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Measurements of the Vapor and Dissociation Pressures of Potassium Sulfate and Carbonate at High Temperatures

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The dissociation reactions of potassium sulfate and potassium carbonate were determined using a quadrupole-type mass spectrometer with a Knudsen-cell-type ion source. The vapor and dissociation pressures of potassium sulfate and the dissociation pressure of potassium carbonate were obtained, by the use of the Knudsen effusion method at temperatures from 900 to 1700°K, as follows:

$$\log P = -1.253 \times 10^4\left(\frac{1}{T}\right) + 7.724 \quad (K_2SO_4)$$

$$\log P_d = -3.275 \times 10^4\left(\frac{1}{T}\right) + 20.83 \quad (K_2SO_4)$$

$$\log P_d = -1.135 \times 10^4\left(\frac{1}{T}\right) + 9.257 \quad (K_2CO_3)$$

The equilibrium constants of the dissociation reaction were estimated from the above data and from those of Kröger and Stratmann:[1]

$$\log K_p = -6.94 \times 10^4\left(\frac{1}{T}\right) + 38.8 \quad (K_2SO_4)$$

$$\log K_p = -1.38 \times 10^4\left(\frac{1}{T}\right) + 9.80 \quad (K_2CO_3)$$

An easily ionizable material (seed) must be added to the combustion products of fuels to achieve a sufficient degree of ionization of the gases in a magnetohydrodynamic (MHD) generator. The problem of seed recovery in open-cycle MHD power plants is of critical importance for the successful economic realization of MHD power generation. In general, the seed used for open-cycle MHD power generation is a potassium compound. Hart *et al.*[2] suggested that the potassium compounds which were contained in exhaust gases from the MHD generator were potassium sulfate and potassium carbonate when a sulfur-contained fuel was used.

Unfortunately, the physical and chemical properties of the potassium compounds are not yet clear because of their strong reactivity at high temperatures. Therefore, a seed-recovering technique has not been established.

This paper will give experimental data on the dissociation reactions and some thermodynamic constants of potassium sulfate and potassium carbonate at high temperatures.

Experimental

Mass Spectrometric Studies. *Apparatus*: Details of the mass spectrometer used have been described in a previous paper.[3] The Knudsen cell, made of Pt-5%Rh alloy, was heated with a tantalum heater. The temperature of the cell was measured with a calibrated Pt/Pt-13%Rh thermocouple at the bottom of the cell.

The vapor effusing from the Knudsen cell entered directly into the ionization chamber, which was mounted on top of

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[1] C. Kröger and J. Stratmann, *Glastech. Ber.*, **34**, 311 (1961).

[2] A. B. Hart, G. C. Gradner, W. D. Halstead, J. W. Laxton, and D. Tidy, "International Symposium on Magnetohydrodynamic Electrical Power Generation," Paris (1964), No. 89.

[3] T. Kosugi, *Kogyo Kagaku Zasshi*, **73**, 148 (1970).

the analyzer tube. In the ionization chamber, neutral atoms and molecules were bombarded with electrons of controlled energy and thus ionized. A secondary electron multiplier was used for ion detection. The out-put of this multiplier was amplified and recorded.

Materials: A special grade of potassium compound was used. Impurities in the powder were checked by means of emission spectroscopy. The results of qualitative analysis showed a trace of Na and no evidence of As, Ca, Mg, Pt, Fe, Al, Sn, Ag, Cu, and Pb. Further sample purification was not carried out.

Preparation of the Sample: The method of sample preparation was the same as given in a previous paper.[3]

After preparation, the cell was cooled to below 50°C. Then, the ion intensity of each dissociaton product was measured by means of the mass spectrometer at each experimental temperature. Then peaks at masses 32, 39, 48, 64, and 94 were attributed to O_2^+, K^+, SO^+, SO_2^+, and K_2O^+ respectively for the potassium sulfate on the basis of the detected mass number and the atomic construction of the sulfate. On the other hand, the peaks at masses 12, 16, 28, 39, 44, and 94 for the carbonate were associated with C^+, O^+, $CO,^+$ K^+, CO_2^+, and K_2O^+ respectively. Throughout these experiments, no potassium-oxygen compounds other than K_2O were observed. SO_3 was also not observed from the potassium sulfate.

The product $(I_x^+ \cdot T)$ is proportional to the partial pressure of the species x,[4] where I_x^+ is the measured ion intensity. Thus, the thermal dissociation reaction was discussed on the basis of the relation between $\log(I_x^+ \cdot T)$ and $1/T$. The vapor and dissociation pressures were measured independently of the results of the mass-spectrometric studies.

The values of $\log(I_x^+ \cdot T)$ *vs.* $1/T$ are shown in Fig. 1 for the sulfate and in Fig. 2 for the carbonate.

As is obvious from Fig. 1, the chemical species marked O_2^+, SO_2^+, and K_2O^+ showed the same temperature dependency. In the case of the carbonate, CO^+, K^+, CO_2^+, and K_2O^+ exhibited similar slopes, as is shown in Fig. 2.

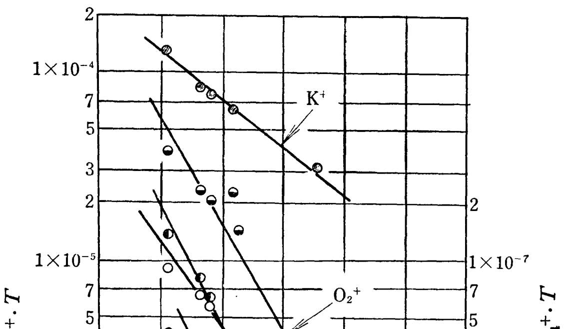

Fig. 1. Plots of $I_x^+ \cdot T$ *vs.* $1/T$ for thermal dissociation products of potassium sulfate.

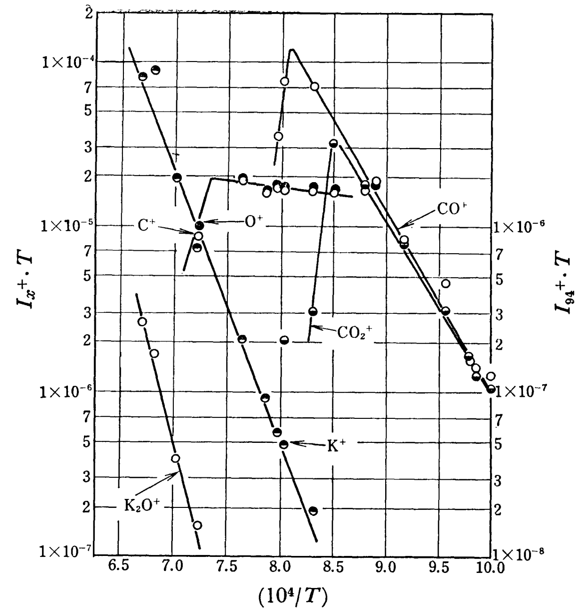

Fig. 2. Plots of $I_x^+ \cdot T$ *vs.* $1/T$ for thermal dissociation products of potassium carbonate.
(x=molecular weight)

It should be noted that the thermal dissociation reaction of the carbonate is effected completely below 1,250°K and that the temperature dependencies of C^+, and O^+ are very slight.

Effusion-rate Measurements by Knudsen Method. The cell was made of Pt-5%Rh alloy; the orifice diameter was 0.5 mm, and the thickness of the orifice was 0.25 mm. The inner diameter of the cell was 9.5 mm.

The effusion weight of the sample was calculated as the weight change in the cell before and after each run, because the evaporation rate of the platinum was very small (*ca.* 1×10^{-11} g/cm²/sec at 1,700°K).[5] The cell weight was measured to be about 0.01 mg by means of a semi-microbalance.

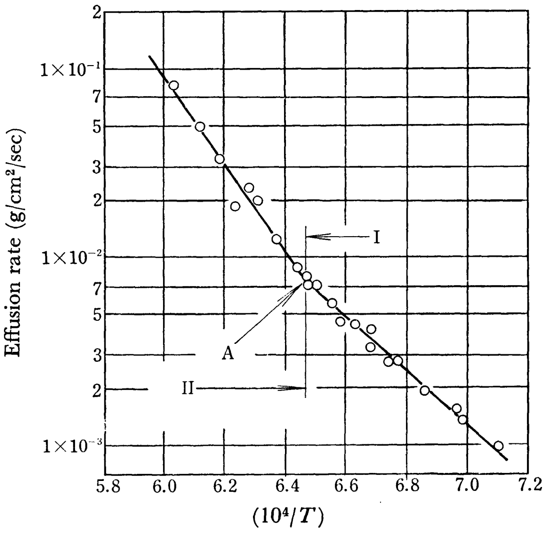

Fig. 3. Plots of effusion rate *vs.* $1/T$ of K_2SO_4.

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[4] D. White, K. S. Seshadri, and D. F. Dever, *J. Chem. Phys.*, **39**, 2463 (1963).

[5] H. A. Jones, I. Langmuir, and D. H. J. Mackey, *Phys. Rev.*, **30**, 201 (1927). See T. Okada and R. Goto, "Hakkinzoku to Kogyoteki Riyo," Sangyo Tosho, Tokyo (1956), p. 91.

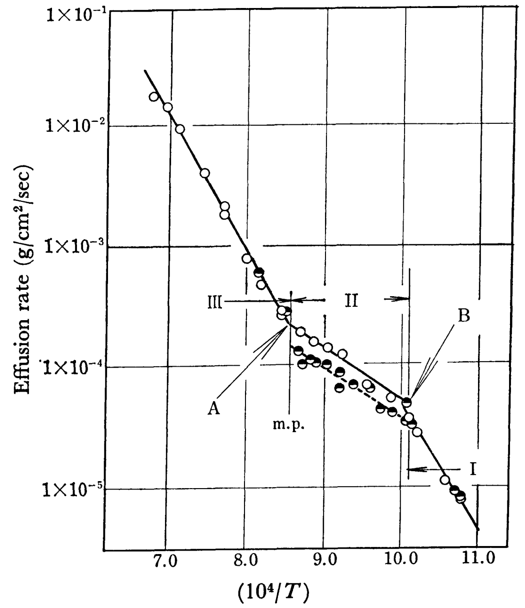

Fig. 4. Plots of effusion rate *vs.* $1/T$ of K_2CO_3.

In the precise calculation of the effusion rate, the orifice area change caused by the thermal expansion of the cell material must be calibrated. However, as the thermal expansion of platinum at 1,700°K is about 1.5%,[6] the orifice-area change was disregarded and a value measured at room temperature was used in this experiment. The preparations of the samples and cell were described previously.[7,8]

The effusion rates of the sulfate and carbonate are plotted in Figs. 3 and 4 as log G *vs.* $1/T$ where G is the effusion rate. It was obvious that the effusion rate of the sulfate showed a temperature-dependency change at Point A and that the slope of the curve in the higher temperature region (II) was larger than that in the lower temperature region (I).

The effusion-rate change of the carbonate was very complicated compared with that of the sulfate. The effusion rate was changed by the maximum degassing temperature in the (II) region indicated in Fig. 4.

Discussion

Thermal Dissociation Reaction of the Samples. The detected species will be generated by several reactions for example, as primary thermal dissociation reaction products of the sample, consecutive reaction products of the above primary reaction products might be detected. Therefore, it is impossible to conclude that all the detected species are generated from the primary dissociation reaction of the sample or that those species indicating larger ion intensities were the primary dissociation products.

Thus, the identification of the primary dissociation products was made by a comparison of the heats of formation of all the species in this study.

Now, let us assume the following primary dissociation reaction:

$$ABC \longrightarrow A + B + C \qquad (1)$$

In this reaction, the heat of formation of A, B, and C species must be equal to the heat of dissociation of the starting material, ABC. Therefore, the slopes of the relations of $\log(I_A{}^+ \cdot T)$, $\log(I_B{}^+ \cdot T)$, and $\log(I_C{}^+ \cdot T)$ *vs.* $1/T$ should be equal. From this point of view, chemical species as O_2, SO_2, and K_2O were assumed to be the primary dissociation products of potassium sulfate (from Fig. 1).

Then, the dissociation reaction of the sulfate can be estimated as:

$$K_2SO_4 \longrightarrow K_2O + SO_2 + \frac{1}{2}O_2 \qquad (2)$$

Regarding the carbonate the species which have the same slope in Fig. 2 are K, K_2O, CO, and CO_2. Of these, the potassium atoms indicate the same temperature dependency as was observed for the sulfate shown in Fig. 5. In addition, the heat of formation of the potassium atom is very close to that of the K_2O molecules, from the following reaction:

$$2K + \frac{1}{2}O_2 \longrightarrow K_2O \qquad (3)$$

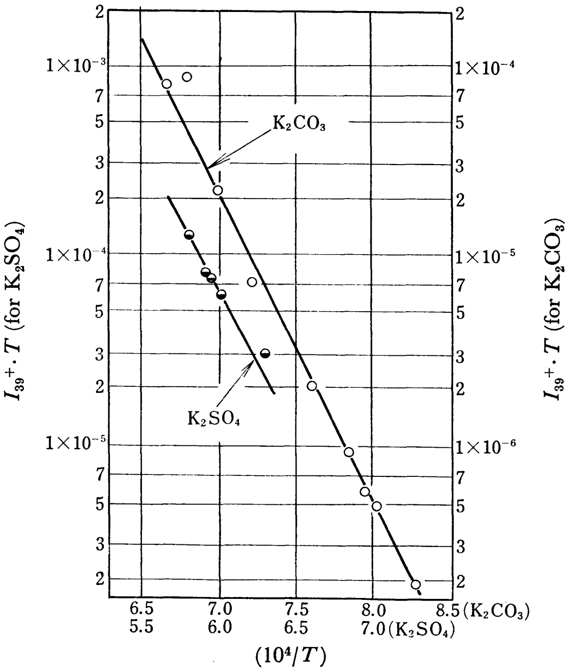

Fig. 5. Plots of $I_{39}{}^+ \cdot T$ *vs.* $1/T$ for K^+ in K_2SO_4 and K_2CO_3.

Therefore, it can be considered that the potassium atoms are produced by thermal dissociation of the potassium oxide in the two samples. On the basis of the above discussion and the mass balance between the starting material and the dissociation products, the thermal dissociation reaction of the carbonate was estimated as follows:

$$K_2CO_3 \longrightarrow K_2O + CO_2 \qquad (4)$$

Recently, a mass spectrometric study of the dissociation reaction of alkali metal compounds was reported by Ficalora *et al.*[9] They proposed the following dissociation reaction for the sulfate on the basis of a com-

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[6] J. W. Edwards, R. Speiser, and H. L. Johnston, *J. Appl. Phys.*, **22**, 424 (1951).

[7] T. Kosugi, *Kogyo Kagaku Zasshi*, **70**, 2089 (1967).

[8] T. Kosugi, *ibid.*, **71**, 1581 (1968).

[9] P. U. Ficalora, O. M. Uy, D. W. Muenow, and J. L. Margrave, *J. Amer. Ceram. Soc.*, **51**, 574 (1968).

parison of the measured ion intensities:

$$K_2SO_4 \longrightarrow 2K + SO_2 + O_2 \qquad (5)$$

In this study, however, the heat of formation of a potassium atom was different from that of the SO_2 and O_2 molecules shown in Fig. 1. This implies that the potassium atom differs from the SO_2 and O_2 molecules in its formation mechanism. The generation mechanism of a potassium atom should, then, be considered as a dissociation product of K_2O molecules as has been described above.

Kellogg[10] proposed that the dissociation reaction of sodium sulfate porceeded as:

$$Na_2SO_4 \longrightarrow Na_2O + SO_3 \qquad (6)$$

However, it is difficult to consider that the dissociation reaction of potassium sulfate proceeds in that way for the following two reasons:

1) Sulfur trioxide was not detected in this study. In addition, it is considered, from the above description, that sulfur dioxide might be one of the true primary dissociation products.

2) It was estimated, on the basis of a previous report,[11] that sulfur trioxide was not stable in this experimental temperature range, and that only sulfur dioxide was present.

On the basis of the above considerations, Eqs. (5) and (6) can be said not to be adequate for indicating the dissociation mechanism of potassium sulfate.

Vapor and Dissociation Pressures. Potassium Sulfate: The relationship of log G *vs.* $1/T$ should be linear if the dissociation reaction is not observed. The experimental results for the sulfate, however, show a change in the slope at Point A (*ca.* 1,555°K) in Fig. 3. The slope is steeper in the higher-tempearture region. It is estimated that the main effused species are changed near Point A; *i.e.*, the primary dissociation products are only detected by the mass spectrometer above 1,555°K.

Therefore, it is assumed that the measured G value consists of two components: the K_2SO_4 molecules (G_1) and all the dissociation products (G_2). Thus, we assumed the measured G value to be:

$$G = G_1 + G_2 \qquad (7)$$

where:

$$\log G_1 = -A\left(\frac{1}{T}\right) + B$$

$$\log G_2 = -C\left(\frac{1}{T}\right) + D$$

$$G_2 = G_3 + G_4 + G_5$$

$$G_1 = G(K_2SO_4)$$

$$G_3 = G(K_2O)$$

$$G_4 = G(SO_2)$$

$$G_5 = G(O_2)$$

A, B, C, D: constants

These constants were calculated by least-means-square method from the measured G values using a computor (HITAC-5020F). The resulting values were 1.220×10^4 for A, 5.638 for B, 3.245×10^4 for C, and 18.36 for D. The vapor pressure equation derived from G_1 using the Knudsen equation[12] for the sulfate is, then:

$$\log P = -1.253 \times 10^4\left(\frac{1}{T}\right) + 7.724 \text{ (Torr)} \qquad (8)$$

The average heat of vaporization in the experimental temperature range is estimated to be 57.3±8.6 kcal/mol, and the entropy of vaporization at the melting point (1,342°K) is estimated to be 42.7±6.4 e.u. from the extrapolation of the vapor-pressure equation.

The vapor-pressure data measured in this experiment were in good agreement with the data of Nettleton *et al.*[13] obtained from the evaporation-rate measurement of a droplet of the sulfate melted under several atmospheric conditions. However, they disagree with the data reported by Kröger and Stratmann.[1]

The dissociation pressure of the sulfate was estimated by using the G_2 values and the ideal gas equation; it can be represented by the following equation:

$$\log P_d = -3.275 \times 10^4\left(\frac{1}{T}\right) + 20.83 \text{ (Torr)} \qquad (9)$$

The average heat of dissociation was 150±22.5 kcal/mol. The vapor and dissociation pressures are shown in Fig. 6, together with the published data.

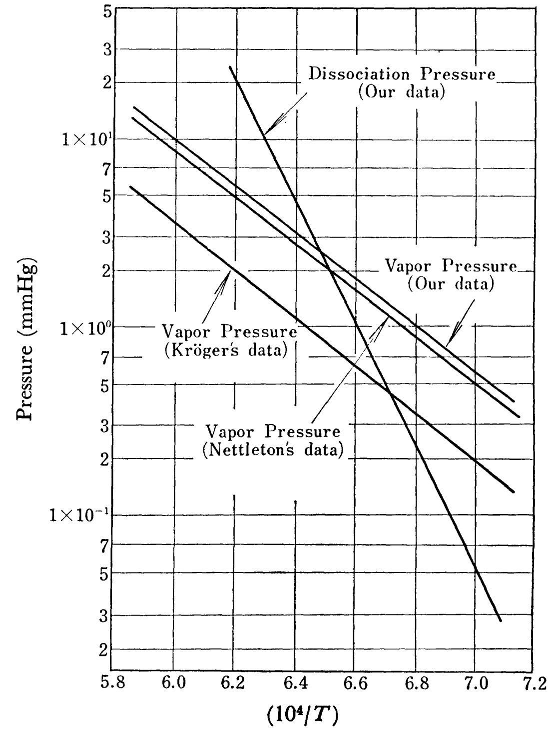

Fig. 6. Vapor and dissociation pressure of K_2SO_4.

Potassium Carbonate: From the results of the mass-spectrometric study and Wöhler's report,[14] it should be considered that the major effusing vapors are dissociation products of the sample throughout the experimental-temperature range.

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[10] H. H. Kellogg, *Trans. Met. Soc.*, AIMT **230**, 1622 (1964).

[11] F. Hals, L. Keefe, and A. E. Bindari, An ASME publication 64-WA/ENER-5 (1964).

[12] A. N. Nesmeyanov, Edited by Gray, "Vapor Pressure of the Chemical Elements," Elsevier Publishing Company (1963).

[13] M. A. Nettleton and E. Raask, *J. Appl. Chem.*, **17**, 18 (1967).

[14] L. Wöhler, *Z. Elektrochem.*, **11**, 836 (1905).

From a previous discussion,[8] it can be considered that the slope in the (I) region of Fig. 4 depends mainly on the activation energy of Eq. (4).

Then, the true effusion rate of the primary dissociation products of the carbonate was calculated from the measured effusion rate at the lowest experimental temperature (925°K) and the temperature dependency of the CO_2 molecule obtained from the mass-spectrometric experiment.

The relationship of the effusion rate and the temperature, assuming that there was no reaction between the sample vapor and the cell, was:

$$\log G = -1.105 \times 10^4\left(\frac{1}{T}\right) + 6.989 \qquad (10)$$

where:

$$G = G(K_2O) + G(CO_2)$$

Thus, the dissociation pressure of the carbonate was estimated to be:

$$\log P_d = -1.135 \times 10^4\left(\frac{1}{T}\right) + 9.257 \text{ (Torr)} \qquad (11)$$

using the method described for the sulfate. The average heat of dissociation in the experimental temperature range was found to be 51.9±8.1 kcal/mol. The dissociation pressure is shown in Fig. 7 along with the data reported by Kröger and Stratmann,[1] measured by the same method as the present data, and the data of Howarth and Turner,[15] measured by the static method. All the data agree well.

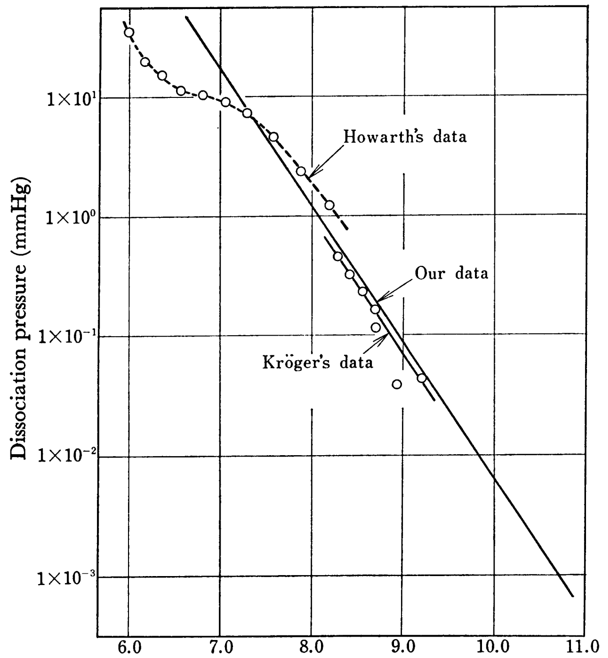

Fig. 7. Dissociation pressure of K_2CO_3.

Equilibrium Constants of The Dissociation Reaction. From the above discussion, the equilibrium constants of the two samples can be said to be:

$$K_p(K_2SO_4) = P(K_2O)\cdot P(SO_2)\cdot P(O_2)^{1/2}\cdot P(K_2SO_4)^{-1} \qquad (12)$$

$$K_p(K_2CO_3) = P(K_2O)\cdot P(CO_2)\cdot P(K_2CO_3)^{-1} \qquad (13)$$

For the sulfate, the relation between the measured dissociation pressure and the partial pressure of each dissociation product is:

$$P_d = P(K_2O) + P(SO_2) + P(O_2) \qquad (14)$$

Therefore, $K_p(K_2SO_4)$ is expressed as follows, using the measured vapor and dissociation pressures:

$$\log K_p(K_2SO_4) = -6.94 \times 10^4\left(\frac{1}{T}\right) + 38.8 \text{ (atm}^{1.5}\text{)} \qquad (15)$$

$K_p(K_2CO_3)$ can be calculated by the same method; however, vapor pressure of the carbonate could not be obtained in the present work. Consequently, the vapor-pressure data of Kröger and Stratmann[1] were used for $P(K_2CO_3)$. The following relation was thus estimated:

$$\log K_p(K_2CO_3) = -1.38 \times 10^4\left(\frac{1}{T}\right) + 9.80 \text{ (atm)} \qquad (16)$$

Both relations are shown in Fig. 8.

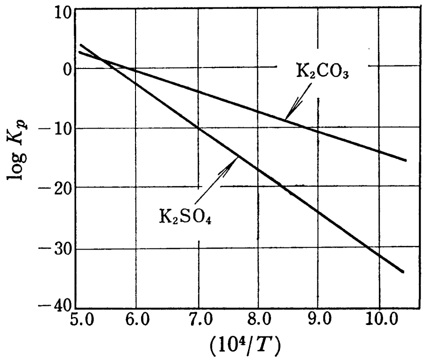

Fig. 8. Equilibrium constants of dissociation reaction.

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The useful suggestions of Dr. K. Shinriki and Dr. N. Kawashima of this laboratory are greatly appreciated.

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[15] J. T. Howarth and W. E. S. Turner, *J. Soc. Glass Tech.*, **15**, 360 (1931).