropriate redox agents along with the capability to control oxygen partial pressures during the experiments. This subsection is devoted to a brief discussion of various redox agents and their required attributes as well as methods to control oxygen partial pressures.

Oxygen partial pressures have traditionally been controlled by using glove-boxes/atmospheric control chambers. The use of prepurified inert gasses (e.g.  $N_2(g)$ , Ar(g)) assures that the oxygen can be controlled at about 10 ppm, which translates to about  $10^{-7}$  atmospheres of  $O_2(g)$ . Although this is a great improvement over what is present in air (~ $10^{-0.68}$  atmospheres), is not low enough to maintain many of the

ideally suited for the solubility method because their solubility can be approached from both the over- and under-saturation directions. Some of the solid phases (e.g. crystalline tetravalent actinides dioxides) do not readily form at room temperature and because the actinides are radioactive and due to radiolysis they may become amorphous at room temperatures ([18]). Relatively high temperature (e.g., 90°C) overcomes these effects and the tetravalent hydrous oxides do convert to crystalline oxides ([5] and [4]). Therefore if the solubility product of a given crystalline tetravalent dioxide needs to be investigated by the solubility method, then it would be necessary to conduct these experiments at relatively higher temperatures so that solubility can be approached from both the over-saturation and under-saturation directions.

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reduced oxidation states of different actinides (e.g., it would require ~  $10^{65}$  atm. for maintaining U(IV) and ~  $10^{-42}$  atm. for Np(IV)).

We have been able to maintain very low oxygen partial pressures, close to what is required for maintaining U(IV), by passing the glove box air through distilled water and Fe-powder suspensions and passing this over dri-rite to remove moisture that can be problematic for operation of the chamber. It should be mentioned that simply controlling the oxygen partial pressures is not sufficient to maintain the required oxidation state; it must be accompanied by appropriate redox agents. In addition, the sample tubes must always be kept sealed and open to glove box atmosphere as short a time as possible to make certain that traces of oxygen are not inadvertently introduced in the sample tubes.

Many different aspects of redox agents need to be understood. These include 1) mode of operation and desirable attributes, 2) available data for redox agents, 3) selection criteria, and 4) experimentally evaluated redox agents for redox sensitive radioactive elements. The modes of operation of redox agents include 1) interacting with oxygen so that inadvertent addition of oxygen in samples does not cause oxidation of the element of interest, 2) acting as an oxidant or reductant for the element of interest, and/or 3) acting as a redox buffer which can maintain specific Eh value for controlling a given oxidation state.

Desirable redox agents are those that 1) are kinetically active, 2) do not form strong complexes with elements of interest or if they do thermodynamic data for these interactions are available, 3) do not change pH values of the systems, 4) are effective in the range of pH values of interest, 5) are effective at room temperatures, and 6) are soluble for enhanced reactivity. Information regarding available redox agents is reported in several publications (e.g. Handbook of physics and chemistry [19], and those suitable for actinides in Newton [20]).

To check whether a given redox agent has the required potential, we first need to tabulate the reduction potentials [Eq. 1, reactions with the oxidized species (Ox) on the left side of the equation and reduced species (Red) on the right side of equation and where  $ne^-$  represents the number of electrons involved in the reaction] or the equilibrium constants ( $K^0$ ) of the reactions involving redox agents and of the species to be controlled.

$$Ox + ne^{-} = Red$$
(1)

If only the values of the equilibrium constants are available, these can be converted to reduction potentials in volts ( $E^0$ ) using Eq. 3 for 25<sup>o</sup>C derived from Eq.2, where *F* is the Faraday constant (96485.309 Jules volt<sup>-1</sup> equivalent<sup>-1</sup>, *R* is the gas constant (8.31451 Jules Kelvin<sup>-1</sup> mol<sup>-1</sup>), and *T* is the temperature in degrees Kelvin (298.15 at 25<sup>o</sup>C) [21]. The reduction potential value of the reaction involving species of interest can then be compared with the reduction potentials of the redox agents to determine whether a

given redox agent is potentially suitable to control the given oxidation state.

$$-nFE^{0} = -RT (\ln K^{0})$$
(2)  
$$E^{0} = (\log K^{0})/(16.9 \text{ n})$$
(3)

For example 1) the reduction potential of reactions involving dithionite  $(S_2O_4^{2-})$ ; metallic Fe, Zn, and Pb; and Fe<sup>2+</sup> are all lower than the reduction of Pu<sup>4+</sup> to Pu<sup>3+</sup> (Table 2), therefore all of these reducing agents can potentially produce Pu(III) from Pu(IV), and 2) the reduction potential of the Fe(III)/Fe(II) couple is higher than the U(VI)/U(IV) couple (Table 2), therefore the Fe(III)/Fe(II) couple would potentially oxidize U(IV) to U(VI) rather than reduce U(VI) to U(IV). It needs to be stated that a given redox couple/reaction can act as a reducing or oxidizing agent; it depends on the relative redox potentials of the two couples in question. If the reduction potential of the couple is lower than an another couple it then acts as a reducing agent [as Fe(III)/Fe(II) in the above example for Pu(IV)/PU(III)], but if on the other hand the reduction potential of the couple is higher than the other couple then it acts as an oxidizing agent [as Fe(III)/Fe(II) in the above example for U(VI)/U(IV)].

The effectiveness of the redox/oxidizing agent depends not only on its relative potential but also on the kinetics of reaction. In other words, just because a redox agent has a desirable potential, it does not mean that it is effective under all conditions. For example,  $H_2(g)$ , Pb-metal, and Zn-metal all have low enough potentials to reduce U(VI) to U(IV) (Table 2), but  $H_2(g)$  requires higher temperatures and is effective at room temperature only under very acidic conditions [22] and Zn-metal was not as effective as some of the other agents tested (e.g. Fe-metal,  $S_2O_3^{2-}$ , and EuCl<sub>2</sub> see [4, 22, 23]).

Actinides are important components of nuclear wastes. Therefore, many studies have been conducted on redox-sensitive actinides to obtain thermodynamic data for different oxidation states that require controlling or maintaining the given oxidation state. In general, if the oxidation state we are interested in is either the most reduced (e.g., Pu(III) for Pu) or most oxidized (e.g.Pu(VI) for Pu) then it is relatively easy to control these states by using a large number of reducing agents or oxidizing agents. It is generally much more difficult to precisely control the intermediate states (e.g., Pu(IV) or Pu(V)). To help in selecting the redox agents, a few general observations regarding oxidation states of redox sensitive actinides are discussed below. In the case of U, U(VI) is stable in oxygenated environments, U(V) is difficult to control, and U(IV) can be controlled by using strong reducing agents. In the case of Np, Np(V) is the stable oxidation state under oxygenated environments, Np(VI) will require strong oxidizing agents to make certain that selected agent does not reduce Np all the way to Np(III). In the case of Pu, Pu(VI) requires strong oxidizing agents and Pu(III) requires reducing agents, and it is generally difficult to control Pu(V) through the use of redox agents.

As mentioned earlier, several factors determine the suitability of a redox agent to control a certain oxidation state. Because of the possible kinetic sluggishness of the redox agents under different conditions, the effectiveness of a redox agent to control a given oxidation state must be verified experimentally. Redox agents that we used in our experiments and have been verified for use with specific elements, and their oxidation states are summarized in Table 3.

#### 4.4 Quantification of hydrogen ion

Many geologically important minerals and solids of radioactive elements are either oxides or hydroxides. In addition many salts (salts of organic acids such as ethylenediaminetetraacetic acid and isosaccharinic acid, and most notably salts of inorganic weak acids such as phosphate and carbonate) react with hydrogen, and potentiometric methods are extensively used to determine equilibrium constants in aqueous solutions. As Rand et al. [21] point out, the measurement of  $H^+$  activities/concentrations is fraught with many problems that have not been taken into account by many investigators. Therefore, to develop reliable thermodynamic data for many systems, studies require accurate quantification of H/OH concentrations/activities. Ultimately, values of  $H^+$  activities are required to obtain thermodynamic data at zero ionic strength for application to systems other than the one used to obtain concentrations along with thermodynamic models (such as Pitzer and SIT) that can be used to convert  $H^+$  concentrations to activities are required. These methods are briefly described in this chapter. A large amount of the discussion in this section is based on Rai et al. [24].

Hydrogen ion activities are generally quantified by pH (negative logarithm of hydrogen ion activity  $= -\log_{10} a_{H+}$ , where *a* refers to activity of the subscripted species) using a combination glass electrode with a pH meter. Glass electrodes work as ion-selective electrodes for hydrogen ions when the concentration of interfering alkali ions is low; in this case the dependence of measured electrochemical potential on pH shows a linear behavior. Most glass electrodes can be used reliably to measure pH values of relatively dilute solutions (<~0.1 mol.L<sup>-1</sup> ionic strength) in a pH value range of about 1 - 12. If the experiments involve very acidic or very basic conditions, then it is best to use a standard acid or base to adjust H<sup>+</sup> or OH<sup>-</sup> concentrations, and a geochemical code can then be used to calculate the pH values.

For studies involving pH it is very often necessary to have data points that not only have a broad range in pH values but also are evenly spaced along the pH scale. To obtain such a range in pH values it is necessary to adjust the pH of the solid-liquid suspensions multiple times on successive days before there will be a minimum drift in the final experimental pH values. After this period of pH adjustments, further adjustments in pH values *must not* be made, and the equilibration period is counted from the last pH manipulation. A similar approach, in addition to the methodology discussed below, should also be taken to adjust H<sup>+</sup> concentrations for suspensions involving concentrated electrolytes.

In cases where the studies to obtain thermodynamic data are conducted at high fixed ionic strengths such as 1, 2, 3, or >3 mol.L<sup>-1</sup> to keep the activity coefficients constant or in salt brines, the measured potentials with glass electrode are no longer linear and thus electrodes cannot be used to quantify pH. In these cases alternative methods are required to quantify hydrogen ion concentrations/activities. There are two reliable methods that can be used to quantify H<sup>+</sup> concentrations in concentrated salt solutions using ion selective electrodes (ISE). These methods are described below and involve the use of ISEs with or without liquid junctions.

#### 4.4.1 Determining H<sup>+</sup> concentration using ISEs without liquid junctions

Knauss et al. [25] discussed in detail the use of cells without liquid junctions (also see [26, 27]). They used these cells in combination with a variety of ion selective electrodes to directly measure thermodynamic quantities like  $a_{\text{HCl}}$  or activity rations such as  $a_{\text{H+}}/a_{\text{Na+}}$  which, in conjunction with analytical concentrations of the ions to which the ion-selective electrode responds and the use of SIT or Pitzer models, can be used to calculate the value of the molality of H<sup>+</sup>. For example, for high ionic strength chloride solutions the  $a_{\text{HCl}}$  (Eq. 4, [21]) can be measured with a cell consisting of H<sup>+</sup> and Cl<sup>-</sup> ion selective electrodes without liquid junctions. All the quantities in Eq.4, with the exception of  $\log_{10} m_{\text{H+}}$ , are either measured or calculated with SIT or Pitzer models, and thus  $\log_{10} m_{\text{H+}}$  can be evaluated

$$\log_{10} a_{\rm HCl} = \frac{1}{2} \left( \log_{10} m_{\rm H^+} + \log_{10} m_{\rm Cl^-} + \log_{10} \gamma_{\rm H^+} + \log_{10} \gamma_{\rm Cl^-} \right)$$
(4)

from Eq.4. Thermodynamic models can then be used to convert  $\log_{10} m_{H^+}$  to  $\log_{10} a_{H^+}$ . The disadvantages of this method are that it requires an ion selective electrode for the counter ion of interest, thermodynamic models to calculate activity coefficients of the various species, and the assurance that there are no interferences in the measurements made by the ion selective electrodes.

#### 4.4.2 Determining $H^+$ concentration using ISEs with liquid junctions

Rai et al. [24] proposed and successfully used a relatively simple procedure for estimating hydrogen ion concentrations ( $pC_{H^+} = -\log_{10}$  of H<sup>+</sup> concentration) in the Na<sup>+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O system using commercially available combination glass electrodes with liquid junctions. The method was tested over a wide range of electrolyte concentrations (0.15 to 6 mol.kg<sup>-1</sup>) and  $pC_{H^+}$  values (2 to 12) using pure and mixed NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions. A step-by-step procedure is described for Gran-type titrations of brines with HCl and/or NaOH to determine hydrogen ion concentrations from the measured/observed pH meter readings. The method can also be adapted to and has been used for other electrolytes (discussed later) including complex brines not specifically investigated by Rai et al. [24]. We recommend using this method because it is easy to use, versatile, and fairly reliable (with uncertainty of ± 0.05 pC<sub>H+</sub>).

Discussed below are the fundamental equations, a brief description, a detailed example for determining the hydrogen ion concentration in a 5.5 mol.kg<sup>-1</sup> NaCl solution, and general comments on the

use of this method for electrolytes other than NaCl. For details the reader is referred to the study by Rai et al. [24].

The EMF of a glass electrode with liquid junctions is represented as in Eq. 5, (where  $E_{(x \text{ or } s)}$  is the liquid junction potential,  $E^*$  is a constant representing the sum of all other electrostatic potential differences such as between Pt wires, R is a gas constant, T is the temperature, F is Faraday's constant, and  $a_{H^+(x \text{ or } s)}$  is the H<sup>+</sup> activity) for a given solution (x) and standards (s). The operational definition of pH is given in Eq. 6. It can be shown from Eqs. 5 and 6 that the  $pC_{H^+}$  of a given concentrated electrolyte is related to the observed pH (pH<sub>ob</sub>) measured with a glass electrode calibrated against standard buffers by equation Eq. 7 [24], where  $\gamma_{H^+}$  is the convention dependent molality-scale activity coefficient of H<sup>+</sup>,  $\Delta E_j$  the difference in liquid junction potentials between standards and a given electrolyte solution.

$$E_{(x \text{ or } s)} = E^* - (RT/F) \ln a_{H^+(x \text{ or } s)} + E_j^{(x \text{ or } s)}$$
(5)

$$pH_{(x)} = pH_{(s)} + (E_{(x)} - E_{(s)})(F/2.303RT)$$
(6)

 $pC_{H+} = pH_{ob} + \log_{10} \gamma_{H+} + (\Delta E_j)(F/2.303RT)$ (7)

Neither  $\log_{10} \gamma_{H^+}$  nor  $(\Delta E_j)(F/2.303RT)$  is individually measurable, but their combination "A" [A =  $\log_{10} \gamma_{H^+} + (\Delta E_j)(F/2.303RT)$ ] can be measured through Gran-type titrations because A remains constant in a given electrolyte solution as the H<sup>+</sup> concentration changes. Substituting A for  $(\log_{10} \gamma_{H^+} + (\Delta E_j)(F/2.303RT))$  in Eq. 7 (Eq. 8), rewriting Eq. 8 in terms of logarithms (Eq. 9), and taking the antilog of both sides and rearranging yields Eq. 10. The constant A is then obtained by a modified Gran titration procedure, as described in Appendix A, in which the moles of added free acid per liter are plotted against  $H_{ob}^+$  (i.e.,  $10^{-pHob}$ ). The logarithm of the slope of this curve provides the correction factor "A" needed to convert the pH<sub>ob</sub> reading to pC<sub>H+</sub> using the Eq. 8.

$$pC_{H+} = pH_{ob} + A \tag{8}$$

$$-\log_{10}C_{H^+} = -\log_{10}H_{ob}^+ + A \tag{9}$$

$$H_{ob}^{+} = 10^{A} C_{H}^{+}$$
(10)

The experimental procedure [24] to obtain the values of factor "A" is described in Appendix A and was used as an example to determine the correction factor A for determining the H<sup>+</sup> concentrations from measured pH values of 5.5 mol.kg<sup>-1</sup> NaCl solutions using the combination glass electrode. For this purpose 25 mL of 5.5 mol.kg<sup>-1</sup> NaCl solution was titrated with 0.1040 mol.L<sup>-1</sup> HCl solution at 20°C. The raw experimental data are listed in Table 4 and are plotted in Fig. 4. The slope of the plotted line ([H<sup>+</sup><sub>free</sub>, add] 10<sup>3</sup> (mol.L<sup>-1</sup>) vs. [H<sup>+</sup><sub>ob</sub>]10<sup>3</sup> (mol.L<sup>-1</sup>)) was 8.357; using this slope the value of correction factor A (A = log<sub>10</sub> (8.357) = 0.922) was calculated. This value was then used in Eq. 8 to calculate the H<sup>+</sup> concentration of unknown 5.5 mol.kg<sup>-1</sup> NaCl solutions from the measured pH values of these solutions using the

electrode that was used in titration data listed in Table 4.

The data presented in Rai et al. [24]) shows that the values of the correction factors can also be determined using a base such as NaOH instead of the acid (HCl), and the values thus obtained are similar to the values obtained using HCl. If NaOH is used as the titrant, it is necessary to use thermodynamic models to calculate the  $K_w$  of water for the given electrolyte, and the value of  $H^+_{free, add}$  needed for evaluating the correction factor A can then be calculated from the relationship  $[H^+_{free, add} = K_w/(NaOH)$ added in  $mol(L^{-1})$ ]. In the past some authors have used the same concentrated electrolyte in the salt bridge as the electrolyte used in the experiments to minimize or eliminate the liquid junction potentials. However, this does not eliminate the need to determine the value of the correction factor A to accurately determine the  $H^+$  concentrations. This is because the correction factor depends not only on the liquid junction potentials but also on the activity coefficients of H<sup>+</sup>, and the latter can be significantly different than in the buffer solutions. For example, when titrations were performed for 6 mol.kg<sup>-1</sup> NaCl with an electrode that contained 6 mol.kg<sup>-1</sup> NaCl in the salt bridge, the value of the correction factor was found to be 1.27 [24]. For electrolytes (such as NaCl, CaCl<sub>2</sub>, NaClO<sub>4</sub>, MgCl<sub>2</sub>) that do not chemically react with H<sup>+</sup> the procedure described in Appendix A, where acid is used for titrations, can be used with one modification: the salt bridge should be filled with NaClO<sub>4</sub> for titrations of electrolytes involving perchlorate to avoid precipitation of KClO<sub>4</sub> when using standard electrodes that normally contain KCl as the salt bridge. Extra precautions are required to determine correction factors for electrolytes that react with  $H^+$  (e.g., sulfates which would react with  $H^+$  to produce HSO<sub>4</sub>) or with OH<sup>-</sup> (e.g., electrolytes containing Mg that would react with  $OH^{-}$  to produce  $Mg(OH)_{2}(s)$ ). The calculation of correction factors in these cases requires that the amount of  $H^+$  or  $OH^-$  consumed by these side reactions be accurately determined. For example in the case of titrations of sulfate electrolytes with H<sup>+</sup>, the total amount of hydrogen added  $(H_{add}^+)$  can be converted to  $H_{free, add}^+$  (Eq. 11) from the apparent equilibrium constant (K<sub>app</sub>, calculated using thermodynamic equilibrium models for the given electrolyte) for the HSO4<sup>-</sup> formation reaction  $(H^+ + SO_4^{2-} = HSO_4)$  and the knowledge that total  $H^+_{add}$  is the sum of  $H^+_{free, add}$  and the amount of HSO<sub>4</sub><sup>-</sup> produced in titration.

$$H^{+}_{free,add} = (H^{+}_{add}) / [1 + K_{app} (SO_{4}^{2})]$$
(11)

The procedure described in Appendix A has been successfully used for a large number of relatively dilute to concentrated (as high as 9 mol.kg<sup>-1</sup>) simple electrolytes, mixtures of electrolytes, and synthetic brines. For examples, the procedure has been used for NaCl [24, 28-30], NaClO<sub>4</sub> ([30]), CaCl<sub>2</sub> [31, 32], MgCl<sub>2</sub> [29], mixtures of NaCl and Na<sub>2</sub>SO<sub>4</sub> [24], and synthetic brines containing Na, K, Ca, Mg, Cl, SO<sub>4</sub>, and Br [33, 34].

4.4.3 Use of Thermodynamic Models to Set up Experiments for Relatively Concentrated Electrolytes Containing Known H<sup>+</sup> Activities

Thermodynamic models (e.g., Pitzer and SIT) can be used to determine molality of a particular acid required for a given electrolyte or mixture of electrolytes to obtain a certain pH value. These combinations of acids and electrolytes can then be used to set experiments to obtain thermodynamic data. This method can be used for all electrolytes or mixtures of electrolytes whether or not they react with  $H^+$  or OH<sup>-</sup>. This method is most accurate when used for relatively acidic or basic conditions. Rai et al. [1, 13, 35] used this method to calculate the HCl molalities at different NaH<sub>2</sub>PO<sub>4</sub> molalities ranging up to 1.0 mol.kg<sup>-1</sup> required to obtain a constant pH value of 2.5 for studies involving solubilities of PuPO<sub>4</sub> and NdPO<sub>4</sub> or 1.4 for studies involving BiPO<sub>4</sub>. An example of the use of this method for fixing pH 2.5 for studies involving PuPO<sub>4</sub> is discussed below. For these calculations Rai et al. [13] used the Pitzer model (GMIN code, [36]) that included appropriate ion-interaction parameters and the required thermodynamic data (Tables 5 and 6). Based on these calculations the HCl molalities required for different NaH<sub>2</sub>PO<sub>4</sub> molalities to control pH value at 2.5 were determined (Table 1). Rai et al.'s [13] data involving these solutions showed that the measured pH values (although measured pH values in the relatively high NaH<sub>2</sub>PO<sub>4</sub> concentrations are not expected to be reliable) were very similar to the calculated pH (2.5) for these solutions, thereby showing that this method is reliable.

#### 4.5 Experiments involving carbonate as a ligand

Carbonate makes stable solid phases and strong complexes with many elements. Therefore, it is equally important to be aware of the need to keep carbonate out of the experimental systems as it is to control its concentrations. Carbonate impurities in experiments can result from two different sources, 1) experiments conducted in air in relatively acidic to alkaline conditions, which can be avoided by conducting experiments in atmospheric control chambers with inert gaseous atmospheres, and 2) experiments using relatively large quantities of bases that normally contain significant soluble carbonate impurities, which can be avoided by using carbonate-free bases either purchased or through in-house preparations<sup>2</sup>.

Carbonate concentrations can be controlled in two different ways, by1) controlling partial pressure of  $CO_2(g)$  primarily in studies involving relatively acidic conditions, and 2) the addition of standard carbonate solutions. It should be mentioned that when studies are conducted as functions of  $CO_2(g)$ , it is important that soluble total carbonate concentrations in the experimental solutions are analytically determined and are compared to calculated values based on thermodynamic data, pH, and  $CO_2(g)$  partial pressures to make

<sup>2</sup> Based on analytical carbonate concentration in the base, it can be reacted with  $BaCl_2$  solution containing 10% more  $BaCl_2$  than the carbonate equivalent and by removing the precipitated  $BaCO_3$  and storing the base in a  $CO_2(g)$ -free gaseous atmosphere (e.g., see [37]). However, it should be made certain that the excess carbonate-precipitating agent, Ba in this case, will not significantly interfere with the reactions investigated. If the carbonate-precipitating agent is expected to interfere, then one can choose to add only the equivalent amount of this reagent to the carbonate equivalent amount in the base.

certain the solutions are in equilibrium with the given  $CO_2(g)$  partial pressures; sometimes due to kinetic effects and/or experimental constraints the solutions may not truly be in equilibrium with the given  $CO_2(g)$  pressures (e.g., see [38]). Additionally, the solid-water suspensions can be spiked with known quantities of standard carbonate solutions, calculated as stated above, to make certain that the suspensions are indeed in equilibrium with the given  $CO_2(g)$  pressures. A couple of things must be mentioned in regard to controlling carbonate concentrations through the addition of standard carbonate solutions. Firstly,  $CO_3^{2^2}$  is the dominant species at pH values  $\sim 10.3$ , and secondly, at pH values of <10.3 there will be a mixture of different carbonate species (H<sub>2</sub>CO<sub>3</sub>(aq), HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) and the dominant species will depend on the pH. These experiments should be conducted in sealed containers (preferably glass) to avoid either in-gassing or out-gassing of  $CO_2(g)$ . Since carbonate species depend on the pH, especially at pH values <10.3, it is important that the pH values either are precisely known or are calculated from the geochemical codes. Experiments with carbonate solutions at pH  $>\sim10.3$  are relatively easy, and precise pH values can be calculated from the molalities of the base and the carbonate solutions used in experiments.

#### 5 Expected results

It is important to anticipate different possible results of the experiments that are to be conducted. In this regard, one can do a preliminary modeling based on the available thermodynamic data. The reason it is important to know about the expected results is so that one can before hand anticipate problems that may be encountered during the experimentation and take steps to address these problems. Here are several examples, along with ways to handle the problems. 1) To maintain a certain range in oxidizing/reducing conditions, it is important to test/acquire beforehand redox agents or equipment that will help maintain these stringent conditions. 2) With solid phases that are expected to show very low solubility, it is important to make certain that sensitive analytical methods will be available. 3) Certain ligands (e.g. Si) are highly soluble only in high pH but not in low pH. Because the equilibrated solutions are routinely acidified during analyses using analytical techniques such as ICP-MS, it is necessary to plan for this type of problem beforehand; otherwise the analytical results will be unreliable. 4) In conditions where the original solid phase may convert to a different solid phase (e.g., as a function of pH, or as a result of increase in ligand concentration which may result in double salt), anticipating such changes will help develop/use appropriate analytical and modeling methods or plan for selecting appropriate ranges in variables. Having discussed the usefulness of anticipated results for practical planning and analyses use, I want to emphasize a fact that every researcher must be constantly careful about. We are very likely to see the results we expect because we have that mindset. It is extremely important to look at the results with a completely open mind.

#### 6 General equipment requirements

Depending on the metal-ligand systems under investigation, there is a large list of equipment that may be required for these studies. For examples, 1) analytical equipment for measuring total metal concentrations (generally ICP-MS for elements and radio-counting equipment for radioactive elements),

ligand concentrations, and pH, 2) equipment for measuring oxidation states and species (such as solvent extractions, various kinds of spectrophotometers, EXAFS), 3) equipment for characterization of solid phases (X-ray diffraction, EXAFS, SEM equipped with EDAX, wet chemistry laboratory facility for total chemical analyses), 4) atmospheric control chambers for redox-sensitive experiments and where partial pressure of different gases needs to be controlled, and 5) filtration and sample preservation methodology and equipment. It is assumed that either the appropriate equipment is available or the researchers have access to such equipment for analyses of samples.

#### 7 Conducting experiments

Examples of methodology that can be used to conduct experiments in several different types of systems are: for  $H^+/OH^-$  [15, 37, 39]; for carbonate [8, 9, 12, 38, 40, 41]; for sulfate [40, 42]; for phosphate and EDTA [13, 17, 35, 43, 44]; and for brines [33]. These are just examples and this is by no means an exhaustive list. Nor does it mean that all studies in these systems should follow the procedures outlined, but rather that the procedures used in these studies can be adapted to other similar studies. It is generally best to review the literature to determine what methodology others have used under similar conditions and to determine for yourself whether the methodology previously used is sound or needs improvements. For these reasons only a very general and brief description is provided here for conducting experiments.

For the selected solid-ligand system, a finite quantity<sup>3</sup> of the solid phase is added to a vessel, usually a 50-mL centrifuge tube (because it is convenient to be able to centrifuge the sample for aid in separating the solid phase from the aqueous phase) containing a stir bar and about 40 mL of the standard ligand/ionic-medium solution<sup>4</sup>. Several different samples in a given set and different sets with standard ligand solutions at fixed or variable pH values may be required for developing a reasonable quantity of experimental data to obtain reliable values for thermodynamic constants. For systems sensitive to H<sup>+</sup> concentration, it may be necessary before initiating the equilibration period to periodically adjust the pH values of the samples to either obtain a broad range in pH values evenly spaced along the pH scale or to obtain a fixed pH value. In these cases, it is necessary to accurately record the amount of the acid (usually HClO<sub>4</sub>) or base (usually NaOH) used to accurately calculate the total aqueous concentrations of Na and the anionic component of the acid in aqueous solutions. The samples should be equilibrated in atmospheric

<sup>&</sup>lt;sup>3</sup> For radioactive solid phases it is desirable to use the smallest amount of the solid phase necessary in order to avoid unwanted side effects due to radiolysis. An ideal amount of the solid is approximately 5 to 10 mg in excess of the maximum amount of the solid that can dissolve under the given experimental conditions. If, however, the solid phase will need to be characterized, the amount of solid phase will have to be increased.

<sup>&</sup>lt;sup>4</sup> A 40-mL amount is usually sufficient to analyze the samples 3-4 times to check for an approach to equilibrium. The experiments may involve low ionic strength ligand solutions or ligands in a high constant ionic strength non-complexing ionic media such as NaClO<sub>4</sub> or NaCl as may be needed to represent geological environmental conditions.

control chambers, but can be equilibrated on bench top if it is determined that the  $CO_2(g)$  and or  $O_2(g)$  partial pressures in the air will not interfere with the experimental variables.

The samples thus prepared are continuously shaken under controlled temperature conditions until analyzed. Periodically the samples are analyzed (generally at intervals of one week, two weeks, and four weeks which is sufficient for samples to reach equilibrium, but a given system may require either considerably shorter or longer equilibration period to reach equilibrium) until at least two successive analyses show similar metal concentrations as a function of pH/ligand concentrations. At each equilibration period the pH and/or Eh values (as appropriate for the given system) of the suspensions are measured using electrodes standardized against buffers covering the range in values expected in the samples<sup>5</sup>. At each equilibration period, the samples are centrifuged and a finite amount of the sample is filtered through as fine a membrane filter as possible. It is always desirable but in some cases it is absolutely necessary<sup>6</sup> to adjust the pH values of the filters by equilibrating them with water adjusted to the pH values of given samples and to filter a small portion of sample and discard the filtrate before collecting the filtrate for analyses as described in [42, 45]. It is always also a good idea to conduct a few simple experiments with filters to check how effectively they separate the solids from solutions, as for example discussed in Rai et al. [46]. The filtrates are analyzed for total chemical composition, oxidation states, and speciation. At least at the end of the experiment but preferably at other equilibration periods as well, the solid phase should be characterized.

### 7.1 Quality control

If the experiments are worth doing then it is worthwhile to be sure that 1) the experimental systems and samples used are well described, 2) that the experimental procedures used are the best that are available, and 3) that they are well documented. A few of the necessary quality control issues are discussed below.

It may seem trivial, but it is very important that the sample designations used are unique for each sample in any set and convey something about the experiment without having to look up the sample numbers in a laboratory book. I learned early in my career that poor sample designations can have very bad consequences. For example, while collecting fairly dry soil samples we had written sample numbers

<sup>&</sup>lt;sup>5</sup> The solid/liquid suspensions should be continuously and slowly stirred during these measurements. There is generally a continuous slow drift in these measured values. Rather than assuming that these values have stabilized at an undefined time, we have consistently taken these readings at 2-minutes and 5-minutes and have found them to be similar in most cases. The 2-minute and 5-minute readings can be used as guides to ascertain whether the values have stabilized. We have noticed that rarely more than 5-minutes are needed before the values stabilize.

<sup>&</sup>lt;sup>6</sup> It is necessary to take these steps. We found by experience that the filters were changing the pH values of the samples which in turn changed the aqueous metal concentrations.

in ink on pieces of paper which we inserted into the plastic sacks along with the soil. When we opened the plastic bags a few days later in the laboratory all our sample numbers were illegible. We would have had to go on another sampling trip if we had not also put tags on the outside of each sampling bag. On other occasions we designated samples with 1-20 and a few months later we started another similar set with 1-20 sample numbers. We had not planned to carry these experiments over several years, but we ended up doing so. The end result was that we had a very difficult time connecting the analyses to a particular set and even determining the year we started them. Of course this was before the computer age and when only written notes were made. Since then we have developed a very comprehensive system of designating the samples which has helped us keep the sample numbers and associated analyses straight. I will briefly describe the system we used. I do not mean to suggest that this is the only system, but rather that some elements of this system should be incorporated in sample designation. Any scheme of sample designation can be used so long as it would help the researcher himself (and also someone else who might look at the results) to know which set/sets of experiments correspond with the given analyses.

The sample designation scheme we have successfully used is as follows: dd/mm/yy - Element/site - Chemical system under investigation - Sample number - Equilibration period. For example, we start two different sets with 15 samples each. The first set begins on November 10, 2012 on PuO<sub>2</sub>(am) solubility as a function of EDTA at a fixed pH value of 12, and the second set begins on the same day but as a function of pH at fixed EDTA concentration of 1mM. We analyze both sets after seven days. Our sample designations for the first sample of these sets will be: 101112-Pu-vEDTA pH12-1 for set I and 101112-Pu-vpH-1mMEDTA-100 for set II. For the seven day analyses of these samples the designations will be 101112-Pu-vEDTA-pH12-1-7 and 101112-Pu-vpH-1mMEDTA-100-7 respectively (where v stands for variable). Note that not only the designations differ but also that the starting sample number in each set is drastically different from each other (1 and 100 in the above example) so there is no possibility that the analyses for first set could ever be confused with analyses for the second set. The two most important aspects of sample labeling are 1) the number will include identifying information (such as Pu-vEDTA-pH12 in above sample) and 2) no two samples will ever have the same sample number.

The experimental procedures, standard solutions and buffers used in experiments should be well documented. The standards should be current and not expired. It is also the responsibility of the scientists that the records of calibrations of different instruments are maintained. The detection limits for analytical analyses by different instruments must be verified for systems under investigation. Appropriate standard protocols for good practices should be followed. For example, when the analyses are done by ICP or ICP-MS, several different dilutions of the given sample must be made and analyzed to be sure that the results are reliable and that the results are replicated. When the concentrations are near the detection limits it may be necessary to use the known additions method to verify that the results are reliable.

#### 8 Interpreting experimental data

The experimental data are plotted with metal concentration as the Y-axis and the independent variable such as ligand concentration as the X-axis. In most cases, the metal concentrations are dependent on more than one variable in the experiment (e.g., pH and some other ligand). In a case where the experimental information is available for the system as a function of pH at fixed different concentrations of the ligand, several different plots of pH vs. metal ion concentrations are made corresponding to each different concentration of the ligand. If the available data is as a function of the ligand at different fixed values of pH, several different plots of ligand vs. metal ion concentrations are made corresponding to each different pH value (e.g. see [1]). For convenience in interpreting the data, metal ion and ligand concentrations are plotted in  $\log_{10}$  of the concentration in mol.kg<sup>-1</sup>. If the system is very simple (i.e., low ionic strength and different regions in the graph are represented by only one dominant reaction), then it is relatively easy to interpret data by using simple electrolyte models to calculate ionic activities (e.g., Debye Huckel or Davies equation) and linear regressions. However, only occasionally are the experimental systems simple enough that this approach can be used. Most often the experimental systems are very complicated in that the ionic strengths may vary and be high with multiple reactions that are involved in any given region, so it is necessary to use complicated electrolyte models (e.g., SIT and Pitzer) with many different terms and many different species that may vary as a function of pH and/or ligand concentration. In cases such as these, simple calculations cannot be used to interpret the data but require computerized fitting codes that use SIT and Pitzer formulism (e.g., NONLIN-SIT, [21]; INSIGHT, [47]). These fitting codes can be used to predict concentrations with a given chemical model or to fit not only the chemical potentials of the chemical species of interest but also the ion-interaction parameters from multiple samples and data sets simultaneously and allow the calculation of activities of different ions/species to obtain values of thermodynamic constants.

It must be emphasized that it is absolutely necessary not only to accurately interpret the experimental data but also to develop a consistent and comprehensive thermodynamic model based on these data and the literature data that are reliable. Very often, the authors just report values of equilibrium constants reported in the literature for the reactions they evaluated. This is not sufficient. If the values reported in the literature are reliable then they must be used in the model to interpret the current experimental data or to verify the literature values. If, on the other hand, the experimental data reported in the literature are of good quality but the original authors misinterpreted the data<sup>7</sup> or did not interpret it at all, then it is the responsibility of the authors to reinterpret these data and develop a comprehensive thermodynamic model consistent with all of the data (for examples of these aspects and where the reinterpretational tools (such as NONLIN-SIT and INSIGHT) are necessary for these interpretations because of the additional

<sup>&</sup>lt;sup>7</sup> Due to the inclusion of species they should not have, use of an electrolyte model of uncertain quality, or a model that is drastically different from the one being used to interpret the experimental data and which explain literature data.

complications involved in these studies conducted using different techniques (such as solvent extraction and potentiometric titrations) and ionic media.

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$\log_{10}$ [HCl] (mol.kg <sup>-1</sup> )	$\log_{10} [NaH_2PO_4] (mol.kg^{-1})$	$pH_{(observed)}^{a}$
-2.479	-4.000	2.480
-2.479	-3.699	2.493
-2.456	-3.398	2.494
-2.444	-3.097	2.502
-2.420	-2.796	2.480
-2.367	-2.495	2.517
-2.268	-2.194	2.485
-2.143	-1.893	2.484
-1.971	-1.592	2.484
-1.770	-1.291	2.481
-1.538	-1.000	2.485
-1.284	-0.699	2.484
-1.018	-0.398	2.491
-0.842	-0.222	2.491
-0.717	-0.097	2.510
-0.620	0.000	2.502

Table 1. Calculated HCl mol.kg<sup>-1</sup> required to fix a pH value of 2.5 for various NaH<sub>2</sub>PO<sub>4</sub> mol.kg<sup>-1</sup> solutions along with the observed pH meter readings for these solutions [13]

<sup>a</sup> pH values reported by Rai et al. [13]for the solubility of  $PuPO_4(cr, hyd.)$  in the HCl and  $NaH_2PO_4$  solutions equilibrated for 6 days.

Reaction	$\log_{10} K^0$	$E^{0}(\mathbf{V})$
Selected Redox Agents [	19]	
$2SO_3^{2-} + 2H_2O + 2e^{-} = S_2O_4^{2-} + 4OH^{-}$	-37.86	-1.12
$Fe^{2+} + 2e^{-} = Fe$	-13.82	-0.409
$Zn^{2+} + 2e^{-} = Zn$	-25.79	-0.763
$Pb^{2+} + 2e^{-} = Pb$	-4.25	-0.126
$Fe^{3+} + e^{-} = Fe^{2+}$	13.01	0.770
Selected Actinide Reaction	s [49]	
$UO_2^{2+} + 4H^+ + 2e^- = U^{4+} + 2H_2O$	9.038	0.267
$NpO_2^+ + 4H^+ + e^- = Np^{4+} + 2H_2O$	10.212	0.604
$Pu^{4+} + e^{-} = Pu^{3+}$	17.694	1.047
$PuO_2^+ + 4H^+ + e^- = Pu^{4+} + 2H_2O$	17.453	1.033

# Table 2. Redox potentials of selected reactions involving redox agents and actinides

Redox Agent	Effective in	Reference	Comments
	controlling		
Fe powder	U(IV)	[10, 12, 22, 50]	Suitable only for alkaline
	Np(IV)	[6, 50]	pH, effective in dilute
	Pu(III)	[34, 50]	solutions, very sluggish in
			brines
Fe(II)	Pu(III)	[51]	
$Na_2S_2O_4$	U(IV)	[7, 10, 23]	Very effective in a wide
			range of pH
	Np(IV)	[6, 7, 8, 52]	Very effective in a wide
			range of pH
	Tc(IV)	[28]	Alkaline conditions
Zn - metal	U(IV)	[23]	Not very effective
	Np(IV)	[6]	
Pb - metal	Np(IV)	[6]	Not suitable
Ni - metal	Np(IV)	[6]	Not suitable
Cu(I)/Cu(II)	Np(IV)	[53]	Effective in low pH, dilute
			solutions
EuCl <sub>2</sub>	U(IV)	[4, 22, 29]	More suitable in acidic
			conditions
	Tc(IV)	[28]	Acidic conditions
NH <sub>2</sub> OH.HCl	Np(IV)	[8, 54]	Unsatisfactory in alkaline,
			okay in acidic
NH <sub>2</sub> .NH <sub>2</sub>	Np(IV)	[8]	Unsatisfactory in alkaline
			conditions
	Tc(IV)	[28]	Satisfactory in acidic
			conditions
Hydroquinone	Pu(III)	[51]	Effective in acidic
			conditions
NaOCl	Pu(VI)	[55]	Very effective in a wide
			range of pH but higher the
			pH more stable is NaOCl

 Table 3.
 Redox agents used in controlling different actinide oxidation states

pH <sub>ob</sub> <sup>a</sup>	HCl added (mL)	HCl added (mol.L <sup>-1</sup> ) <sup>b</sup>
8.210	0	0.000E+00
7.840	0.025	1.039E-05
7.110	0.05	2.076E-05
6.801	0.053	2.200E-05
6.598	0.055	2.283E-05
6.432	0.057	2.366E-05
6.138	0.06	2.490E-05
5.924	0.062	2.573E-05
5.756	0.064	2.656E-05
5.606	0.066	2.738E-05
5.450	0.069	2.862E-05
5.309	0.071	2.945E-05
5.159	0.074	3.069E-05
4,998	0.077	3.193E-05
4 884	0.08	3 317E-05
4 761	0.083	3 441E-05
4 639	0.086	3 565E-05
4 548	0.09	3 731E-05
4 423	0.094	3.896E-05
4 323	0.098	4 061E-05
4.323	0.000	4 267E-05
4 138	0.105	4.2072-05
4.138	0.114	4 721E-05
3 963	0.12	4.968E-05
3.884	0.12	5 256E-05
3.804	0.127	5 586E 05
3.707	0.135	5.580E-05
3.727	0.144	6 267E 05
3.030	0.154	6 810E 05
2.515	0.105	7.211E.05
3.313	0.1/7	7.067E.05
3.439	0.193	/.96/E-05
3.383	0.209	<u>8.622E-05</u>
3.300	0.231	9.522E-05
3.246	0.249	1.026E-04
3.179	0.2/4	1.127E-04
3.118	0.301	1.23/E-04
3.055	0.334	1.3/1E-04
2.998	0.37	<u>1.51/E-04</u>
2.929	0.414	1.694E-04
2.8/4	0.458	1.871E-04
2.874	0.458	1.871E-04
2.816	0.511	2.083E-04
2.764	0.57	2.318E-04
2.702	0.642	2.604E-04
2.649	0.713	2.884E-04
2.599	0.795	3.205E-04
2.551	0.888	3.567E-04
2.499	0.995	3.981E-04

Table 4.Titration of 25 mL of 5.5 mol.kg<sup>-1</sup> NaCl with 0.0104 mol.L<sup>-1</sup> HCl at 20°C (after [24])

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Table 4	Titration of 25 mL of 5.5 mol.kg <sup>-1</sup>	NaCl with $0.0104 \text{ mol}.L^{-1}$	HCl at 20°C (after
[24])(Contin	ued)		

$pH_{ob}^{a}$	HCl added (mL)	HCl added $(mol.L^{-1})^{b}$			
2.457	1.105	4.402E-04			
2.410	1.236	4.900E-04			
2.368	1.37	5.403E-04			
2.325	1.518	5.953E-04			
2.287	1.673	6.523E-04			
2.254	1.843	7.140E-04			
2.217	2.034	7.825E-04			
<sup>a</sup> The $10^{-\text{pHob}}$ is plotted as $[\text{H}^+_{\text{ob}}]10^3 \text{ (mol.L}^{-1})$ , the Y-axis in Fig. 4					
<sup>b</sup> The HCl (mol.L <sup>-1</sup> ) added [(25 x 0.0104) / (25 + mL of HCl added)] is plotted as					
$[H^+_{free, add}]$ 10 <sup>3</sup> (mol.L <sup>-1</sup> ), the X-axis in Fig. 4.					

Binary parameters					
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{\phi}$	Reference
$Na^+-H_2PO_4^-$	-0.0533	0.0396	0.00	0.00795	[56]
Na <sup>+</sup> -HPO <sub>4</sub> <sup>2-</sup>	-0.0583	1.4655	0.00	0.02938	[56]
$Na^{+}-PO_{4}^{3-}$	0.17813	3.8513	0.00	-0.05154	[56]
Na <sup>+</sup> -OH <sup>-</sup>	0.0864	0.253	0.00	0.0044	[57]
$Na^+-C1^-$	0.0765	0.2664	0.00	0.00127	[57]
$H^+-C1^-$	0.1775	0.2945	0.00	0.0008	[57]
	]	Fernary para	umeters <sup>c</sup>		
H <sub>3</sub> PO <sub>4</sub> -H <sub>3</sub> PO <sub>4</sub>	0.0503				[58]
$H_3PO_4-H_2PO_4^-$	-0.4				[58]
$H_3PO_4-H^+$	0.29				[58]
$H^+$ -N $a^+$	0.036				[57]
$H^+$ -Na <sup>+</sup> -C1 <sup>-</sup>	-0.004				[57]
Cl <sup>-</sup> -OH <sup>-</sup>	-0.05				[57]
$Cl^{-}-H_2PO_4^{-}$	0.1				[58]
$Cl^{-}-OH^{-}-Na^{+}$	-0.006				[57]

Table 5.Ion-interaction parameters for the Pitzer model used to calculate HCl mol.kg<sup>-1</sup> required to fix<br/>a pH value of 2.5 for various NaH<sub>2</sub>PO<sub>4</sub> mol.kg<sup>-1</sup> solutions

Species	$\Delta_{\rm f} G_{\rm m}^{0}/{ m RT}$
H <sub>3</sub> PO <sub>4</sub> (aq)	-463.647
$H_2PO_4$	-458.719
$HPO_4^{2-}$	-442.113
$PO_4^{3-}$	-413.676
Cl	-52.932
Na <sup>+</sup>	-105.670
$H_2O(l)$	-95.661
OH	-63.421

Table 6. Dimensionless Gibbs free energies of formation( $\Delta_f G_m^{-0}/RT$ ) used to calculate HCl mol.kg<sup>-1</sup> required to fix a pH value of 2.5 for various NaH<sub>2</sub>PO<sub>4</sub> mol.kg<sup>-1</sup> solutions (all values from [49])



Fig. 1. Total Sn concentrations (solid line) and Sn-OH species in equilibrium with cassiterite (SnO<sub>2</sub>) at pH values of  $\leq \sim 11.7$  and with Na<sub>2</sub>Sn(OH)<sub>6</sub>(s) at pH values  $> \sim 11.7$  for different periods as a function of pH [15]



Fig. 2. Solubility of Fe(OH)<sub>3</sub>(am) in 0.0001 mol.kg<sup>-1</sup> EDTA as a function of pH and equilibrated for 27 days. Solid line represents total Fe concentration and other lines represent concentrations of different species as marked in the figure (after [17])



Fig. 3. Solubility of  $PuO_2(am)$  in 0.0001 mol.kg<sup>-1</sup> EDTA as a function of pH. Solid line represents predicted total Pu concentration and the other lines represent concentrations of different species as marked in the figure (after [17])



Fig. 4. Titration of 5.5 mol.kg<sup>-1</sup> NaCl with 0.0104 mol.L<sup>-1</sup> HCl at 20°C using the Orion-Ross combination glass electrode (raw data are listed in Table 4) (after [24]).

### APPENDIX A.

# Determining H<sup>+</sup> concentrations in concentrated electrolytes using combination glass electrode: Procedure

The equipment required for this procedure includes 1) pH meter equipped to read out in pH units to a precision of at least 0.01 units, 2) combination glass pH electrode (e.g., Orion-Ross), 3) pH buffer solutions (2, 4, 7, 10), 4) a buret capable of delivering titrant accurate to 0.001 mL, 5) standardized acid solution (0.01 to 0.1 N, also see next section for selecting exact normality of acid), 6) transfer pipette,  $25.0 \pm 0.1$  mL, 7) titration vessel with cover, and 8) purified N<sub>2</sub> gas for sparging. The steps (i- v) involved in this procedure along with the method of calculating the correction factor A (described in text Eq. 8) from the data generated using these steps are described below.

### Steps in the procedure

- Calibrate pH electrode and meter using pH buffer solution at 4 and 7, referring to the pH meter manual as a guide. Measure and record the electrode response in pH 2 and 10 buffers to note the reliability of measured values but do not adjust the meter.
- ii. Deliver  $25.0 \pm 0.1$  mL of the electrolyte for which calibration is required into the titration vessel and sparge this solution with purified N<sub>2</sub> gas for 5 minutes before beginning the titration. Continuously sparge and stir the solution throughout the titration procedure.
- iii. Measure and record the temperature of the solution to a precision of  $\pm 1^{\circ}$ C.
- Add the standardized acid to the titration vessel containing the sparged electrolyte solution until an appropriate pH change is observed. Select the normality of the acid so that 1) the volume of the acid can be accurately measured to observe pH changes of about 0.2 to 0.4 for pH units above 4.5 and of 0.1 pH units for pH <4.5, and 2) the total volume of acid used by the end of titration is less than 10% of the original volume of electrolyte used for titration. Record the normality of the standard acid (N), measured pH (pH<sub>ob</sub>), and the corresponding volume in mL of added standardized acid (V<sub>i</sub>).
- v. Repeat step iv until a final pH value of about 2 is observed. Different electrolytes will depress the measured pH values by different amounts, thereby requiring some adjustment to the measured pH range over which the data is taken.

### Calculations

- i. Calculation of acid added and measured
  - a. Equivalents of  $H^+/L$  measured,  $Y_i = 10^{-pH}$

- b. Equivalents of  $H^+_{free, add}/L$  added to titration vessel,  $X_i$ .  $X_i = (V_iN)/(Z + V_i)$ : Normality (N) of standard acid per liter is added to the titration vessel containing Z mL of electrolyte solution for electrolytes such as NaCl that do not chemically react with added  $H^+$ ; in these cases the added  $H^+$  equals  $H^+$  free added ( $H^+_{free, add}$ ). The Z in most situations is selected to be about 25 mL (as stated in procedure step ii), and the normality of the acid is selected in such a way that the total volume of acid added by the end of titration does not exceed about 10% of the volume (Z) of electrolyte used in titration. Note that the value of  $X_i$  will involve a different equation for electrolytes such as Na<sub>2</sub>SO<sub>4</sub> that chemically react with added  $H^+$  (see [24] for details)
- ii. Data set selection for calculation of correction factor A

Plot  $Y_i$  as the Y-axis and  $X_i$  as the X-axis. For further calculations select those  $(X_i, Y_i)$  data pairs that yield a linear relationship by visual inspection.

- iii. For the selected  $(X_i, Y_i)$  data pairs, use a linear correlation to calculate the slope of the line  $(\text{slope} = (X_iY_i (X_iY_i/n))/(X_i^2 X_i^2/n)).$
- iv. Calculate  $pC_{H^+}$  from the following relationship:

$$pC_{H+}=pH_{ob}+log_{10}(slope)$$
(8)  
where log\_{10} (slope) = A, the correction factor described in Eq. 5.

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表 1. SI 基本单位				
甘木昌	SI 基本単位			
本平里	名称	記号		
長さ	メートル	m		
質 量	キログラム	kg		
時 間	秒	s		
電 流	アンペア	А		
熱力学温度	ケルビン	Κ		
物質量	モル	mol		
光度	カンデラ	cd		

表2.基本単位を用いて表される	SI組立単位の例
a d d d d d d d d d d d d d d d d d d d	基本単位
和立重 名称	記号
面 積 平方メートル	m <sup>2</sup>
体 積 立法メートル	m <sup>3</sup>
速 さ , 速 度 メートル毎秒	m/s
加速度メートル毎秒毎	秒 m/s <sup>2</sup>
波 数 毎メートル	m <sup>-1</sup>
密度, 質量密度キログラム毎立方	メートル kg/m <sup>3</sup>
面 積 密 度キログラム毎平方	メートル kg/m <sup>2</sup>
比体積 立方メートル毎キ	ログラム m <sup>3</sup> /kg
電 流 密 度 アンペア毎平方	メートル $A/m^2$
磁界の強さアンペア毎メー	トル A/m
量濃度(a),濃度モル毎立方メー	トル mol/m <sup>3</sup>
質量濃度 キログラム毎立法	メートル kg/m <sup>3</sup>
輝 度 カンデラ毎平方	メートル $cd/m^2$
屈 折 率 <sup>(b)</sup> (数字の) 1	1
比 透 磁 率 (b) (数字の) 1	1

(a) 量濃度(amount concentration)は臨床化学の分野では物質濃度(substance concentration)ともよばれる。
 (b) これらは無次元量あるいは次元1をもつ量であるが、そのことを表す単位記号である数字の1は通常は表記しない。

表3. 固有の名称と記号で表されるSI組立単位

			SI 組立里位	
組立量	名称	記号	他のSI単位による 表し方	SI基本単位による 表し方
平 面 隹	ラジアン <sup>(b)</sup>	rad	1 <sup>(b)</sup>	m/m
· 体 催	ステラジア、(b)	er <sup>(c)</sup>	1 (b)	$m^{2/m^2}$
周 波 数	ヘルツ <sup>(d)</sup>	Hz	1	s <sup>1</sup>
力 力	ニュートン	N		m kg s <sup>-2</sup>
压力, 応力	パスカル	Pa	N/m <sup>2</sup>	m <sup>-1</sup> kg s <sup>-2</sup>
エネルギー、仕事,熱量	ジュール	J	N m	$m^2 kg s^2$
仕事率,工率,放射束	ワット	w	J/s	m <sup>2</sup> kg s <sup>-3</sup>
電荷,電気量	クーロン	С		s A
電位差(電圧),起電力	ボルト	V	W/A	$m^2 kg s^{-3} A^{-1}$
静電容量	ファラド	F	C/V	$m^{-2} kg^{-1} s^4 A^2$
電気抵抗	オーム	Ω	V/A	$m^2 kg s^{-3} A^{-2}$
コンダクタンス	ジーメンス	s	A/V	$m^{-2} kg^{-1} s^3 A^2$
磁東	ウエーバ	Wb	Vs	$m^2 kg s^{-2} A^{-1}$
磁束密度	テスラ	Т	Wb/m <sup>2</sup>	$kg s^{2} A^{1}$
インダクタンス	ヘンリー	Н	Wb/A	$m^2 kg s^2 A^2$
セルシウス温度	セルシウス度 <sup>(e)</sup>	°C		K
光東	ルーメン	lm	cd sr <sup>(c)</sup>	cd
照度	ルクス	lx	$lm/m^2$	m <sup>-2</sup> cd
放射性核種の放射能 <sup>(f)</sup>	ベクレル <sup>(d)</sup>	Bq		s <sup>-1</sup>
吸収線量,比エネルギー分与,	グレイ	Gv	J/kg	m <sup>2</sup> s <sup>-2</sup>
カーマ		, and	0.115	
線量当量,周辺線量当量,方向	SUNCE (g)	Sv	J/kg	m <sup>2</sup> a <sup>-2</sup>
性線量当量, 個人線量当量		50	orkg	III 8
酸素活性	カタール	kat		s <sup>-1</sup> mol

(a)SI接頭語は固有の名称と記号を持つ組立単位と組み合わせても使用できる。しかし接頭語を付した単位はもはや

(a)SE接頭語は固有の名称と記号を持つ組立単位と組み合わせても使用できる。しかし接頭語を付した単位はもはや コヒーレントではない。
 (b)ラジアンとステラジアンは数字の1に対する単位の特別な名称で、量についての情報をつたえるために使われる。 実際には、使用する時には記号rad及びsrが用いられるが、習慣として組立単位としての記号である数字の1は明示されない。
 (c)測光学ではステラジアンという名称と記号srを単位の表し方の中に、そのまま維持している。
 (d)ヘルツは周期現象についてのみ、ベクレルは放射性抜種の統計的過程についてのみ使用される。
 (e)セルシウス度はケルビンの特別な名称で、セルシウス温度を表すために使用される。
 (e)セルシウス度はケルビンの特別な名称で、セルシウス温度で表すために使用される。
 (f)数単位を通の大きさは同一である。したがって、温度差や温度問隔を表す数値はとちらの単位で表しても同じである。
 (f)数単性核種の放射能(activity referred to a radionuclide)は、しばしば誤った用語で"radioactivity"と記される。
 (g)単位シーベルト(PV,2002,70,205)についてはCIPM勧告2(CI-2002)を参照。

表4.単位の中に固有の名称と記号を含むSI組立単位の例

	S	I 組立単位	
組立量	名称	記号	SI 基本単位による 表し方
粘质	パスカル秒	Pa s	m <sup>-1</sup> kg s <sup>-1</sup>
カのモーメント	ニュートンメートル	N m	$m^2 kg s^2$
表 面 張 九	ニュートン毎メートル	N/m	kg s <sup>-2</sup>
角 速 度	ラジアン毎秒	rad/s	m m <sup>-1</sup> s <sup>-1</sup> =s <sup>-1</sup>
角 加 速 度	ラジアン毎秒毎秒	$rad/s^2$	$m m^{-1} s^{-2} = s^{-2}$
熱流密度,放射照度	ワット毎平方メートル	$W/m^2$	kg s <sup>-3</sup>
熱容量、エントロピー	ジュール毎ケルビン	J/K	$m^2 kg s^{2} K^{1}$
比熱容量, 比エントロピー	ジュール毎キログラム毎ケルビン	J/(kg K)	$m^2 s^{-2} K^{-1}$
比エネルギー	ジュール毎キログラム	J/kg	$m^{2} s^{-2}$
熱伝導率	ワット毎メートル毎ケルビン	W/(m K)	m kg s <sup>-3</sup> K <sup>-1</sup>
体積エネルギー	ジュール毎立方メートル	J/m <sup>3</sup>	m <sup>-1</sup> kg s <sup>-2</sup>
電界の強さ	ボルト毎メートル	V/m	m kg s <sup>-3</sup> A <sup>-1</sup>
電 荷 密 度	クーロン毎立方メートル	C/m <sup>3</sup>	m <sup>-3</sup> sA
表 面 電 荷	クーロン毎平方メートル	C/m <sup>2</sup>	m <sup>-2</sup> sA
電 束 密 度 , 電 気 変 位	クーロン毎平方メートル	$C/m^2$	m <sup>-2</sup> sA
誘 電 率	ファラド毎メートル	F/m	$m^{-3} kg^{-1} s^4 A^2$
透 磁 率	ヘンリー毎メートル	H/m	m kg s <sup>-2</sup> A <sup>-2</sup>
モルエネルギー	ジュール毎モル	J/mol	$m^2 kg s^2 mol^1$
モルエントロピー,モル熱容量	ジュール毎モル毎ケルビン	J/(mol K)	$m^{2} kg s^{2} K^{1} mol^{1}$
照射線量(X線及びγ線)	クーロン毎キログラム	C/kg	kg <sup>-1</sup> sA
吸収線量率	グレイ毎秒	Gy/s	$m^{2} s^{-3}$
放射 強度	ワット毎ステラジアン	W/sr	$m^4 m^{-2} kg s^{-3} = m^2 kg s^{-3}$
放射輝 度	ワット毎平方メートル毎ステラジアン	$W/(m^2 sr)$	m <sup>2</sup> m <sup>-2</sup> kg s <sup>-3</sup> =kg s <sup>-3</sup>
酵素活性濃度	カタール毎立方メートル	kat/m <sup>3</sup>	m <sup>-3</sup> s <sup>-1</sup> mol

表 5. SI 接頭語					
乗数	接頭語	記号	乗数	接頭語	記号
$10^{24}$	э 9	Y	$10^{-1}$	デシ	d
$10^{21}$	ゼタ	Z	$10^{-2}$	センチ	с
$10^{18}$	エクサ	Е	$10^{-3}$	ミリ	m
$10^{15}$	ペタ	Р	$10^{-6}$	マイクロ	μ
$10^{12}$	テラ	Т	$10^{-9}$	ナーノ	n
$10^{9}$	ギガ	G	$10^{-12}$	ピョ	р
$10^{6}$	メガ	М	$10^{-15}$	フェムト	f
$10^{3}$	キロ	k	$10^{-18}$	アト	а
$10^{2}$	ヘクト	h	$10^{-21}$	ゼプト	z
$10^{1}$	デ カ	da	$10^{-24}$	ヨクト	У

表6.SIに属さないが、SIと併用される単位					
名称	記号	SI 単位による値			
分	min	1 min=60s			
時	h	1h =60 min=3600 s			
日	d	1 d=24 h=86 400 s			
度	۰	1°=(п/180) rad			
分	,	1'=(1/60)°=(п/10800) rad			
秒	"	1"=(1/60)'=(п/648000) rad			
ヘクタール	ha	1ha=1hm <sup>2</sup> =10 <sup>4</sup> m <sup>2</sup>			
リットル	L, 1	1L=11=1dm <sup>3</sup> =10 <sup>3</sup> cm <sup>3</sup> =10 <sup>-3</sup> m <sup>3</sup>			
トン	t	$1t=10^{3}$ kg			

\_

表7.	SIに属さないが、	SIと併用される単位で、	SI単位で
	まとわて粉は	ぶ 中 瞬時 ほう や て そ の	

衣される剱旭が夫破的に待られるもの				
名称記		SI 単位で表される数値		
電子ボルト	eV	1eV=1.602 176 53(14)×10 <sup>-19</sup> J		
ダルトン	Da	1Da=1.660 538 86(28)×10 <sup>-27</sup> kg		
統一原子質量単位	u	1u=1 Da		
天 文 単 位	ua	1ua=1.495 978 706 91(6)×10 <sup>11</sup> m		

表8.SIに属さないが、SIと併用されるその他の単位				
	名称		記号	SI 単位で表される数値
バ	1	ル	bar	1 bar=0.1MPa=100kPa=10 <sup>5</sup> Pa
水銀	柱ミリメー	トル	mmHg	1mmHg=133.322Pa
オン	グストロー	- 4	Å	1 Å=0.1nm=100pm=10 <sup>-10</sup> m
海		里	М	1 M=1852m
バ	-	$\sim$	b	1 b=100fm <sup>2</sup> =(10 <sup>-12</sup> cm)2=10 <sup>-28</sup> m <sup>2</sup>
1	ッ	ŀ	kn	1 kn=(1852/3600)m/s
ネ	-	パ	Np	
ベ		N	В	▶ 51 単位との 叙 値的 な 阕徐 は 、 対 数 量の 定 義 に 依 存.
デ	ジベ	N	dB -	

表9. 固有の名称をもつCGS組立単位					
名称	記号	SI 単位で表される数値			
エルグ	erg	1 erg=10 <sup>-7</sup> J			
ダイン	dyn	1 dyn=10 <sup>-5</sup> N			
ポアズ	Р	1 P=1 dyn s cm <sup>-2</sup> =0.1Pa s			
ストークス	St	$1 \text{ St} = 1 \text{ cm}^2 \text{ s}^{\cdot 1} = 10^{\cdot 4} \text{ m}^2 \text{ s}^{\cdot 1}$			
スチルブ	$^{\mathrm{sb}}$	$1 \text{ sb} = 1 \text{ cd} \text{ cm}^{-2} = 10^4 \text{ cd} \text{ m}^{-2}$			
フォト	ph	1 ph=1cd sr cm <sup>-2</sup> 10 <sup>4</sup> lx			
ガル	Gal	$1 \text{ Gal} = 1 \text{ cm s}^{-2} = 10^{-2} \text{ ms}^{-2}$			
マクスウェル	Mx	$1 \text{ Mx} = 1 \text{ G cm}^2 = 10^{-8} \text{Wb}$			
ガウス	G	$1 \text{ G} = 1 \text{Mx cm}^{2} = 10^{4} \text{T}$			
エルステッド <sup>(c)</sup>	Oe	1 Oe ≙ (10 <sup>3</sup> /4π)A m <sup>-1</sup>			

(c) 3元系のCGS単位系とSIでは直接比較できないため、等号「 ▲ 」 は対応関係を示すものである。

	表10. SIに属さないその他の単位の例					
	3	名利	尓		記号	SI 単位で表される数値
キ	ユ		IJ	ĺ	Ci	1 Ci=3.7×10 <sup>10</sup> Bq
$\scriptstyle  u$	$\sim$	ŀ	ゲ	$\sim$	R	$1 \text{ R} = 2.58 \times 10^{-4} \text{C/kg}$
ラ				ド	rad	1 rad=1cGy=10 <sup>-2</sup> Gy
$\scriptstyle  u$				ム	rem	1 rem=1 cSv=10 <sup>-2</sup> Sv
ガ		$\boldsymbol{\mathcal{V}}$		7	γ	1 γ =1 nT=10-9T
フ	I		N	11		1フェルミ=1 fm=10-15m
メー	- トル	系	カラゞ	ット		1メートル系カラット = 200 mg = 2×10-4kg
ŀ				ル	Torr	1 Torr = (101 325/760) Pa
標	準	大	気	圧	atm	1 atm = 101 325 Pa
力			IJ	ļ	cal	1cal=4.1858J(「15℃」カロリー), 4.1868J (「IT」カロリー)4.184J(「熱化学」カロリー)
Ξ	ク			ン	μ	$1 \mu = 1 \mu m = 10^{-6} m$

この印刷物は再生紙を使用しています