(UC-25: Metallurgy and Ceramics
TID-4500, 13th Ed., Suppl.)

CALCULATED EQUILIBRIUM CONSTANTS FOR METAL-OXYGEN
REACTIONS IN MOLTEN URANIUM ALLOYS

by

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November 1957

Contract AT-11-1-GEN-14

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REACTIONS IN MOLTEN URANIUM ALLOYS

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CALCULATED EQUILIBRIUM CONSTANTS FOR METAL-OXYGEN REACTIONS IN MOLTEN URANIUM ALLOYS

by

E. H. Roland

INTRODUCTION

An understanding of the chemical reactions occurring between oxygen dissolved in molten uranium alloys and alloying additions and impurities is of major importance in the development of high purity nuclear fuel alloys. Such knowledge may be applied to control the oxygen or other impurity content of uranium alloys to be used in reactors, or it may be applied with equal effectiveness to the purification of spent fuels. In any event, the need for experimental work designed to study such reactions is quite pressing if uranium fuel alloy technology is to advance at a maximum rate.

The oxygen and the metallic impurities are present as a result of the reactions of the molten alloy with the crucible materials and the furnace atmosphere. There is little or no experimental information available upon which to base equilibrium studies of oxidation reactions occurring in molten uranium alloys. However, the equilibrium constants for oxidation reactions occurring in molten uranium alloys can be estimated from thermodynamic principles. This report is concerned with such calculations.

THERMODYNAMIC CONSIDERATIONS

For the generalized equation

the equilibrium constant for the reaction is written

$$K_a = \frac{a_M^x \cdot P_{O_2}^{y/2}}{a_{M_xO_y}} \quad (2)$$

where a = chemical activity and

P_{O_2} = partial pressure of oxygen gas. The equilibrium constant is related to the standard free energy ΔF° by the relationship

$$\Delta F^\circ = - RT \ln K_a \quad (3)$$

The reaction of impurities and alloying additions in molten uranium with dissolved oxygen are of interest in this study. The generalized equation for this case is written

where the dash under the chemical symbol designates solution of that element in the liquid uranium. The equilibrium constant then becomes

$$K_s = \frac{[w/o M]^x [w/o O]^y}{a_{M_{x y} O_{x y}}} \quad . \quad (5)$$

The equilibrium constant given in equation (5) above differs from equation (2) in that here the activities relate to different standard states than for equation (2) and the reaction is occurring in a solvent of liquid uranium. The equilibrium constant when the reaction occurs in the liquid uranium solvent is designated K_s .

The concentration units in which the equilibrium constants will be evaluated have been chosen as weight percent of metal and oxygen in molten uranium. For the metal the standard state becomes a solution containing 1 w/o metal where the activity of the metal is unity, and for the dissolved oxygen a solution containing 1 w/o oxygen where the activity of the oxygen is unity.

For the uranium and uranium-base alloys there are no experimental determinations upon which the equilibrium constant and the associated free energy relationships can be based. In lieu of experimental determinations, the relationships of interest for equation (4) will be estimated by using thermodynamic concepts and available standard free energy values.

So that the standard free energy value for equation (4) can be calculated, the standard free energy values for the following reactions must be known:

for which the standard free energies have been tabulated by various authors.

The source used for this paper is Metallurgical Thermochemistry by Kubaschewski and Evans.¹ The free energy relationship fits the form $\Delta F^\circ = A + BT \log T + CT$.

For the reaction

$$M \text{ (liquid, } N = 1) = M \text{ (solution)} = \underline{M} \quad , \quad (7)$$

by which the pure liquid metal goes into solution in uranium, the activities are unknown, and it is assumed that Raoult's Law is applicable (i.e., the solute behaves ideally or $\overline{\Delta F}^\circ = RT \ln N$). The standard state is that of pure liquid metal where the mol fraction N is equal to unity. However, for the purpose of this study it is desirable that the standard state be a dilute solution of 1 w/o metal in molten uranium. For the new standard state there will be a new standard free energy which is related to the old standard free energy by:

$$\overline{\Delta F}_M^\circ = F^\circ(\%) - F^\circ(\text{mol fraction}) = -RT \ln \frac{a(\%)}{a(\text{mol fraction})} \quad (8)$$

or for the uranium-base alloys

$$\overline{\Delta F}_M^\circ = -RT \ln(1 + 0.416 M_s) \quad , \quad (9)$$

where M_s is the molecular weight of the solute.

The final reaction of interest is that for solution of gaseous oxygen according to the reaction

The standard free energy for this reaction has never been evaluated experimentally and is estimated on the following premises:

1. The saturated solution of oxygen in molten uranium is in equilibrium with pure solid UO_2 . The solubility data for oxygen in solution are taken from the uranium-oxygen phase diagram.⁵

2. The partial pressure of oxygen can be evaluated from the free energy of formation of UO_2 .

The standard free energy for equation (4), the reaction of interest, can now be evaluated by the summation of the free energies for equations (6), (7), and (10) multiplied by appropriate constants as follows:

$$M_x O_y (\text{solid}) = xM (\text{liquid}) + \frac{y}{2} O_2 (\text{gas}) \quad (6)$$

$$\Delta F^\circ (\text{oxide}) = A + BT \log T + CT$$

$$xM (\text{liquid}) = x\bar{M} \quad (7)$$

$$\overline{\Delta F}_M^\circ = x [-4.576 T \log (1 + 0.416 M_s)]$$

$$\frac{y}{2} \text{O}_2 (\text{gas}) = y\underline{\text{O}} \quad (10)$$

$$\underline{\Delta F}_0^\circ = \frac{y}{2} (-224,300 + 40.3 T)$$

Adding the equations give

$$\text{M}_x\text{O}_y (\text{solid}) = x\underline{\text{M}} + y\underline{\text{O}} \quad , \quad (4)$$

the reaction of interest in this study.

The standard free energy for the reaction

$$\text{O}_2 (\text{gas}) = 2\underline{\text{O}} \quad (10)$$

is evaluated from solubility data given in Fig. 1 and the free energy of formation for uranium dioxide.

Fig. 1 Uranium-Oxygen Phase Diagram*

*Reference 5

For the reaction

the standard free energy change as given by Kubaschewski and Evans¹ is

$$\Delta F^\circ = 264,920 + 6.2 T \log T - 64.5 T \quad (12)$$

for the temperature range from the melting point of pure uranium to 2000°K, where T in the above equation is given in degrees Kelvin.

It is further assumed, however, that equation (12) is valid up to 2273°K (2000°C). The equilibrium constant is written

$$K = \frac{a_U \cdot P_{\text{O}_2}}{a_{\text{UO}_2}} \quad (13)$$

where $a_U = a_{\text{UO}_2} = 1$, since both the pure uranium (the slight solubility of oxygen in uranium can be neglected) and the oxide are in their standard states. The equilibrium constant is written

$$K = P_{\text{O}_2} \quad (14)$$

The partial pressure of oxygen, P_{O_2} , is related to the standard free energy change by

$$\Delta F^\circ = - RT \ln P_{\text{O}_2} \quad .$$

From this relationship the partial pressure of oxygen in equilibrium with a saturated solution of oxygen in uranium can be calculated. Table I lists both the oxygen potential above the melt and the oxygen content of the uranium-oxygen alloy along with the calculated equilibrium constant.

The equilibrium constant for the reaction

is written

$$K_{\text{O}} = \frac{[\text{w/o O}]^2}{P_{\text{O}_2}} \quad , \quad (15)$$

and the calculated values are listed in Table I.

TABLE I

SOLUBILITY OF OXYGEN, OXYGEN POTENTIAL, AND CALCULATED EQUILIBRIUM
CONSTANT FOR SOLUTION OF GASEOUS OXYGEN IN LIQUID URANIUM

$T, ^\circ\text{C}$	w/o O	P_{O_2}	K
1200	0.0033	3.2×10^{-30}	3.40×10^{24}
1400	0.0055	1.5×10^{-25}	2.02×10^{20}
1600	0.0110	5.6×10^{-22}	2.16×10^{17}
1800	0.0187	4.7×10^{-19}	7.44×10^{14}
2000	0.0286	1.2×10^{-16}	6.82×10^{12}

If $\log K_{\text{O}}$ is plotted versus $1/T$, as shown in Fig. 2, it is seen that the

Fig. 2 $\log K_{\text{O}}$ vs. $1/T$ for the Reaction $\text{O}_2 (\text{gas}) = 2\text{O}$

data can best be approximated by a straight line relationship through the calculated points. Applying the method of least squares to the data, $\log K_{\underline{O}}$ as a function of temperature becomes

$$\log K_{\underline{O}} = \frac{49018}{T} - 8.808 \quad (16)$$

and is shown graphically in Fig. 2. Since

$$\overline{\Delta F_{\underline{O}}^{\circ}} = -RT \ln K_{\underline{O}}, \quad (17)$$

the standard free energy change becomes

$$\overline{\Delta F_{\underline{O}}^{\circ}} = -224,306 + 40.3 T$$

and is shown graphically in Fig. 3.

Fig. 3 Standard Free Energy Change ($\overline{\Delta F_{\underline{O}}^{\circ}}$) vs. Temperature for Reaction $\text{O}_2 (\text{gas}) = 2\underline{\text{O}}$

DEOXIDATION REACTIONS IN MOLTEN URANIUM

Oxygen is an unwanted impurity in uranium fuel alloys. The purpose of this section is to evaluate from an equilibrium standpoint the ability of various elements to be used as deoxidizers for the uranium alloys. The calculations serve a twofold purpose in that they also predict the best crucible material.

The chemical reactions of interest in this study are

For all of the above reactions except (20) the pure oxide is in its standard state where the activity is equal to unity and the equilibrium constant is written

$$K'_s = \frac{a_{\text{M}_x\text{O}_y}}{[\text{w/o M}]^x [\text{w/o O}]^y} = \frac{1}{[\text{w/o M}]^x [\text{w/o O}]^y} \quad (24)$$

As an example, the calculation of the deoxidation constant for the reaction

will be given. For ease of computation the reverse of reactions (18) through (23) are used. The equilibrium constant is then written for the reaction

and

$$K_s = \frac{1}{K'_s} = [\text{w/o M}]^x [\text{w/o O}]^y \quad (21)$$

The sample calculation is shown below:

Chemical Reaction	Free Energy
$\text{BeO (s)} = \text{Be (l)} + 1/2 \text{ O}_2 \text{ (g)}$	$\Delta F^\circ_{\text{BeO}} = 145,000 + 1.66 T \log T - 29.66 T$
$\frac{1}{2} \text{ O}_2 \text{ (g)} = \underline{\text{O}}$	$\overline{\Delta F^\circ_{\text{O}}} = -112,153 + 20.15 T$
$\text{Be (l)} = \underline{\text{Be}}$	$\overline{\Delta F^\circ_{\text{Be}}} = -4.576 T \log (1 + 0.416 M)$
	$= -3.12 T$

where s = solid

l = liquid

g = gas

- = in solution

The addition of the above three reactions and free energy values gives

Since

$$\Delta F^\circ = -RT \ln K$$

$$\log K_s = \frac{7386}{T} - 0.363 \log T + 2.738,$$

where

$$K_s = [\text{w/o Be}][\text{w/o O}]$$

The calculated values of $\log (1/K_s')$ vs. temperature for the deoxidation reactions are shown graphically in Fig. 4 and are given in Table II.

The associated standard free energy change for the reaction can be calculated through the relationship

$$\Delta F^\circ = -RT \ln K_s = -4.576 T \log K_s \quad (22)$$

The standard free energy change for the deoxidation reactions are shown graphically as a function of temperature in Fig. 5 and given in Table III.

The relative ability of the various alloying additions as deoxidizers can be estimated from Figs. 4 and 5. Figure 6 illustrates an easier manner by which the deoxidizing potential of the different alloying additions can be estimated. Here weight percent metal is plotted versus weight percent oxygen in solution at 1500°C for the deoxidation reactions previously considered. The values for

Fig. 4 Log K vs. $1/T$ for Deoxidation Reactions Occurring in Molten Uranium of Type $M_x O_y$ (solid) = $x \underline{M} + y \underline{O}$

Fig. 5 Standard Free Energy Charge (ΔF°) vs. Temperature for the Deoxidation Reactions Occurring in Molten Uranium of Type $M_x O_y = x \underline{M} + y \underline{O}$

TABLE II

CALCULATED VALUES OF LOG K AS A FUNCTION OF TEMPERATURE
FOR DEOXIDATION REACTIONS OCCURRING IN MOLTEN URANIUM

Reaction	$\log K' = \log 1/K$
$2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 \text{ (solid)}$	$\log [\text{w/o Al}]^2 [\text{w/o O}]^3 = -\frac{15144}{T} - 0.819 \log T + 11.117$
$\text{Be} + \text{O} = \text{BeO (solid)}$	$\log [\text{w/o Be}][\text{w/o O}] = -\frac{7386}{T} - 0.363 \log T + 2.738$
$\text{C} + \text{O} = \text{CO (gas)}$	$\log \frac{[\text{w/o C}][\text{w/o O}]}{P_{\text{co}}} = \frac{18760}{T} - 8.208; (P_{\text{co}} \text{ in atm})$
or	$\log [\text{w/o C}][\text{w/o O}] = \frac{18760}{T} - 11.091 + \log P_{\text{co}}; (P_{\text{co}} \text{ in mm Hg})$
$\text{Ca} + \text{O} = \text{CaO (solid)}$	$\log [\text{w/o Ca}][\text{w/o O}] = -\frac{9047}{T} - 2.343$
$\text{Mg} + \text{O} = \text{MgO (solid)}$	$\log [\text{w/o Mg}][\text{w/o O}] = -\frac{8517}{T} - 1.611 \log T + 8.348$
$\text{Zr} + 2\text{O} = \text{ZrO}_2 \text{ (solid)}$	$\log [\text{w/o Zr}][\text{w/o O}]^2 = -\frac{8796}{T} - 2.28 \log T + 10.081$

TABLE III

STANDARD FREE ENERGY CHANGE FOR DEOXIDATION
REACTIONS OCCURRING IN MOLTEN URANIUM

Reaction	F°
$\text{Al}_2\text{O}_3 \text{ (solid)} = 2\text{Al} + 3\text{O}$	$\Delta F^\circ = 69,299 + 3.75 T \log T - 50.87 T$
$\text{BeO (solid)} = \text{Be} + \text{O}$	$\Delta F^\circ = 33,798 + 1.66 T \log T - 12.53 T$
$\text{CO (gas)} = \text{C} + \text{O}$	$\Delta F^\circ = -85,846 + 37.56 T; (P_{\text{CO}} \text{ in atm})$
or	$\Delta F^\circ = -85,846 + 50.75 T (P_{\text{CO}} \text{ in mm of Hg})$
$\text{CaO (solid)} = \text{Ca} + \text{O}$	$\Delta F^\circ = 41,399 - 10.72 T$
$\text{MgO (solid)} = \text{Mg} + \text{O}$	$\Delta F^\circ = 38,974 + 7.37 T \log T - 38.20 T$
$\text{ZrO}_2 \text{ (solid)} = \text{Zr} + 2\text{O}$	$\Delta F^\circ = 40,250 + 10.15 T \log T - 46.13 T$

$2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 \text{ (solid)}$ fall off the range of this graph and can be considered as a very poor choice either for a deoxidizer or as a crucible material. From this graph and also from Fig. 5 it can be seen that the elements Ca and Be would be the best deoxidizers to use from an equilibrium viewpoint.

The information presented in Figs. 4 and 5 does not give the complete story for the carbon-oxygen equilibria. It is absolutely necessary to take into account the partial pressure of carbon monoxide above the melt. This will be discussed in the following section.

CARBON-OXYGEN REACTION IN MOLTEN URANIUM

The carbon-oxygen reaction differs from the other deoxidation reactions in that the oxide phase formed is in a gaseous state rather than solid. The chemical activity of the carbon monoxide gas is equal to its partial pressure above the melt. For the reaction

the equilibrium constant is given by

$$K_{\text{CO}} = \frac{[\text{w/o C}][\text{w/o O}]}{P_{\text{CO}}} \quad (24)$$

The role played by the pressure of CO on the impurity level of carbon and oxygen in uranium and its alloys is very important. A small change in pressure will

Fig. 6 Weight Percent Oxygen vs. Weight Percent of Various Metals Showing Effect of Deoxidation Product on Crucible Material on Impurity Level of Uranium at 1500°C

Fig. 7 Weight Percent Oxygen vs. Weight Percent Carbon Showing Effect of Carbon Monoxide Pressure on Impurity Level of Uranium at 1500°C

cause an appreciable change in the carbon-oxygen level. This effect is illustrated in Fig. 7, where weight percent carbon is plotted versus weight percent oxygen at 1500°C for various partial pressures of CO. From Fig. 7 it can be seen that changing the pressure from 1 micron (10^{-3} mm Hg) to 10 microns (10^{-2} mm Hg) at constant carbon content will cause a marked increase in the oxygen content. Similarly, a slight pressure change at constant oxygen content will increase the carbon content appreciably.

This shows that the variability of furnace pressures over the working range in vacuum-melting techniques can account for the differences in oxygen and carbon contents from melt to melt.

SUMMARY

It is essential to restate, so that the importance of the numerical values derived will not be overemphasized, that values for the standard free energy and the associated equilibrium constants are based on the following conditions:

1. The solubility of oxygen in uranium is that given by the phase diagram in The Chemistry of Uranium, by Katz and Rabinowitch.⁵
2. The oxygen-saturated liquid uranium phase is in equilibrium with solid UO_2 of stoichiometric composition.
3. The partial pressure of oxygen in equilibrium with the liquid phase is calculable from the standard free energy of formation of UO_2 .
4. The solution of the solute metals in liquid uranium obeys Raoult's Law.

This study has provided preliminary qualitative information on two important points: (a) the relative ability of various elements to deoxidize uranium, and (b) the relative stability of the oxides formed as a result of deoxidation. Point (b) serves as a guide to the selection of these oxides for possible application as crucible materials. Ideas have been obtained as to the extent to which one might be able to purify uranium by the conventional melting techniques. This analysis provides information necessary for interpreting present experimental data as well as for designing new experiments to enable better understanding of the complex problems encountered in melting uranium alloys.

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