

Thermodynamics of $Mg_yU_{1-y}O_{2+x}$ by EMF Measurements.

II. Properties at Low Magnesium Concentrations

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Received October 3, 1978

Thermodynamic properties of a solid solution, $Mg_yU_{1-y}O_{2+x}$, at low magnesium concentrations have been investigated using the solid galvanic cell technique. The emf values were found to vary linearly with temperature in the range 850–1050°C, from which the linear temperature dependence of partial molar free energy of oxygen, $\Delta\bar{G}_{O_2}$, and the temperature independence of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ were derived. These thermodynamic quantities were obtained as a function of x and y . Agreement of these values with those from theoretical considerations was examined. The effect of magnesium incorporation on $\Delta\bar{G}_{O_2}$ was expressed using $\Delta\bar{G}_{O_2}$ of UO_{2+x} as $-\Delta\bar{G}_{O_2}(Mg_yU_{1-y}O_{2+x}) = -\Delta\bar{G}_{O_2}(UO_{2+x}) - 0.0035 T \ln[1 + 0.07(y^{1/2}/x)] - 60y$.

Introduction

In a previous paper (1), the phase stability and thermodynamic properties of a solid solution, $Mg_yU_{1-y}O_{2+x}$, were investigated at high magnesium concentrations, $0.05 \leq y \leq 0.33$. The lattice constant of this cubic solid solution was studied as a function of x and y , and relations between them were determined. It was found that the lattice constant was better described for each of two regions, $x \geq 0$ and $x < 0$, and the single-phase range of the solid solution in relation to the y value, temperature, and oxygen pressure was discussed. Solid state emf measurements on $Mg_yU_{1-y}O_{2+x}$ revealed that both partial molar entropy and enthalpy of oxygen are temperature independent and that $-\Delta\bar{S}_{O_2}$ and $\Delta\bar{H}_{O_2}$ increase with x and y of $Mg_yU_{1-y}O_{2+x}$. The negative partial molar free energy, $-\Delta\bar{G}_{O_2}$, was found to decrease more rapidly with increasing temperature for the solid solution of larger y values.

In the present paper emf measurements were carried out on $Mg_yU_{1-y}O_{2+x}$ at low magnesium concentrations. The investigation of the thermodynamic properties of the solid solution is important at low concentrations as a guide to assess the effects of foreign ions on the stability of UO_2 .

Experimental

1. $Mg_yU_{1-y}O_{2+x}$ Samples

The $Mg_yU_{1-y}O_{2+x}$ samples with low magnesium concentrations were prepared by heating the mixtures of MgU_3O_{10} and UO_2 either in a helium stream or under vacuum. Reactions in helium were performed at temperatures between 1100 and 1350°C as described earlier (1, 2). Reactions under vacuum were carried out at 1500°C for 15 hr in 5×10^{-6} mm Hg. All mixtures of MgU_3O_{10} and UO_2 having a variety of mixing ratios, 0.002, 0.01, 0.02, and 0.05, were made by a stepwise mixing technique (1).

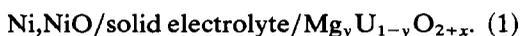
In the case of low magnesium concentrations, it is especially important to examine the magnitudes of the effects of impurities. The result of the emission spectrographic analysis for the samples was as follows: Si < 60; Cr < 14; Al < 10; Fe < 10; Ni < 10; V < 10; and Mo < 3 ppm. The above concentrations are negligibly small in comparison with the lowest concentration of magnesium, 200 ppm. Therefore, the effect of metal impurities was disregarded in the following discussion on the emf values.

2. Coulometric Titration

After measurements of emf at a certain oxygen concentration were finished, the lead wires for the measurement of emf were changed to connect with a dry battery of 1.5 V. The sample in the cell was held at 1050°C during the titration. The new x value of the sample is calculated with accuracy from the integration of current with time. After the titration the sample was annealed for 10 hr at 1050°C. The oxygen concentration of the sample was checked after a series of experiments by the weight change and the X-ray method which were described elsewhere (1). The results from these three methods agreed well with each other.

3. Measurement of Electromotive Force

Measurement of emf was performed using the following solid cell:



The arrangement of the cell has already been described (1). The emf was measured for samples of $y = 0, 0.002, 0.01, 0.02,$ and 0.05 at temperatures of 850, 900, 950, 1000, and 1050°C.

The partial molar free energy of oxygen is obtained by

$$\begin{aligned} \Delta\bar{G}_{\text{O}_2}(\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}) &= 4EF \\ &+ \Delta\bar{G}_{\text{O}_2}(\text{Ni, NiO}), \end{aligned} \quad (2)$$

where E is the emf and F is the Faraday constant. For $\Delta\bar{G}_{\text{O}_2}$ (Ni, NiO) the following equation was used (3):

$$\begin{aligned} \Delta\bar{G}_{\text{O}_2}(\text{Ni, NiO}) &= -113\,300 + 41.5T(\text{K}) \\ &(\text{cal}_{\text{th}} \text{mole}^{-1}). \end{aligned} \quad (3)$$

The $\Delta\bar{G}_{\text{O}_2}$ values obtained were found to vary approximately linearly with temperature. Therefore, the negative partial molar entropy of oxygen, $-\Delta\bar{S}_{\text{O}_2}$, was worked out as the least-squares calculated slope, $\Delta(\Delta\bar{G}_{\text{O}_2})/\Delta T$, in the linear region. The partial molar enthalpy of oxygen, $\Delta\bar{H}_{\text{O}_2}$, was obtained by the equation

$$\Delta\bar{H}_{\text{O}_2} = \Delta\bar{G}_{\text{O}_2} + T \cdot \Delta\bar{S}_{\text{O}_2}. \quad (4)$$

Results and Discussion

1. Dependence of Partial Molar Free Energy on x and y Values

Figure 1 shows plots of $-\Delta\bar{G}_{\text{O}_2}$ against temperature for typical cases of $y = 0.01$ with x values as parameters. The $-\Delta\bar{G}_{\text{O}_2}$ values were obtained from emf by Eq. (2). It is seen from the figure that the linear relationship holds well between them, which means that $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ have no temperature dependence in the temperature range of 850 ~ 1050°C. The values of $-\Delta\bar{G}_{\text{O}_2}$ as a function of x of $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$ at 1000 and 800°C are shown in Figs. 2 and 3, respectively. The y values are treated as parameters. In Figs. 4 and 5, the $-\Delta\bar{G}_{\text{O}_2}$ curves are shown as a function of y , which are obtained from smoothed curves in Figs. 2 and 3, respectively. It is seen from Figs. 2 and 3 that the $-\Delta\bar{G}_{\text{O}_2}(\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x})$ curves for a variety of y values have features similar to those of the $-\Delta\bar{G}_{\text{O}_2}(\text{UO}_{2+x})$ curve. As will be discussed later, the former curves can be expressed by parallel transformation of the latter. From Figs. 4 and 5, it is clear that the negative partial molar free energy, $-\Delta\bar{G}_{\text{O}_2}$, decreases with increasing magnesium concentration and that the

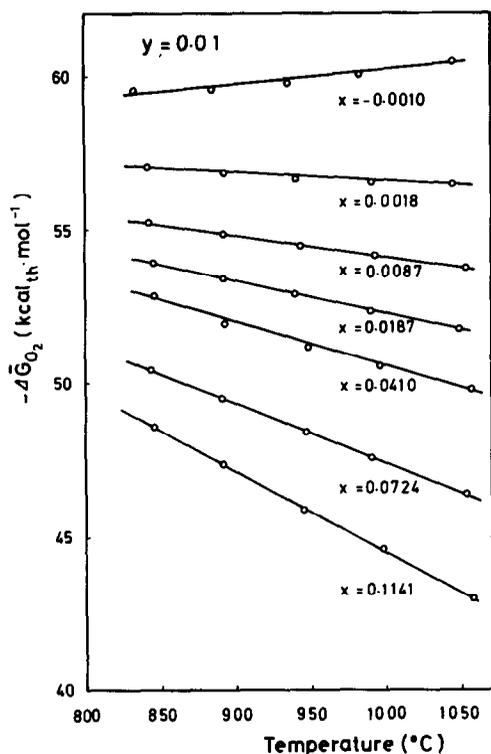


FIG. 1. An example showing linearity between partial molar free energy and temperature.

degree of its decrease is larger for smaller x values. In other words, the $-\Delta\bar{G}_{O_2}$ of the solid solution at higher oxygen concentrations is less sensitive to the dissolved magnesium.

Markin and Bones have measured the emf of UO_{2+x} and have discussed its properties (4). Comparing the present work with their results for certain x values, we find that our $-\Delta\bar{G}_{O_2}(UO_{2+x})$ values are lower by about $3 \text{ kcal}_{th} \text{ mole}^{-1}$ than those of Markin and Bones. The difference may originate from the experimental apparatus; the single-compartment cell was used in this work, while they used a separate-type cell for low oxygen concentrations ($x < 0.01$). In our case, when the oxygen potential is extremely low, the oxygen might transfer from the Ni, NiO mixture pellet to the sample via the helium atmosphere.

2. Dependence of Partial Molar Enthalpy and Entropy on x and y Values

$-\Delta\bar{H}_{O_2}$ against x and against y are shown in Figs. 6 and 7, respectively. $-\Delta\bar{S}_{O_2}$ against

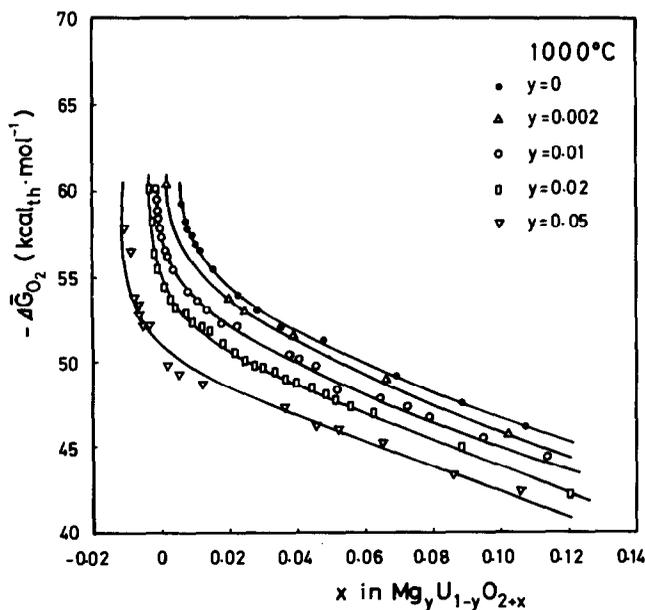


FIG. 2. Plots of negative partial molar free energy of $Mg_yU_{1-y}O_{2+x}$ against x with parameters of various y values at 1000°C .

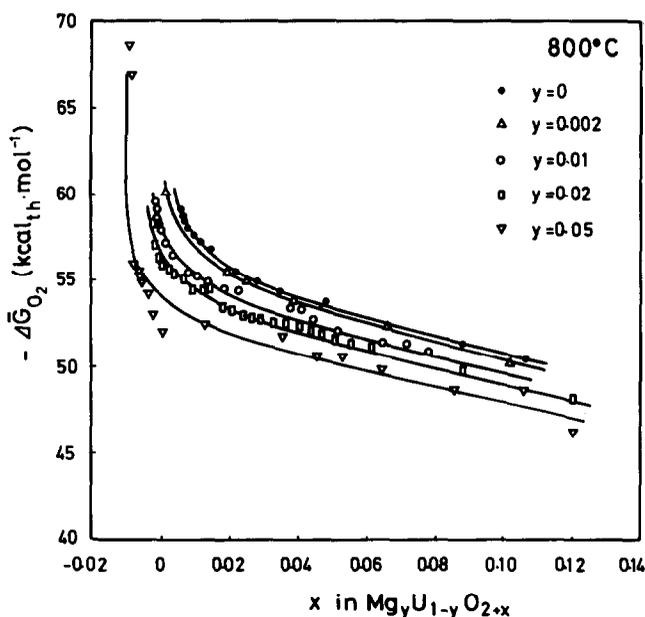


FIG. 3. Plots of negative partial molar free energy against x at 800°C .

x and against y are shown in Figs. 8 and 9, respectively. The curves as a function of y value were obtained in the same way as described for $\Delta\bar{G}_{\text{O}_2}$ curves. The curves of

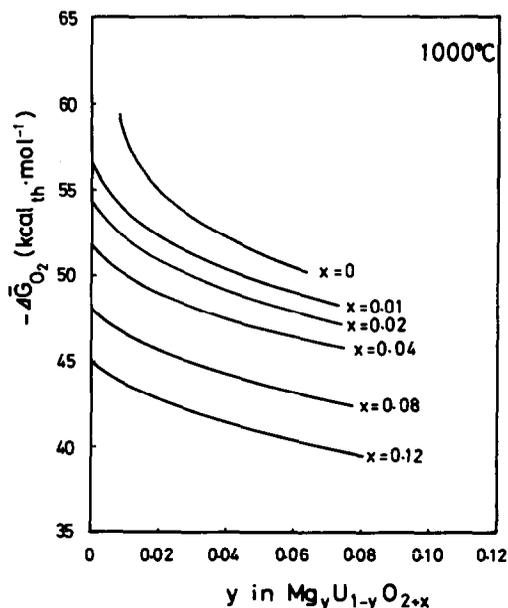


FIG. 4. Negative partial molar free energy as a function of y with parameter x at 1000°C .

$-\Delta\bar{H}_{\text{O}_2}$ vs x have aspects similar to those of $-\Delta\bar{S}_{\text{O}_2}$ vs x as are seen in Figs. 6 and 8. In the previous report (1) it was pointed out that these thermodynamic quantities can be expressed approximately by logarithmic functions of x and y .

In the earlier paper (1) was proposed a relation which describes the entropy as a function of x and y using a statistical model showing that part of the uranium atoms are oxidized to U(V) not only by excess oxygen but also by magnesium substituted in the uranium site of the crystal as

$$\Delta\bar{S}_{\text{O}_2} = -2R \ln[x/(1-x)] - 4R \ln[2(x+y)/(1-2x-3y)] + Q \quad (5)$$

When we put $Q = -46 \text{ e.u. mole}^{-1}$, the coincidence between this equation and the $-\Delta\bar{S}_{\text{O}_2}$ values obtained in the present work is very high except for a low oxygen concentration region such as $x < 0.0015$.

It has been reported that $-\Delta\bar{H}_{\text{O}_2}$ and $-\Delta\bar{S}_{\text{O}_2}$ of UO_{2+x} reverse with a sharp peak near $x = 0$. According to Markin and Bones

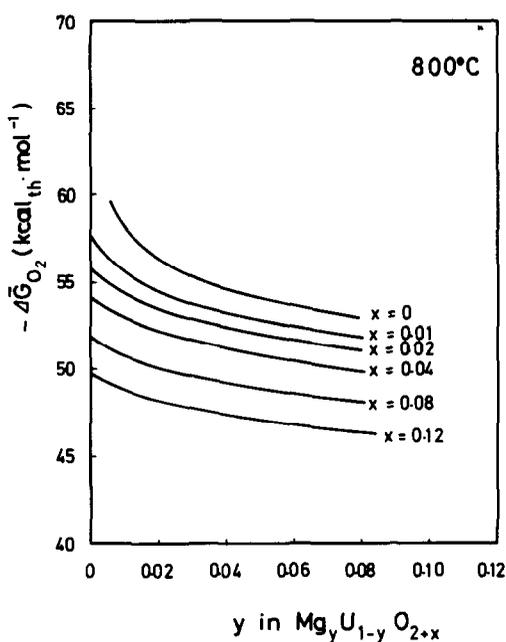


FIG. 5. Negative partial molar free energy as a function of y at 800°C .

this peak appears at about $x = 0.01$, while Gerdanian and Dode showed by calorimetric measurements that this extreme value is located at about $x = 0.002$ (5). In the present results, however, $-\Delta\bar{H}_{O_2}$ and $-\Delta\bar{S}_{O_2}$ of UO_{2+x} have no such anomaly. Instead, somewhat broader peaks are observed in the respective curves of $-\Delta\bar{H}_{O_2}$ and $-\Delta\bar{S}_{O_2}$ at $x = -0.005$ for the sample of relatively high magnesium concentration, $y = 0.05$. This fact can be understood as evidence of behavior of defects in $Mg_yU_{1-y}O_{2+x}$ similar to that in UO_{2+x} . It may be that the reason why peaks were not seen in this work in UO_{2+x} and $Mg_yU_{1-y}O_{2+x}$ of smaller y values is that $-\Delta\bar{G}_{O_2}$ was too large to be measured by the present single-compartment cell.

3. Description of $\Delta\bar{G}_{O_2}(Mg_yU_{1-y}O_{2+x})$ by x and y Values

There have been some reports on the effects of the third ions such as magnesium on

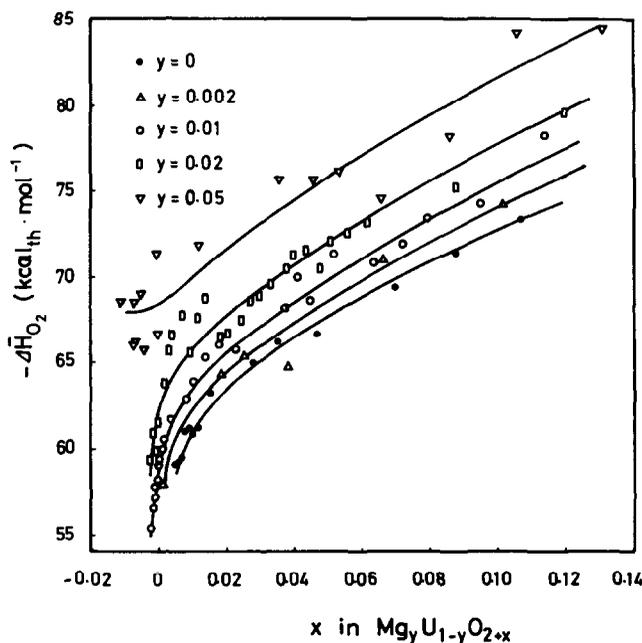


FIG. 6. Plots of negative partial molar enthalpy of $Mg_yU_{1-y}O_{2+x}$ against x with parameters of various y values.

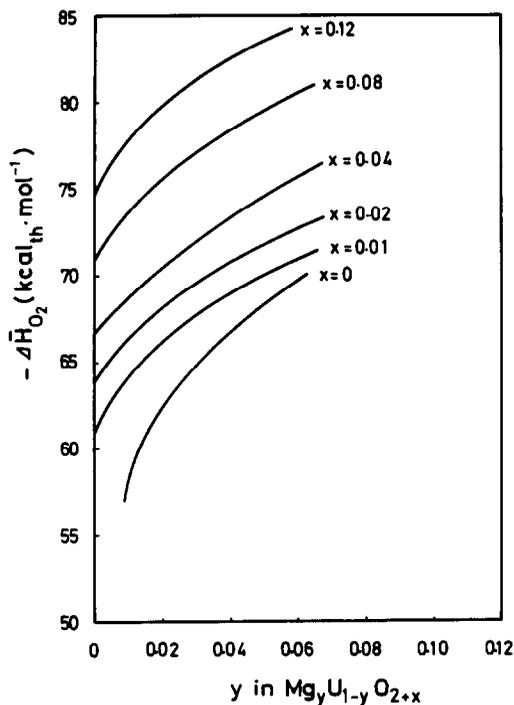


FIG. 7. Negative partial molar enthalpy as a function of y with parameter x .

the partial molar free energy, $\Delta\bar{G}_{O_2}$, of the solid solution. The typical effect may be that of the mean valence model which asserts that the partial molar free energy depends on only the mean valence of the uranium ions in the solid solution (6, 7). Then, if $-\Delta\bar{G}_{O_2}$ values are plotted against the mean valence, z , the values should fall on a single curve for various y values. In the case of $Mg_yU_{1-y}O_{2+x}$, the mean valence is given by

$$z = 2(2 + x - y)/(1 - y). \quad (6)$$

Plots of $-\Delta\bar{G}_{O_2}$ vs z showed that the mean valence model did not hold well for the solid solution, $Mg_yU_{1-y}O_{2+x}$. This may be because the third ion is not tetravalent in the present case.

In the preceding section it was pointed out that the $-\Delta\bar{G}_{O_2}(Mg_yU_{1-y}O_{2+x})$ curve can be expressed by transferring the $-\Delta\bar{G}_{O_2}(UO_{2+x})$ curve in Fig. 2 or 3. A treatment based on this fact is described as following. For simplicity we express $-\Delta\bar{G}_{O_2}(Mg_yU_{1-y}O_{2+x})$ as $g(x, y)$. Then,

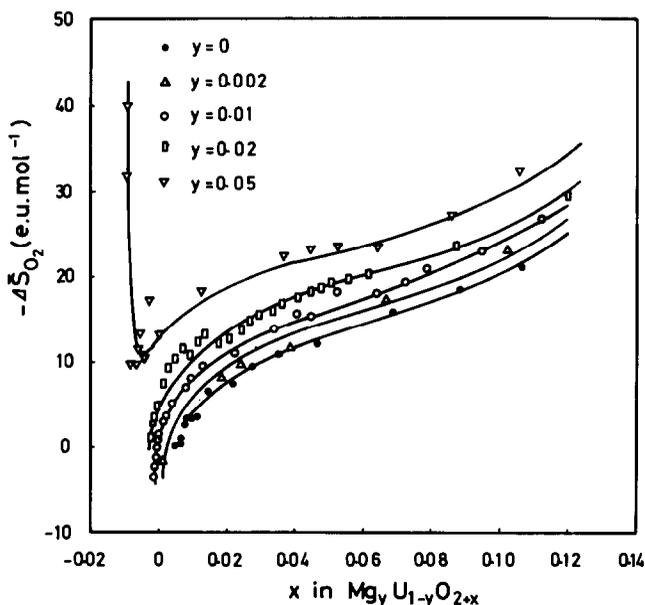


FIG. 8. Plots of negative partial molar entropy of $Mg_yU_{1-y}O_{2+x}$ against x with parameters of various y values.

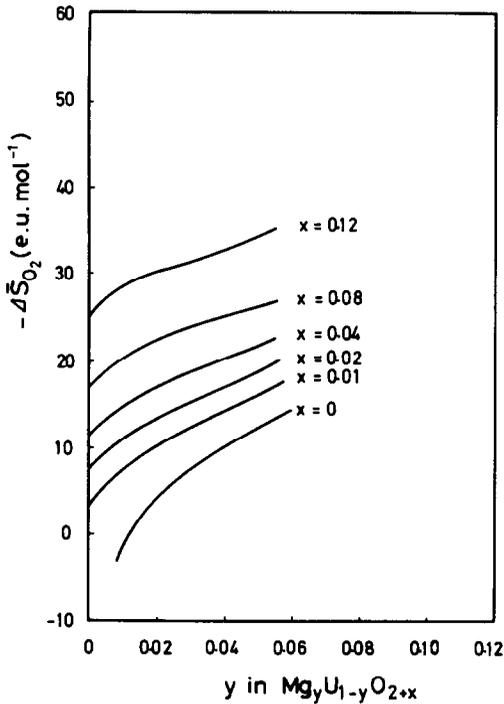


FIG. 9. Negative partial molar entropy as a function of y with parameter x .

$-\Delta\bar{G}_{O_2}(UO_{2+x})$ is expressed as $g(x, 0)$. In Fig. 2, each of the $g(x, y)$ curves, where $y = 0.002, 0.01, 0.02,$ and 0.05 , coincides with the $g(x, 0)$ curve by transferring η parallel to the $-\Delta\bar{G}_{O_2}$ -axis and then by transferring ξ parallel to the x -axis. Hence, we have the relation

$$g(x, y) = g(x + \xi, 0) - \eta. \quad (7)$$

In Fig. 10, the dependence of η and ξ on y is shown. These values are obtained by the parallel transformation of the curves in Figs. 2 and 3. From this figure η and ξ can be written as a function of y as

$$\eta = 60y \quad \text{and} \quad \xi = 0.07y^{1/2}. \quad (8)$$

Here, let us introduce an approximation that the partial molar free energy of UO_{2+x} is given by a logarithmic function of x ,

$$g(x, 0) = -A \ln x + B, \quad (9)$$

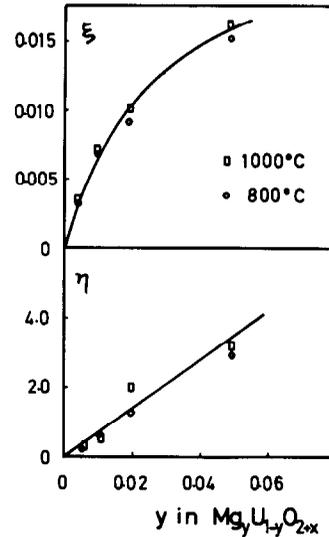


FIG. 10. Degree of parallel transformation required for the $-\Delta\bar{G}_{O_2}(Mg_yU_{1-y}O_{2+x})$ curve to coincide with the $-\Delta\bar{G}_{O_2}(UO_{2+x})$ curve in Fig. 2 or 3. η , parallel to the $-\Delta\bar{G}_{O_2}$ -axis; ξ , parallel to the x -axis.

where A and B are the constants to be determined. A will be proportional to temperature, T , as

$$A = \alpha T. \quad (10)$$

Combination of Eqs. (7) and (9) gives

$$g(x, y) = -A \ln(x + \xi) + B - \eta. \quad (11)$$

Subtraction of Eq. (9) from Eq. (11) leads to

$$g(x, y) - g(x, 0) = -A \ln\left(\frac{x + \xi}{x}\right) - \eta. \quad (12)$$

Substituting Eq. (8) into Eq. (12) we have

$$\begin{aligned} -\Delta\bar{G}_{O_2}(x, y) + 4.5 \ln\left(1 + 0.07 \frac{y^{1/2}}{x}\right) + 60y \\ = -\Delta\bar{G}_{O_2}(x, 0), \end{aligned} \quad (13)$$

where 4.5 was used as the value of A at 1000°C . In the above equation, $-\Delta\bar{G}_{O_2}(Mg_yU_{1-y}O_{2+x})$ and $-\Delta\bar{G}_{O_2}(UO_{2+x})$ are written as $-\Delta\bar{G}_{O_2}(x, y)$ and $-\Delta\bar{G}_{O_2}(x, 0)$, respectively. The values of the left-hand side of Eq. (13) are plotted for various y values in Fig. 11. The experimental

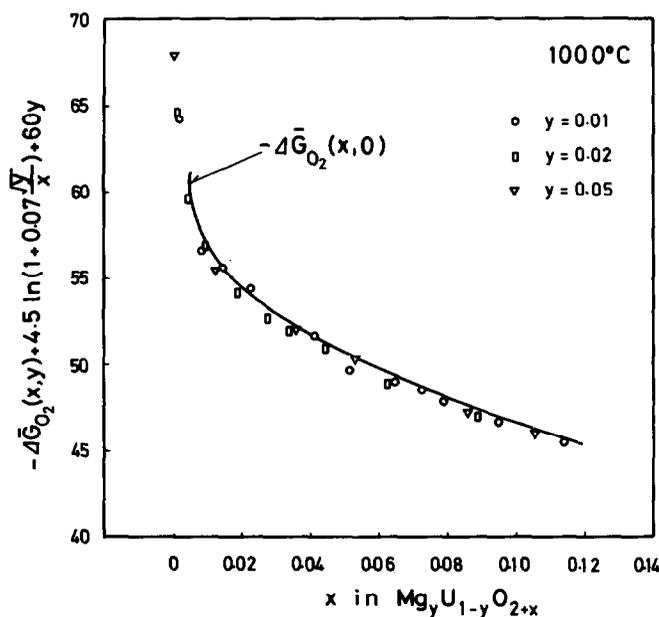


FIG. 11. Plots of the values, $-\Delta\bar{G}_{O_2}(x, y) + 4.5 \ln[1 + 0.07(y^{1/2}/x)] - 60y$, against x at 1000°C . Experimental curve for $-\Delta\bar{G}_{O_2}(x, 0)$ adopted from Fig. 2 is also shown as a solid line.

curve of $-\Delta\bar{G}_{O_2}(x, 0)$ is shown as a solid line. Good coincidence is seen in Fig. 11; this fact exhibits that Eq. (13) is a good approximation equation for the partial molar free energy of the solid solution $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$ at 1000°C .

Using Eq. (10), Eq. (13) can be rewritten in the more general form of the function of

$$\begin{aligned} &-\Delta\bar{G}_{O_2}(\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}) \\ &= -\Delta\bar{G}_{O_2}(\text{UO}_{2+x}) \\ &\quad - 0.0035 T \ln\left(1 + 0.07 \frac{y^{1/2}}{x}\right) - 60y, \end{aligned} \quad (14)$$

where 0.0035 was taken as the α value of Eq. (10). However, the approximation of Eq. (10) is not very exact. We must use $\alpha = 0.0030$ for 800°C , for example. Hence, it is recommended to use the value of A which is calculated from the $-\Delta\bar{G}_{O_2}(\text{UO}_{2+x})$ vs $\ln x$ curve obtained experimentally at a fixed temperature.

For uranium dioxide containing more than one foreign metal, $\text{M}(1)_{y_1}\text{M}(2)_{y_2} \cdots \text{M}(i)_{y_i}\text{U}_{1-y}\text{O}_{2+x}$ ($y = \sum y_i$), where $\text{M}(i)$ expresses i th cation which behaves like a magnesium ion in the solid solution of UO_2 , Equation (14) may be generalized to

$$\begin{aligned} &-\Delta\bar{G}_{O_2}[\text{M}(1)_{y_1}\text{M}(2)_{y_2} \cdots \text{M}(i)_{y_i}\text{U}_{1-y}\text{O}_{2+x}] \\ &= -\bar{G}_{O_2}(\text{UO}_{2+x}) \\ &\quad - 0.0035 T \ln\left[1 + \frac{(\sum a_i y_i)^{1/2}}{x}\right] - \sum b_i y_i, \end{aligned} \quad (15)$$

a_i and b_i being the constants to be determined experimentally for each component. This generalized equation may be useful for estimating the thermodynamic properties of irradiated UO_2 fuel in the nuclear reactor.

Acknowledgment

The authors wish to thank Dr. K. Takashima for the emission spectrographic analysis.

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