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EXPERIMENTAL STUDY ON EQUILIBRIUM PARTITION COEFFICIENT OF VOLATILE FISSION PRODUCTS BETWEEN LIQUID SODIUM AND THE GAS PHASE

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EXPERIMENTAL STUDY ON EQUILIBRIUM PARTITION COEFFICIENT OF VOLATILE FISSION PRODUCTS BETWEEN LIQUID SODIUM AND THE GAS PHASE

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ABSTRACT

A series of tests has been conducted to obtain gas-liquid equilibrium partition coefficient Kd of volatile fission products such as cesium, iodine, and tellurium in sodium. In the test a sodium pool mixed with an FP simulant was heated by an electric furnace and the solvent of trapped vapors by filters was quantitatively analyzed. The results are, (1) Cs shows the highest Kd (20-100), (2) Kd of iodine scatters as wide as 0.02-0.5 at 450°C and 0.3-0.8 at 650°C, (3) the Kd values of Cs and I agree well with the theoretical ones reported by Castleman et al., and (4) if a sodium-telluride which is hard to vaporize than pure Te is assumed, measured Kd of Te agrees with that theoretical.

INTRODUCTION

Fission products released to the coolant during the operation of a Liquid Metal Fast Breeder Reactor (LMFBR) will be distributed over the sodium coolant, reactor cover gas, primary-system surfaces, and trapping devices in the system. Some volatile fission-product elements may be transported to the cover gas by vaporization from the liquid sodium. The presence of these radioisotopes in the cover gas may lead to subsequent problems in cover-gas storage, effluent disposal, or personnel exposure in the event of leakage from the top shield.

The purpose of this paper is to present the results of vaporization-equilibrium studies which were conducted to obtain relative volatility data for three volatile fission products, namely, cesium, iodine and tellurium.

EQUILIBRIUM PARTITION COEFFICIENT

Analytical Description of Equilibrium Partition Coefficient

The equilibrium-vaporization behavior of a binary system is often described by an equilibrium partition coefficient Kd. Here, Kd is defined as the ratio of the mole fraction of the solute in the vapor to its mole fraction in the liquid.

When the gas phase is saturated by vapor under flowing condition of carrier gas, the partial pressure of fission product (FP) material and that of sodium are expressed as follows, respectively :

$$p_i = \frac{n_i}{n_i + n_a + n_g} \cdot P, \qquad (1)$$

$$p_a = \frac{n_a}{n_i + n_a + n_g} \cdot P, \qquad (2)$$

where P = total pressure of gas phase
n_i, n_a, n_g = mole number of FP_i, sodium, the carrier gas in gas phase.

The equilibrium partition coefficient of FP_i is described as,

$$Kd[i] = \frac{n_i}{(n_i + n_a)\, x_i} = \frac{p_i}{(p_i + p_a)\, x_i}, \qquad (3)$$

where x_i = mole fraction of FP_i in liquid phase.

If $p_i \ll p_a$ and $x_i \ll (1-x_i)$,

$$p_a \doteqdot p_a^0$$

where p_a^0 = vapor pressure of pure sodium.

Thus eq. (3) is rewritten as follow :

$$Kd[i] = \frac{p_i}{p_a^0 \cdot x_i} \qquad (4)$$

$$p_i = Kd[i] \cdot p_a^0 \cdot x_i . \qquad (4)'$$

The equilibrium condition of sodium vapor is attained when the ratio p_a/p_a^0 is close to one. A similar evaluation is made to FP materials. In this case, the activity coefficient γ_i defined by eq. (5) becomes a scale to judge the degree of equilibrium of FP vapors.

$$\gamma_i = \frac{p_i}{p_i^0 \cdot x_i} . \qquad (5)$$

Experiment

Figure 1 shows the test apparatus. A small plate in an evaporator is filled with sodium of about 50g. The sodium mixed with an FP simulant is heated by an electric furnace surrounding the evaporator. The FP simulants are cesium powder, tellurium powder and crystal NaI particles. In almost all iodine tests, the sodium pool was stirred to have an uniform distribution. The concentration of mixed material was about 300ppm, 200ppm, 2000-6000ppm of cesium, iodine, tellurium, respectively.

The evaporator is a stainless-steel horizontal tube as depicted in Fig.2. The surface area of sodium is 74cm^2 and the average depth is about 12mm. Five thermocouples were inserted to the liquid phase and gas phase.

The temperature of gas-phase was kept several degrees (3-10°C) higher than that of liquid-phase to prevent mist formation. Argon carrier gas saturated with FP simulant and sodium vapors is led to a sampling line, where sintered stainless-steel filters trap the vapors. The carrier gas is ultimately discharged to a water pool and the flow rate is calculated from the gas volume accumulated in a flask. The solvent of trapped materials is quantitatively analyzed. An atomic absorption analysis is used to cesium and tellurium, and an ion chromatography analysis to iodine. Measurement of sodium mass was mainly made by neutralization titration.

Results and Discussions

[Vapor Saturation in Carrier Gas]

In this experimental technique called "transpiration method" it is important that the vapor is saturated in the carrier gas.

Figure 3 shows an example of relation between degree of vapor saturation and carrier gas flow rate. It indicates that the measured vapor pressure is close to the saturation pressure at small flow rate less than 1ℓ/min. Thus, the data in that range is adoptable to this study.

[Cesium-Sodium System]

Figure 4 is the Arrhenius plots of Kd [Cs] and activity coefficient of cesium γ_C, and Fig.5 compares the measured Kd with those in previous studies. The measured values are well represented by theoretical curves of Castleman et al.[1] and Pollock[2]. This would rationalize the assumption that sodium solvent of cesium shows the characteristics of normal liquid as indicated by Pollock. The agreement between the experiments and theories is reasonable because sodium and cesium are both alkali metals and have a similar atomic structure.

[Iodine-Sodium System]

Figure 6 is the Arrhenius plots of Kd[I] and activity coefficient of iodine γ_I, and Fig.7 compares the measured Kd with those in previous studies. The measured data ranges approximately within one order, and each point scatters widely compared with that of cesium. As indicated by Clough[3], it would be due to a high sensitivity of NaI vaporization to experimental conditions such as container material and purity of sodium. The figures also show the Castleman et al.'s theoretical curves. The Kd[I] curve, which slightly increases with temperature, agrees fairly well with this experiment.

On the other hand, Pollock et al.'s correlation has a strong inverse tendency in the temperature dependence as shown in Fig.7. It would be due to the assumption, on which base is unclear, that the activity coefficient of NaI is an inverse of the solubility. Furthermore, their large values of experimental data upon which the applicability of theoretical curve is claimed would be caused by the argon gas bubbling in the sodium pool during the experiment.

$\gamma_I \gg 1$ means that NaI in sodium has stronger "escaping capability " than that from pure NaI.

[Tellurium-Sodium System]

Figure 8 is the Arrhenius plots of Kd[Te] and an activity coefficient of tellurium γ_T. The measured Kd[Te] relatively agrees with the theoretical curve of Castleman et al.. The experimental value of γ_T was calculated using eq.(5) on the assumption that tellurium vaporization from sodium occurs in the chemical form of pure tellurium whose vapor pressure p_T^0 is given by eq.(6)[4].

$$log\ p_T^0(atm) = 4.7192 - \frac{5960.2}{T}. \qquad (6)$$

γ_T data shows smaller values than the theoretical curve by one or two orders in magnitude. $\gamma_T \langle 1$ means that tellurium in sodium has smaller "escaping capability" than that in pure tellurium, which corresponds to the formation of chemical compound with sodium solvent. In fact, the phase diagram of tellurium-sodium system shows compounds of Na_2Te, Na_2Te_2 and Na_2Te_6.

However, no description is given in the Castleman et al.'s paper on what vapor pressure was used. Hence, if the vapor pressures of sodium tellurides become clear, the telluride in this system will be identified.

[Consideration on Non-equilibrium Partition Coefficient]

Because the cover gas region has an axial temperature drop in actual LMFBR plants, it is useful to examine the non-equilibrium partition coefficient under non-isothermal condition in the gas-phase.

According to Castleman[5] the relation between Kd and non-equilibrium partition coetticient Kd' is written as

$$Kd'/Kd = D_{v,i}/D_{v,a} \cdot \qquad (7)$$

where $D_{v,a}$ = diffusion coefficient of sodium vapor
$D_{v,i}$ = diffusion coefficient of FP i.

In general

$$D \propto \sqrt{1/M} \qquad (8)$$

where M = molecular weight.

Because $D_{v,i} < D_{v,a}$ in sodium-cesium, iodine, and tellurium systems,

$$Kd' < Kd. \qquad (9)$$

The higher the partition coefficient is, the severer results are obtained in the evaluation of FP release into gas-phase, and hence using Kd regardless the tempreture profile in the gas-phase will give a conservative assessment.

CONCLUSIONS

Vaporization of cesium, iodine and tellurium from sodium was studied and the results were put in order in the form of partition coefficient as follows :

(1) Cesium shows the highest equilibrium partition coefficient Kd (20-100). The scatter of cesium data is smallest and the data agree well with the Castleman et al.'s equation based on the phase diagram of sodium/cesium alloy.

(2) Kd of iodine scatters as wide as 0.02-0.5 at 450°C and 0.3-0.8 at 650°C. The results agree fairly well with the Castleman et al.'s equation.

(3) Kd of Te is 10^{-5}-10^{-4}, which was experimentally determined for the first time. The relation between Kd and liquid sodium temperature agrees with the Castleman's equation assuming a sodium-telluride which is hard to vaporize than pure tellurium.

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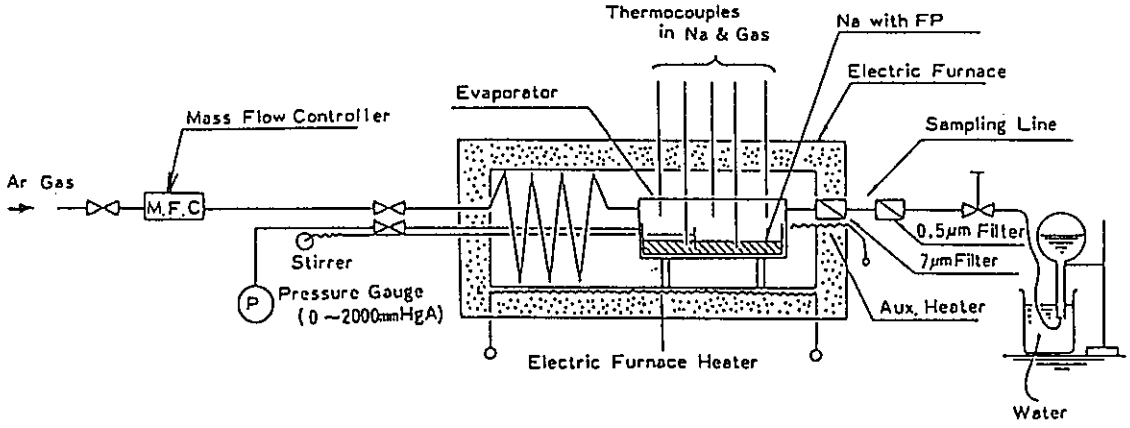
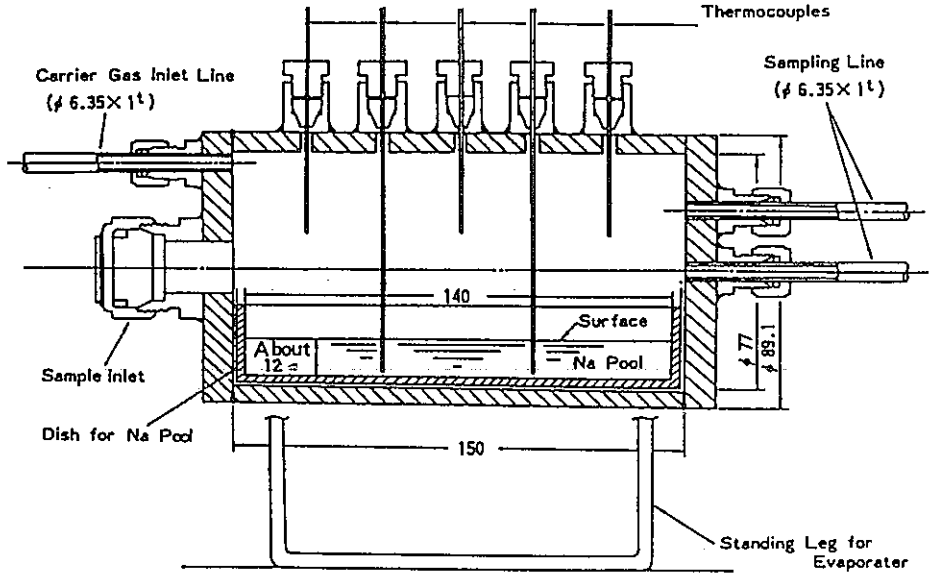


Fig. 1 Test apparatus



Dimension: mm

Fig. 2 Evaporator

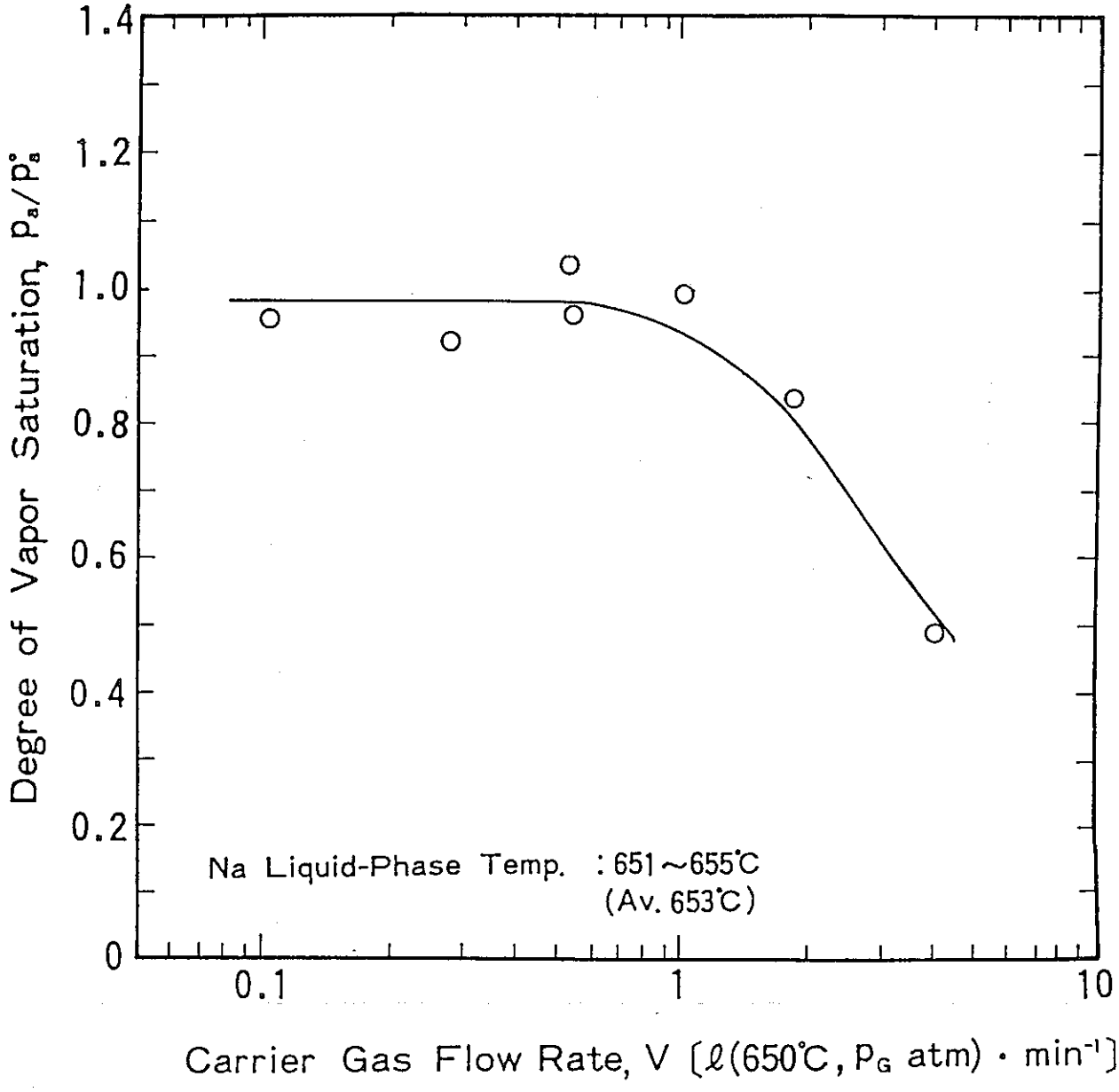


Fig. 3 Carrier gas flow rate versus degree of vapor saturation

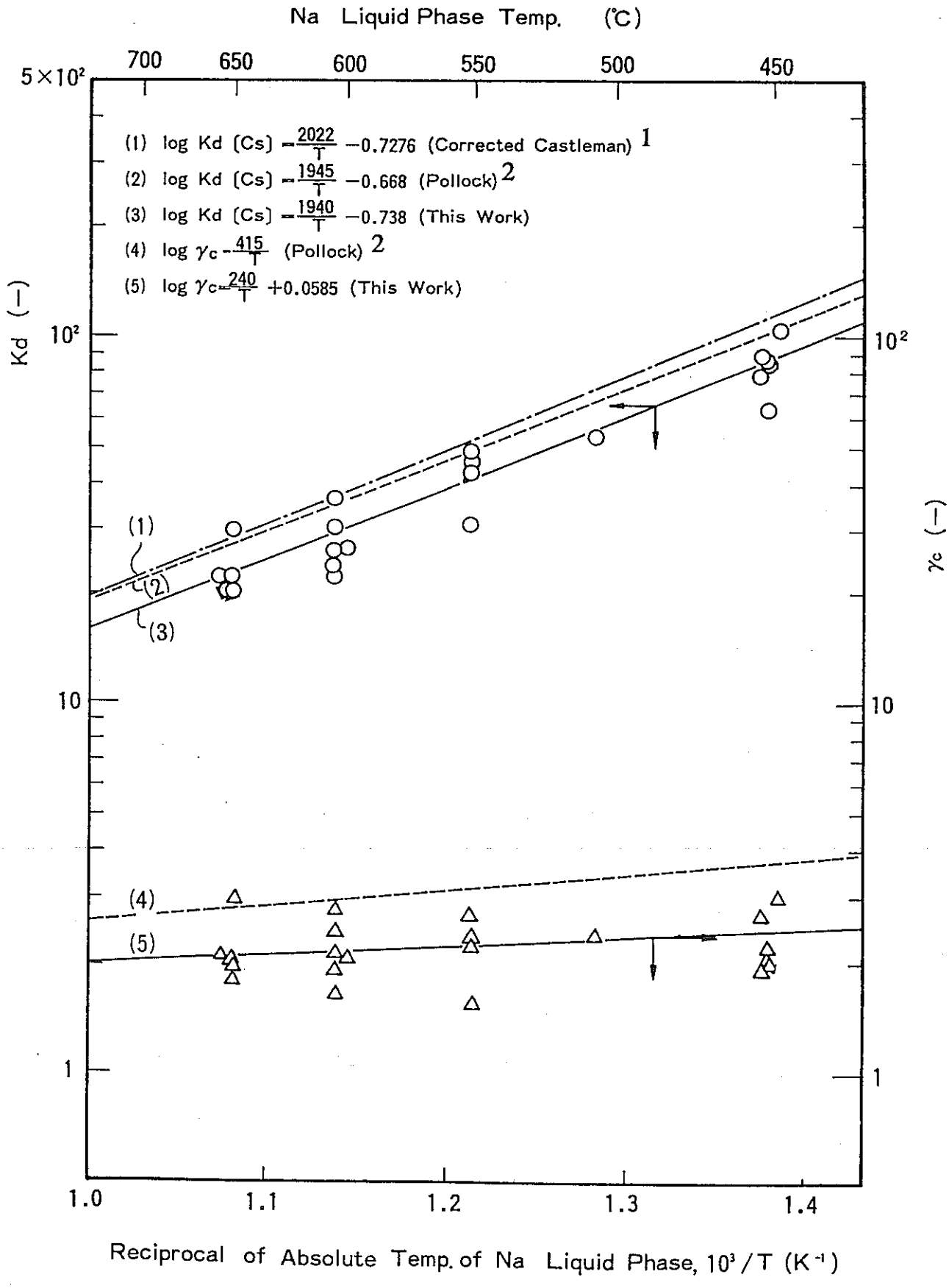


Fig. 4 Measured partition coefficient and activity coefficient of cesium

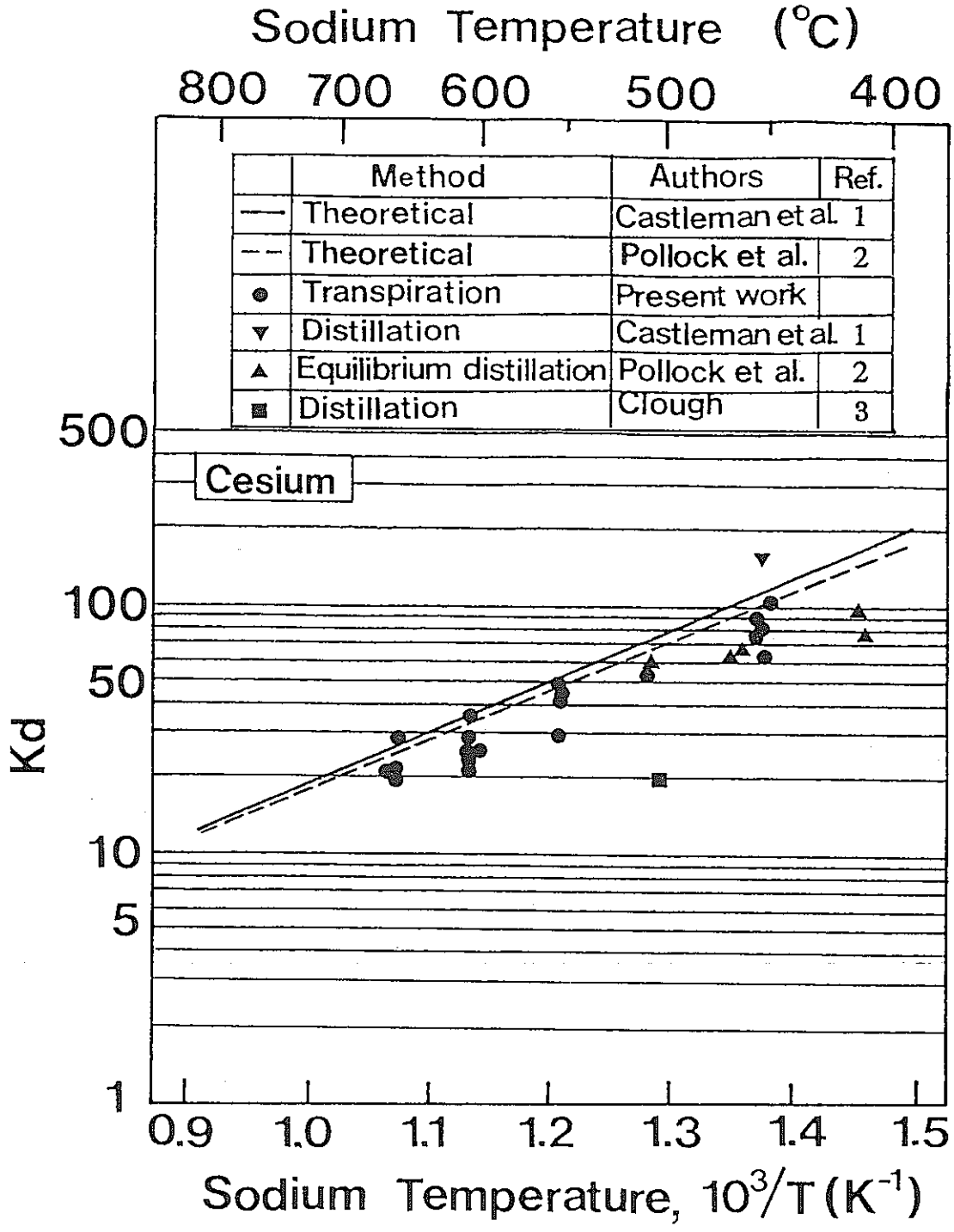


Fig. 5 Comparison measured partition coefficient of cesium with those in previous studies

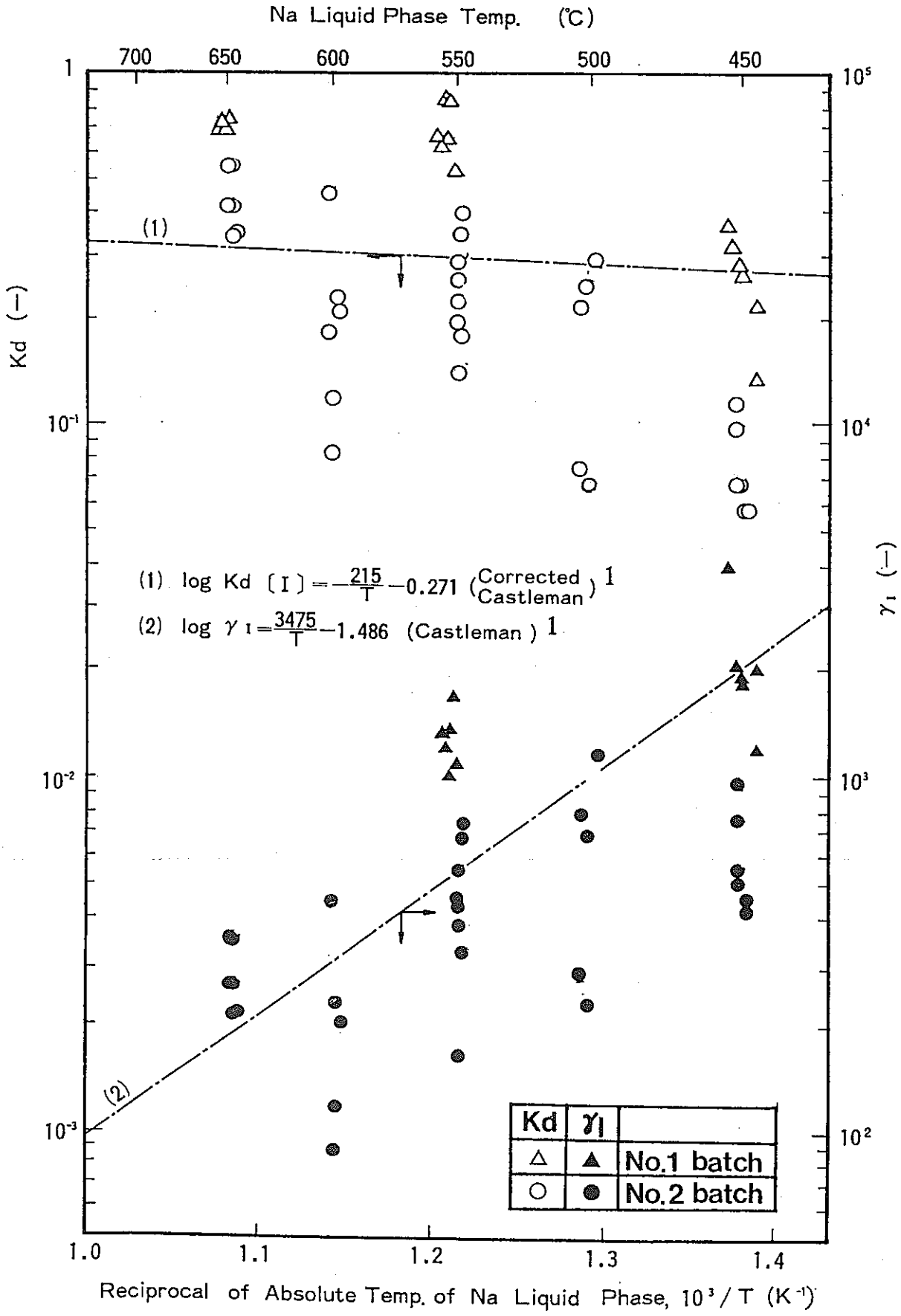


Fig. 6 Measured partition coefficient and activity coefficient of iodine

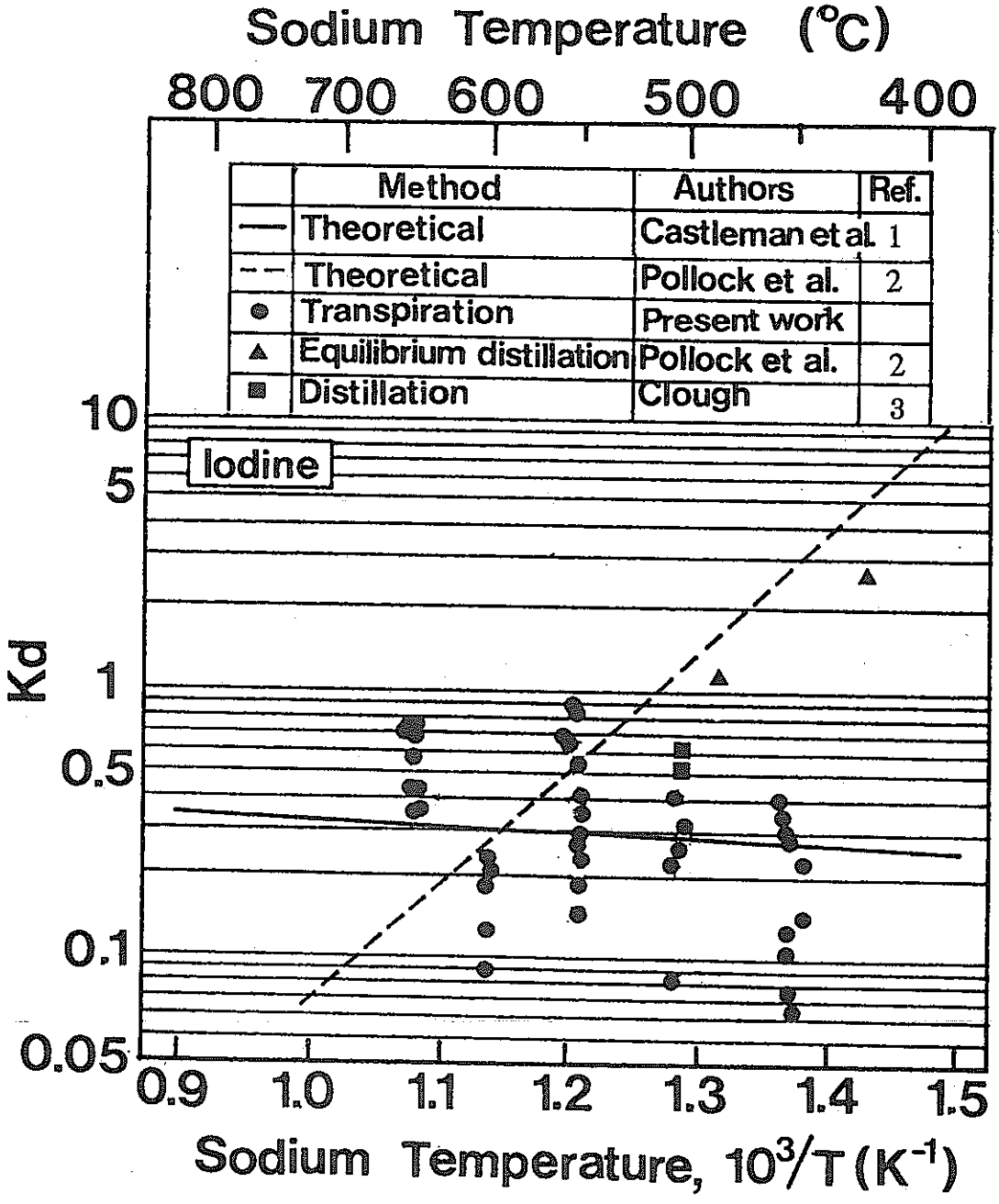


Fig. 7 Comparison of measured partition coefficient of iodine with those in previous studies

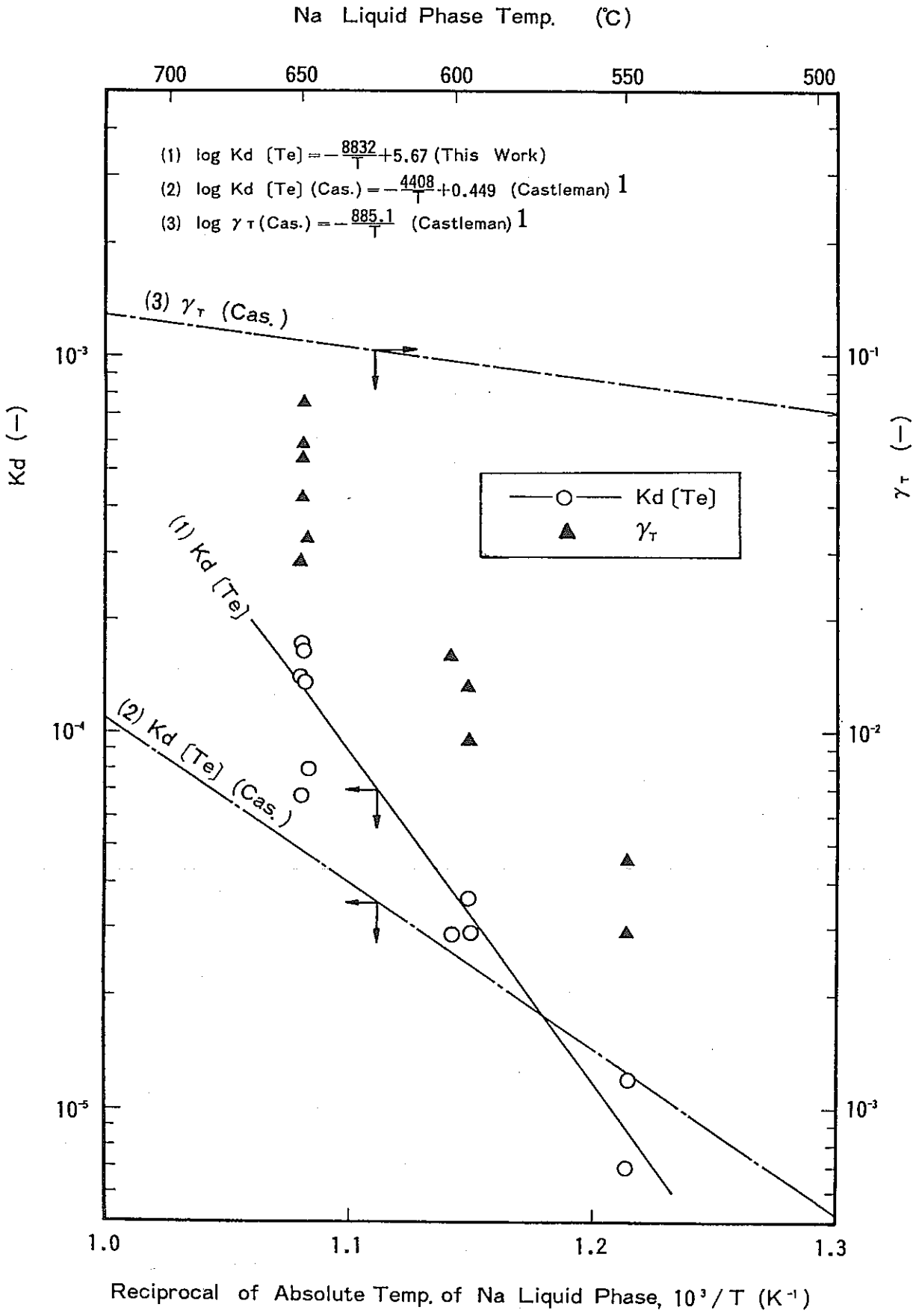


Fig. 8 Measured partition coefficient and activity coefficient of tellurium