研究論文

187. Determination of Enthalpy Change of Oxidation Reaction of Uranium Dioxide by D. T. A.

示差熱分析法による二酸化ウランの酸化反応熱の測定

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The measurement of the heat of oxidation of UO_2 was carried out by differential thermal analysis (D. T. A.) method. The values of ΔH , thus obtained, were as follows,

In addition, a preliminary experiment on the specific heat measurement of UO_2 resulted in $\Delta H_1 = -12.8 \text{ kcal/mol (230}^\circ\text{C)}$ and $\Delta H_2 = -11.0 \text{ kcal/mol (380}^\circ\text{C)}$. These are in good accordance with the D. T. A. results.

Some considerations on the availability of D. T. A. method for calorimetry were also given.

I. INTRODUCTION

The thermodynamic phase studies in the $\text{UO}_2\text{-U}_3\text{O}_8$ region of uranium oxides were carried out by Grønvald⁽¹⁾, Blackburn⁽²⁾ and others, and it was concluded that U_4O_9 exists as a stable phase in addition to UO_2 and U_3O_8 . On the other hand, from the kinetic study and the differential thermal analysis of low temperature oxidation of UO_2 , the metastable intermediate compound, U_3O_7 , was found⁽³⁾⁽⁴⁾.

In this paper, since the thermochemical data for such intermediate oxides are rather scarce, the enthalpy change in the two step reaction, $\text{UO}_2 \rightarrow \text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8$, was determined by D. T. A. (differential thermal analysis) method, as a first step in the thermodynamic study on U_4O_9 and U_3O_7 .

There are many attempts to apply D. T. A. method for calorimetry; such as the peak area method developed by Speil⁽⁵⁾, Kerr-Kulp⁽⁶⁾, Kronig-Snoodijk⁽⁸⁾, Soulé⁽⁹⁾ and Sewell⁽¹⁰⁾, and the slope method developed by Vold⁽⁷⁾. Although the slope-method is applicable to rapid reactions like transition, it is not suitable to apply this method for such relatively slow

reactions as the ordinary chemical reactions in solid.

In this study, the peak area method developed by Sewell was applied.

II. THEORY OF QUANTITATIVE USE

The fundamental equations of the heat transfer were solved by Sewell⁽¹⁰⁾ in the case where the test sample and reference sample were arranged symmetrically and the heating rate of the furnace wall was kept constant. The equations for the base line at steady state and the peak area were given as follows,

$$(\Delta T)_0 = \omega_0 \beta a^2 (-\omega_s / \kappa_s + \omega_r / \kappa_r) \quad (1)$$

$$P = \int_{-\infty}^{\infty} [(\Delta T)_0 - (\Delta T)] \cdot dt = \omega_s \omega_0 L \rho_s a^2 / \lambda_s \quad (2)$$

where,

$(\Delta T)_0$: base line at steady state (temperature difference between the centers of test sample and reference sample)

P : peak area ($^\circ\text{C} \cdot \text{sec}$)

(ΔT) : temperature difference between the centers of test sample and reference

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- sample during reaction
 κ : thermal diffusivity($\lambda/\rho C$)
 ρ : bulk density
 C : specific heat
 β : heating rate (constant)
 λ : thermal conductivity
 a : representative length(radius for cylindrical shape)
 ω_0 : shape factor
 ω_1 : factor representing the effect of thermocouple wire(<1)
 L : heat of reaction per unit mass of total sample
 s : suffix for test sample
 r : suffix for reference sample

It should be noticed that the above Eqs. (1) and (2), are derived on the assumption that the values of λ , ρ , C , κ , h (heat transfer coefficient and L do not vary with temperature and have the same values before and after the reaction. However, in this experiment, the temperature effect was not so sensitive as to modify the equations.

For brevity, Eq. (2) can be written as follows,

$$P = \omega_1 \omega_0 (mQ/m_s) (m_s/V) a^2 (1/\lambda_s) \\ = (\omega_1 \omega_0 a^2 / V \lambda_s) m (\Delta H/M) = Km (\Delta H/M) \quad (3)$$

$$\text{here, } K = \omega_1 \omega_0 a^2 / (V \lambda_s) \quad (4)$$

- where, m_s : weight of the test sample
 m : weight of the reacting material in the test sample
 V : volume of the test sample
 M : molar weight of the reacting material
 Q : heat of reaction per unit mass of the reacting material
 ΔH : heat of reaction per mol. (enthalpy change)
 K : sensitivity

Here, K is defined as sensitivity, since it represents the peak area per unit amount of heat of reaction.

Now, on the basis of Eq. (3), the calorimetry can be made as follows; at first, the sensitivity, K , is to be determined from the slope of P vs. m curve of the reaction in which ΔH is already known, then, the value of ΔH in question is determined by using the value

of K obtained already.

From Eq. (4), since the value of K varies with ω_1 , $\omega_0 a^2$, V and λ_s , it is necessary to keep these values constant always in all the measurements. As regards $\omega_0 a^2$ and ω_1 , this can be attained by maintaining the dimensions and the geometrical arrangements of the sample and the thermocouple wires unchanged. As regards λ_s , its value is expected to differ remarkably with different samples, however, this can be made negligibly small by diluting the sample materials uniformly always in the same Al_2O_3 powder (5~30 w/o) and by tapping carefully.

However, as λ_s varies with temperature, the sensitivity, K , thus obtained will become a function of temperature in spite of the assumption used in the derivation of Eq. (3).

In this experiment, therefore, the sensitivity, K , obtained was plotted against temperature. The enthalpy change ΔH_1 and ΔH_2 of the reactions, $\text{UO}_2 + 1/6 \text{O}_2 \rightarrow 1/3 \text{U}_3\text{O}_7$ and $1/3 \text{U}_3\text{O}_7 + 1/6 \text{O}_2 \rightarrow 1/3 \text{U}_3\text{O}_8$ respectively, were determined by using the values of K at each peak temperature of the reactions.

III. EXPERIMENTAL

1. Apparatus and technique

D. T. A. curves were obtained by using the D. T. A. apparatus manufactured by Rigaku Denki Co. Ltd., Tokyo. In this apparatus, an adiabatically heating method was employed where the nickel block (sample holder) is maintained at the same temperature with the stainless steel ball surrounding it and heated at a constant rate by the internal heater. The arrangement and dimensions of sample holder are shown in Fig 1. Al_2O_3 powder was used as the reference substance for the measurement of differential and reaction temperature. 0.35 mm ϕ Alumel-Chromel thermocouple wires were used. In this experiment, all the measurements were conducted at a heating rate of 5°C/min.

D. T. A. curves were recorded on a potentiometric type recorder. The full range for the differential temperature can be changed as ± 25 , ± 50 , ± 100 , ± 250 , ± 500 and ± 1000 μV .

- ① platinum crucible
- ② nickel block
- ③ internal heater (0.35 mm ϕ Fe-Cr wire)
- ④ thermocouple for differential temperature
- ⑤ thermocouple for adiabatic control
- ⑥ test sample diluted with Al_2O_3
- ⑦ reference Al_2O_3 for differential temperature measurement
- ⑧ reference Al_2O_3 for reaction temperature measurement

The test sample and the reference Al_2O_3 can be inserted without removing the thermocouple wires by using platinum crucibles. Temperature difference between nickel block and stainless steel ball are controlled to within $\pm 0.02^\circ\text{C}$.

Fig. 1 Details of sample holder

As the standard reaction for the calibration of K , the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and the decomposition of PbCO_3 and CdCO_3 were used. After pulverizing these substances, they were uniformly mixed with Al_2O_3 powder at the dilution of 5 ~ 30 w/o. The volume of these powders were maintained constant (0.647 cm^3) in these measurements.

2. Reagents

UO_2 used was prepared by reducing UO_3 with hydrogen at 970° for 2.5 hr. O/U ratio of this sample was 2.00 ± 0.008 .

As for the standards, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (crystal), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (crystal) and PbCO_3 (powder) of AR grade and CdCO_3 (powder) of CP grade were used. The composition of PbCO_3

Fig. 2 D.T.A. curves for the samples diluted with Al_2O_3 powder (10w/o) at heating rate of $5^\circ\text{C}/\text{min}$.

and CdCO_3 was confirmed by the thermal balance data. Al_2O_3 used was prepared by heating the activated Al_2O_3 for chromatographic use (200 ~ 300 mesh) at 1000°C for 6 hr in air.

IV. RESULTS AND DISCUSSION

1. D. T. A. curves

D.T.A. curves of UO_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, PbCO_3 and CdCO_3 and the peak area of each reaction (shaded parts) are shown in Fig. 2. The reaction equation for each peak in Fig. 2, and its enthalpy change, ΔH , at reaction temperature calculated by Kirchhoff's law are shown in Table 1. First peak of UO_2 is considerably broad and there are some ambiguity in the base-line. The cause of the large drift in the base line before the reaction as shown in Fig. 2 is not clear.

Table 1 The reaction equations and ΔH for each reaction peak

Sample	Peak	Reaction equation	$\Delta H(\text{kcal/mol})$	Temp. ($^{\circ}\text{C}$)
UO_2	P_1	$\text{UO}_2 + 1/6 \text{O}_2 \rightarrow 1/3 \text{U}_3\text{O}_7$	—	230
	P_2	$1/3 \text{U}_3\text{O}_7 + 1/6 \text{O}_2 \rightarrow 1/3 \text{U}_3\text{O}_8$	—	380
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	P_1	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$	53.78	112
	P_2	$\text{CuSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$	17.42	278
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	P_1	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot \text{H}_2\text{O} + 6\text{H}_2\text{O}$	79.47	113
	P_2	$\text{MgSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{MgSO}_4 + \text{H}_2\text{O}$	15.62	317
PbCO_3	P	$\text{PbCO}_3 \rightarrow \text{PbO} + \text{CO}_2$	20.23	320
CdCO_3	P	$\text{CdCO}_3 \rightarrow \text{CdO} + \text{CO}_2$	23.23	373

The first group of peaks of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has a complex structure but they were summed up and treated as one peak.

D. T. A. curve of PbCO_3 consists of two peaks and the intermediate product is considered to be $\text{PbO} \cdot \text{PbCO}_3$ from the data of the thermal balance. However, these two peaks were treated also as one peak.

2. Relation between peak area and sample weight

The values of peak areas were plotted

against the weight of reacting materials, where the values of m were referred to the weight of the sample before the reaction.

The linear relations were obtained as shown in Fig. 3. Each point in this curve represents the mean value of the five repetitions. From Eq. (3), the slope obtained indicates the value of K ($\Delta H/M$).

It should be noticed that since the peak area (or the sensitivity, K) is proportional to $1/\lambda$, according to Eq. (3) (or (4)), the P

The values of peak area are measured by a planimeter in the unit of cm^2 directly from the D. T. A. charts and all of these values are referred to the values for which the full scale range is $\pm 25\mu\text{V}$.

Fig. 3 Peak area vs. sample weight curves

vs. m relation is not linear in general. Nevertheless, the linear relationship between *P* and *m* was obtained in this experiment in the range of the dilution of 0~25 w/o as shown in Fig. 3. This indicates that the difference of λ_s between Al_2O_3 powder and the diluted samples can be neglected in this case.

This might arise from the fact that the thermal conductivity, λ_s , is mainly due to that of the gas existing between the powders and the apparent difference between the samples and Al_2O_3 powder becomes very small.

3. Effect of temperature upon the sensitivity

The sensitivity, *K*, can be calculated from the slope of *P vs. m* curve using the value of ΔH shown in Table 1, since the slope indicates the value of *K* ($\Delta H/M$).

The values of *K* obtained are plotted against the peak temperature as shown in Fig. 4. Though these are considerably scattered, there is a tendency in *K* to fall as the temperature rises as a whole. The regression line of *K vs. T* relation, the standard deviation from the line S_e , and the correlation coefficient about six points, *r*, were calculated as follows,

$$\begin{aligned} K &= -2.39 \times 10^{-3}T + 4.73 \text{ (cm}^2/\text{cal)} \\ S_e &= 0.45 \\ r &= -0.48 \end{aligned} \quad (5)$$

here, *T* represents the temperature ($^{\circ}\text{C}$).

The thick solid line shows the regression line of *K vs. T* relation. The fine solid lines show $K \pm S_e$. $1/\lambda_s$ vs. *T* relation is also shown in arbitrary scale by the dotted curve, since $1/\lambda_s$ thus obtained is proportional to *K*.

Fig. 4 Effect of temperature on sensitivity

Since the temperature, dependence of *K* is considered to be due to the variation of λ_s with temperature, the measurement of the temperature dependence of λ_s was attempted by modification of a part of the apparatus and by using Eq. (1). Al_2O_3 powder was charged in a cylindrical hole (9.0 mm $\phi \times 18.0$ mm) worked in the similar nickel block as shown in Fig. 1, and differential temperature between nickel block and the center of Al_2O_3 powder was observed. Since $\kappa(\text{Al}_2\text{O}_3) \ll \kappa(\text{Ni})$, the second term of Eq. (1) can be neglected and Eq. (1) is written as follows,

$$(\Delta T)_0 = -\omega_0 \omega_s \beta a^2 / \kappa_s = -\omega_s \omega_0 \beta a^2 \rho_s C_s / \lambda_s \quad (6)$$

Accordingly, the temperature dependence of λ_s can be observed directly by measuring $(\Delta T)_0$ against temperature, since $(\Delta T)_0$ is inversely proportional to λ_s in this condition.

The results of the measurement of $(\Delta T)_0$ show that $(\Delta T)_0$ decreases slowly with temperature. This means that the thermal conductivity, λ_s , increases as temperature rises.

According to Kingery, *et al.*⁽¹¹⁾, the thermal conductivity of sintered Al_2O_3 falls quickly as temperature rises and has the value of $10^{-1} \sim 10^{-2}$ cal/cm·sec· $^{\circ}\text{C}$ for temperature range from room temperature to 1300°C .

However, in this powdered sample, λ_s increases with temperature as stated above, and the value of λ_s is calculated from Eq. (6) as 4×10^{-4} cal/cm·sec· $^{\circ}\text{C}$ at 200°C , if $\omega_s \sim 1$ and $\omega_0 = 0.245$ (Sewell's value) are assumed. This is smaller by two orders of magnitude than that of the sintered Al_2O_3 at 200°C , i.e. 5×10^{-2} cal/cm·sec· $^{\circ}\text{C}$.

So, it will be concluded that the thermal conductivity of powdered sample is mainly due to the gas existing between powders, leading to the lower value of λ_s and the tendency of λ_s to rise slowly as temperature rises.

Above discussion for Al_2O_3 will also apply to the low concentration mixtures of Al_2O_3

and samples without major alternation.

Since the sensitivity, K , is proportional to $1/\lambda_s$, the temperature dependence of $1/\lambda_s$ was also shown in arbitrary scale in Fig. 4, where $1/\lambda_s$ was obtained by the measurement above mentioned. Agreement between both regression line of K vs. T relation and $1/\lambda_s$ vs. T curve is satisfactory.

Josselin de Jong⁽¹²⁾ who worked on calorimetry by D. T. A. reported that the sensitivity, K , of the sample diluted with powdered Al_2O_3 increased with temperature and its temperature dependence was explained well according to the value of λ_s of sintered Al_2O_3 reported by Kingery, *et al.* However, this conflicts with our results.

4. Enthalpy change of the oxidation of UO_2

From the slope of P vs. m relation in Fig. 3 and the regression line of K vs. T relation in Fig. 4, the enthalpy change of two step oxidation of UO_2 is calculated as follows,

$$\Delta H_1 = -13.8 \pm 1.5 \text{ kcal/mol (230}^\circ\text{C)}$$

$$\Delta H_2 = -10.8 \pm 1.3 \text{ kcal/mol (380}^\circ\text{C)}$$

ΔH_1° and ΔH_2° at standard temperature could not be obtained, since the specific heat of U_3O_7 is unknown. Up to now, ΔH for the reaction, $\text{UO}_2 + 1/3 \text{O}_2 \rightarrow 1/3 \text{U}_3\text{O}_8$ is known to be -25.30 kcal/mol at 25°C and calculated to be -25.12 kcal/mol at 380°C ⁽¹³⁾. Our results of $\Delta H_1(230^\circ\text{C}) + \Delta H_2(380^\circ\text{C}) = -24.6 \pm 2.8$ kcal/mol fairly agrees with the published data.

Error in our result is estimated to be $\pm 12\%$, and as for the cause the following factors can be considered.

(1) Deviation of peak area will be caused from the non-uniformity of mixing, the deviation of the values of ρ_s and λ_s due to the tapping method and the other experimental errors. It is estimated that this causes an error of $\pm 2 \sim 4\%$ in the slope of P vs. m relation or the sensitivity, K .

(2) Errors in ΔH of standard reactions may be considered but these are less than $\pm 1\%$ in general. However, the deviations of ΔH for the reactions at P_2 of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ might reach to several percent

according to the selection of routes in the calculation by Kirchhoff's law.

(3) Because these reactions are accompanied with generation or absorption of gases such as H_2O , CO_2 or O_2 , the λ_s during the reaction is considered to be different from the static thermal conductivity of Al_2O_3 -sample mixtures. Therefore, K is influenced by the type of reaction, *i.e.* hydration, carbonation or oxidation *etc.* Actually, K is lower for dehydration and higher for decomposition of carbonates. This effect will become the main part of the deviation in K . To avoid this effect, it is desirable to calibrate K by the standards of the same type of reaction as the samples to be measured.

Since ΔH of reaction can be also calculated by measuring the specific heat of UO_2 while heating in air, a preliminary experiment on the specific heat measurement of UO_2 was conducted (2°C/min). This resulted in $\Delta H_1 = -12.8$ kcal/mol (230°C) and $\Delta H_2 = -11.0$ kcal/mol (380°C). These values agree fairly well with the D. T. A. results.

V. SUMMARY

(1) Good linear relations were obtained between P and m , and the slopes were easily determined. This means that Eq. (3) is held satisfactorily under the conditions used in this experiment.

(2) K decreases slowly with temperature. This seems to be due to the temperature variation of λ_s , since the thermal conductivity of powdered Al_2O_3 ($\sim 1.0 \text{ g/cm}^3$) increases slowly with temperature.

(3) For the enthalpy change of the oxidation of UO_2 , the following values were obtained.

$$\Delta H_1 = -13.8 \pm 1.5 \text{ kcal/mol (230}^\circ\text{C)}$$

$$\Delta H_2 = -10.8 \pm 1.3 \text{ kcal/mol (380}^\circ\text{C)}$$

$\Delta H_1(230^\circ\text{C}) + \Delta H_2(380^\circ\text{C}) = -24.6 \pm 2.8$ kcal/mol agrees fairly well with the published value, $\Delta H(25^\circ\text{C}) = -25.30$ kcal/mol and $\Delta H(380^\circ\text{C}) = -25.12$ kcal/mol, for the reaction, $\text{UO}_2 + 1/3 \text{O}_2 \rightarrow 1/3 \text{U}_3\text{O}_8$.

(4) A part of the deviation of the value of

K comes from the non-uniformity of mixing, the deviations of ρ_s and λ_s due to the tapping method, the errors in the values of ΔH of the standard reactions and the other experimental errors. However, these will be less than several percent.

(5) λ_s during reaction is considered to be different from the static thermal conductivity, then K will be influenced by the type of reaction. This effect will occupy the greater part of the deviation of K , so it is desirable to calibrate K by the same type of reaction.

(6) Enthalpy change of the oxidation of UO_2 was also obtained preliminarily by the measurement of specific heat of UO_2 during heating in air. The values thus obtained, $\Delta H_1 = -12.8$ kcal/mol (230°C) and $\Delta H_2 = -11.0$ kcal/mol (380°C) agree fairly well with the D. T. A. results.

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研究論文

188. Solvent Extraction of Inorganic Ions with Tri-*n*-octyl Phosphine Oxide

トリ-*n*-オクチルホスヒンオキシド-塩酸および硝酸系
における諸元素の分配

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The extraction behavior of about sixty inorganic ions was studied in the respective systems of tri-*n*-octyl phosphine oxide** -HCl and -HNO₃ for a contribution to the radiochemical separation techniques.

TOPO was dissolved in toluene and used as its 5 % (w/v) solutions. The distribution ratios for each elements were determined in the same way as previous works. The acid dependence curves were obtained

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