UCRL-11957

University of California

Ernest O. Lawrence Radiation Laboratory

MEASUREMENTS OF THE THERMODYNAMIC STABILITIES OF THE NIOBIUM AND TANTALUM OXIDES USING A HIGH-TEMPERATURE GALVANIC CELL

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

IAEA Symposium on Thermodynamics

Paper No. SM-66/66

UCRL-11957

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

MEASUREMENTS OF THE THERMODYNAMIC STABILITIES OF THE NIOBIUM AND TANTALUM OXIDES USING A HIGH-TEMPERATURE GALVANIC CELL

Wayne L. Worrell

June 1965

MEASUREMENTS OF THE THERMODYNAMIC STABILITIES OF THE NIOBIUM AND TANTALUM OXIDES USING A HIGH-TEMPERATURE GALVANIC CELL

Wayne L Worrell

Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California

Thermodynamic data for $Nb_2O_{4.8}$, NbO and Ta_2O_5 have been obtained from six different galvanic cells operating between 1030 and 1300°K. The electrolyte used is a solid-solution of either ThO_2 (94 wt %) - Y_2O_3 or ThO_2 (98.6 wt %) - CaO which remains an ionic conductor at lower oxygen activities and higher temperatures than the more commonly used zirconia-based electrolytes. The $YFeO_3$ phase was detected on the surface of the ThO_2-Y_2O_3 electrolyte where it had been in contact with the Fe, $Fe_{0.95}O$ electrode. More stable readings were obtained using the ThO_2-CaO electrolyte with the Fe, $Fe_{0.95}O$ electrode.

A comparison between the temperature variation of the Gibbs energy of formation of $Nb_2O_{4.8}$ obtained in this study and that of Nb_2O_5 from calorimetric data indicates that the homogeneity range of the pentoxide increases with increasing temperature. Two independent Gibbs-energy-of-formation-equations were determined for NbO. Values from the two equations differ

by 600 calories, but the data from one of the NbO cells is suspected of containing a systematic error. There is considerable disagreement between the enthalpy and entropy values for NbO obtained in this study and those calculated from thermal data. It is suggested that this difference may indicate a homogeneity range for NbO.

The thermodynamic stability of Ta_2O_5 obtained in this study is in excellent agreement with the thermal data.

The effect of the solubility of oxygen in niobium and tantalum on the results for NbO and Ta_2O_5 is discussed.

1. Introduction

In 1957 Kiukkola and Wagner [1] clearly demonstrated the potential use of galvanic cells with solid-oxide electrolytes to obtain reliable thermodynamic data at elevated temperatures. Most investigations since 1957 have used a zirconia-based electrolyte because of the availability of zirconia-calcia tubes which, if of sufficient purity, function quite satisfactorily as electrolytes. However, Schmalzried [2] and Steele and Alcock [7] have shown that n-type electronic conduction becomes significant in the commercially available zirconia-based tubes at oxygen activities below 10^{-15} at 1000°C, and these tubes can not be used to investigate systems with extremely low oxygen activities. Recently several studies [3, 4, 5, 6, 7, 8] have been reported in which a thoria-based electrolyte was used. Because this electrolyte remains a purely ionic conductor in the low oxygen activity region [7], it was used in this galvanic study of the thermodynamic stabilities of the niobium and tantalum oxides.

Niobium forms three stable oxides, Nb_2O_5, NbO_2 and NbO [9]. The pentoxide possesses a homogeneity range which varies from $Nb_2O_{4.8}$ to Nb_2O_5, but no significant homogeneity range has been detected for either NbO_2 or NbO [9]. Because the Nb_2O_5 phase was in equilibrium with NbO_2, the thermodynamic properties obtained in this study apply to the $Nb_2O_{4.8}$ composition.

Although several tantalum oxides have been reported in the literature [10], there is evidence [11, 12] that only tantalum pentoxide is stable. From a study of the defect structure of Ta_2O_5, Kofstad [13] concludes that Ta_2O_5 is essentially a line compound with a very limited range of homogeneity.

2. Experimental Study

2.1 Materials

Niobium, iron, tantalum, Fe_2O_3, Nb_2O_5 and Ta_2O_5 powders(-325 mesh) of 99.9+% purity were purchased from commercial sources. The NbO_2, NbO, and FeO were obtained by hydrogen reduction of Nb_2O_5 and Fe_2O_3. Electrode pellets (0.5 in. diameter and 0.25 in. thick) were prepared by pressing the appropriate metal-oxide mixture at 20 tons/in^2 and oxide-oxide mixture at 10 tons/in^2.

The thoria-based electrolytes were prepared from -325 mesh powders of high purity (99.9 + %) ThO_2 and either Y_2O_3 or CaO. Mixtures of either 98.6 wt. % ThO_2 and 1.4 wt. % CaO or of 94 wt. % ThO_2 and 6 wt. % Y_2O_3 were pressed (10 tons/in^2) into pellets of 0.5 in. diameter and 0.25 in. thick. These compositions correspond to a thoria solid-solution containing 3.25% oxygen ion vacancies, which is the region of maximum ionic conductivity [7]. The pressed pellets were heated inductively to 1900-1950° C and held for 3-4 hours under a vacuum of 1×10^{-5} mm of Hg. During this time the thoria dissolved either the Y_2O_3 or the CaO to form a one phase solid-solution.

2.2 Apparatus

The experimental design was similar to that of Kiukkola and Wagner [1]. The reaction and positioning tubes were high-purity alumina. The reaction tube was encased in platinum foil which was connected to the grounded furnace shell to avoid induced potentials from the resistance windings of the furnace. The reaction tube was positioned vertically in the furnace and sealed at each end with O-rings in brass fittings.

High-purity argon entered the reaction tube after passing through a gas-purification furnace containing Zr-Ti alloy (87½ atomic % Zr) chips at 375°C.

This newly available alloy proved to be an excellent oxygen-getter.

The temperature was measured using a Pt-90% Pt + 10% Rh thermocouple. The cell Emf was measured using a high input resistance (10,000 ohms) electronic galvonometer combined with a Leeds and Northrup K-2 potentiometer.

2.3 Procedure

Two springs positioned at the top and bottom of the reaction tube were used to sandwich the electrolyte pellet between the two electrodes. Platinum lead wires were spot-welded to the platinum disks pressed against each electrode. The Pt-10% Rh wire was also spot-welded to the top platinum disk; thus the upper platinum lead served as both an electrode and a thermocouple lead.

After assembling the cell, the reaction tube was evacuated to five microns and checked for leaks. The argon flow was then started, and the cell was heated to the desired temperature. After obtaining a stable Emf, the temperature was randomly varied to obtain additional measurements.

Occasionally an Emf either higher or lower than the equilibrium value was imposed on the cell. After these polarizations, the Emf always returned to the equilibrium value. The argon flow rate was also increased and decreased to see if the Emf varied with flow rate.

After each run an X-ray diffraction analysis was made of each electrode to confirm that only the initial phases were present.

Using the above procedure, the following galvanic cells were investigated:

NbO_2, $Nb_2O_{4.8}$ / ThO_2 (Y_2O_3) / Fe, $Fe_{0.95}O$	A
NbO_2, $Nb_2O_{4.8}$ / ThO_2 (CaO) / Fe, $Fe_{0.95}O$	A'
NbO, NbO_2 / ThO_2 (CaO) / Fe, $Fe_{0.95}O$	B
NbO_2, $Nb_2O_{4.8}$ / ThO_2 (Y_2O_3) / NbO, NbO_2	C

$Nb, NbO / ThO_2 (Y_2O_3) / NbO, NbO_2$ D

$Nb, NbO / ThO_2 (Y_2O_3) / Ta, Ta_2O_5$ E

A minimum of three experimental runs were made with each of these cells.

3. Results

3.1 NbO_2, $Nb_2O_{4.8}$ versus Fe, $Fe_{0.95}O$

Galvanic cell A was the first cell investigated. Although the Emf appeared very stable, slightly lower values for the Emf were obtained after the first 36 hours. The $ThO_2(Y_2O_3)$ electrolyte was badly stained where it had been in contact with the Fe, $Fe_{0.95}O$ electrode. With reuse, the $ThO_2(Y_2O_3)$ electrolyte gave even lower but steady values for the Emf. After several runs, X-ray diffraction analysis revealed the presence of the $YFeO_3$ phase on the electrolyte surface. Thus a very slow reaction was occurring between the Fe, $Fe_{0.95}O$ electrode and the Y_2O_3 dissolved in the thoria. From a qualitative analysis of the phase relationships in the Y-Fe-O ternary system, it was concluded that the formation of $YFeO_3$ would tend to lower the oxygen activity at the Fe, $Fe_{0.95}O$ electrode, thus bringing it slightly closer to that of the NbO_2, $Nb_2O_{4.8}$ electrode and decreasing slightly the Emf.

Measurements were then made using the $ThO_2(CaO)$ electrolyte (cell A') to confirm the initial Emf readings using the $ThO_2(Y_2O_3)$ electrolyte. These values were very stable over extended periods of time. The $ThO_2(CaO)$ electrolyte was also slightly stained where it had been in contact with the Fe, $Fe_{0.95}O$ electrode. However, the staining was very mild compared to that observed with $ThO_2(Y_2O_3)$, and its X-ray diffraction pattern did not show any extraneous lines.

The results from cells A and A' are shown in Figure 1. Although the initial readings using the $ThO_2(Y_2O_3)$ lie on the accepted line, the later values are one to three millivolts too low.

The Emf obtained at 1000° C by Steele and Alcock [7] using similar cells is also shown. It is interesting to note that Steele and Alcock [7] experienced considerable difficulty stabilizing the Emf in the cell Fe, $Fe_{0.95}O$ / ThO_2 (Y_2O_3) / Nb, NbO. They attributed these difficulties to a very slight electronic conductivity in the electrolyte, possibly caused by the low oxygen activity at the Nb, NbO electrodes. However, the formation of the $YFeO_3$ phase could have been responsible for at least part of the decrease.

Steele and Alcock [7] observed that when the Y_2O_3 in the $ThO_2(Y_2O_3)$ electrolyte was decreased, the drift in the Emf was lessened, and they attributed this to the higher resistivity of the thoria-based electrolytes containing less Y_2O_3. However, the less Y_2O_3 the thoria contains, the less the tendency to form $YFeO_3$. It may be significant that this author experienced no drifting in cells D and E where the oxygen activity is very low but the Fe, $Fe_{0.95}O$ electrode is absent. Thus it appears wise to dissolve as little Y_2O_3 or CaO as possible in the thoria if one is using an Fe, $Fe_{0.95}O$ electrode.

Ignoring the values from the later $ThO_2(Y_2O_3)$ runs, a straight line was fitted to the data from cells A and A'. The equation for this line shown in Figure 2 is:

$$E\ (mV) = 239.5 - 0.075\ T \qquad (1)$$

Using the expression: $\Delta G = -n\ F\ E$ (2)

and equation (1), one obtains:

$$\Delta G\ (cal) = -11,000 + 3.45T \qquad (3)$$

for the reaction:

$$Fe_{0.95}O + 2.5NbO_2 = 0.95Fe + 1.25Nb_2O_{4.8} \qquad \text{I}$$

where ΔG is the Gibbs energy of formation, n is 2 for $O^{=}$, F the Faraday equivalent (23.052 cal/mV), and E the electromotive force.

3.2 NbO, NbO_2 versus Fe, $Fe_{0.95}O$

Several attempts were made to measure the Emf of Cell B. Only one run was successful; in the others the Emf varied appreciably with the argon flow rate.

This variation of the Emf with the argon flow rate most likely indicates a relatively porous electrode-electrolyte interface in which the gaseous atmosphere influences the Emf. It was also observed that the metal-oxide electrodes deformed slightly during a run, and that these ductile electrodes seemed to form a more impervious electrode-electrolyte interface than the more brittle oxide-oxide electrodes. One would thus expect to find the maximum flow rate variation of the Emf in cell C and the least in cell E. The variation of the Emf with argon flow rate was 0.1 mV in cell E, 0.5 mV in cells A, A' and D, and 3 to 5 mV in cells B and C. The uncertainties shown in Figure 1. indicate the extent of the flow rate variation of the Emf.

Alcock and Steele [6] obtained a mirror finish on the surfaces of their electrolytes by polishing with 0.25 μ diamond paste. In this study the surfaces were not polished, which is probably the cause of the difficulty in obtaining non-porous electrode-electrolyte interfaces in cells B and C.

The two Emf values which were obtained using galvanic cell B were combined with the data from cells A and A' and are plotted with the data from

cell C. These are shown as the two triangular points by the NbO, NbO_2 - NbO_2, $Nb_2O_{4.8}$ line of Figure 1.

3.3 NbO, NbO_2 versus NbO_2, $Nb_2O_{4.8}$

The Emf of cell C also varied with the argon flow rate, and relatively large uncertainties (±3-5 mV) have been assigned to these measurements. It should be noted that the maximum change in the Emf was only 5 mV in 270.

The slope of the line drawn through the data of cells C was determined using the third law method. The entropy of NbO_2 is well established [14, 15, 16]. The entropy of $Nb_2O_{4.8}$ was calculated using equation (12) which represents the data obtained from cells A and A'. Because only an estimate was available for the entropy of NbO [14], a value was chosen which would be consistent with the data of cells D and E.

Once the slope was established, a line was drawn through the data giving more weight to the measurements above 1200° K, because these measurements were more precise and reproducible. It should also be noted that several anomalies have been observed in the heat-content curve of NbO_2 between 1090 and 1200° K [17]. The equation for the NbO, NbO_2-NbO_2, $Nb_2O_{4.8}$ line shown in Figure 1 is:

$$E\ (mV) = 242.0 + 0.03\ T \tag{4}$$

Using equation (2) one obtains:

$$\Delta G\ (cal) = -\ 11,150 - 1.38T \tag{5}$$

for the reaction: $NbO + 1.25\,Nb_2O_{4.8} = 3.5NbO_2$ II

3.4 Nb, NbO versus NbO, NbO_2

The measured values from cell D varied only 0.5 mV with the argon flow

rate. The values were also quite stable with time; in some cases the temperature was held constant for 36 hours and no drift in the Emf was detected.

It should be mentioned that the time to approach equilibrium was considerably larger in cells of the type D and E. Longer times are probably necessary for the niobium and tantalum to equilibrate with NbO and Ta_2O_5 respectively. Niobium and tantalum contain 1-3 at. % oxygen when in equilibrium with NbO and Ta_2O_5 [18, 19]. The effect of the oxygen dissolved in tantalum and niobium will be discussed in the next section.

Although the precision of the data from cell D is high, the measured values appear to be 7-8 mV too low. Steele and Alcock's value [7] at 1000° C, shown in Figure 1, is based on several different types of cells. In the subsequent analysis of the data, it also becomes clear that the data from the cell D yield a value for ΔG_f of NbO that is 700 calories less negative than that from cell C. The more negative value is also more consistent with data from cell E.

The NbO used in the electrode pellets contained a small amount of niobium. It appears that the niobium was not oxidized during the galvanic cell runs because a trace of niobium was still evident in the X-ray diffraction patterns of the NbO, NbO_2 electrodes. The oxygen activity may be slightly decreased at the NbO, NbO_2 electrode due to the presence of niobium, and this could account for the lower values observed in this study. Because of these reasons, a dashed line is shown drawn through the data of cell D.

The slope of this line was determined using a third law analysis; the entropy of NbO was chosen to be consistent with the data from cells C and E. The equation for the Nb, NbO - NbO, NbO_2 line shown in Figure 1 is:

$$E\ (mV) = 309.6 - 0.09\ T \tag{6}$$

Using equation (2), one obtains:

$$\Delta G\ (cal) = -14,250 + 4.15\ T \tag{7}$$

for the reaction:

$$NbO_2 + Nb = 2NbO \qquad \text{III}$$

3.5 Nb, NbO versus Ta, Ta_2O_5

The variation of the Emf with the argon flow rate for cell E was negligible (±0.1 mV). The several points shown in Figure 1. with large uncertainties are from an early run in which no spring assembly was used to press the electrodes against the electrolyte.

The slope of the line drawn through the data of cell E was determined using a procedure similar to that for cells C and D. The equation for this line is:

$$E\ (mV) = 87.1 - 0.043\ T \tag{8}$$

Using equation (2), one obtains:

$$\Delta G\ (cal) = -4,020 + 1.98\ T \tag{9}$$

for the reaction: $Nb + 1/5\ Ta_2O_5 = 2/5\ Ta + NbO$ IV

No extraneous lines were observed in the X-ray diffraction patterns of the Ta-Ta_2O_5 and the Nb-NbO electrodes. This observation and the stability of the Emf values indicate that the reported suboxides of tantalum [10] are not stable over the experimental temperature range.

4. Discussion

4.1 Gibbs Energy of Formation of $Nb_2O_{4.8}$

The Gibbs energy of formation of NbO, NbO_2 and $Nb_2O_{4.8}$ could be determined from the measured Gibbs energy changes for reactions I, II and III. However the Gibbs energy change of reaction III is suspected of having a systematic error of 400 to 800 calories. Instead of introducing this error into all three ΔG_f° equations for the niobium oxides, two values for ΔG_f° of NbO were calculated from equations 5 and 7, and ΔG_f° of $Nb_2O_{4.8}$ was calculated from equation 3 using literature values [14, 20] for ΔG_f° of NbO_2.

From the critical evaluation of Schick [14], one obtains the following Gibbs energy equation for NbO_2 between 1100 and 1300° K:

$$\Delta G_f^\circ \text{ (cal)} = -185,600 + 39.0\ T \tag{10}$$

As shown in Figure 2 there is excellent agreement between equation 10 and the high-temperature data [8, 20].

The following Gibbs energy equation for the $Fe\text{-}Fe_{0.95}O$ reaction has been determined by Blumenthal and Whitmore [21] from a critical review of the pertinent data:

$$\Delta G_f^\circ \text{ (cal)} = -63,100 + 15.51\ T \tag{11}$$

Adding equations 11 and 3 yields:

$$\Delta G \text{ (cal)} = -74,100 + 18.96\ T \tag{12}$$

for the reaction: $2.5\ NbO_2 + \frac{1}{2}O_2 = 1.25\ Nb_2O_{4.8}$ V

Using equations 10 and 11, one obtains the following expression for ΔG_f° of $Nb_2O_{4.8}$ between 1050 and 1300° K:

$$\Delta G_f^\circ \text{ (cal)} = -430,480 + 93.17\ T \tag{13}$$

The thermodynamic stabilities [14] of Nb_2O_5 and of $Nb_2O_{4.8}$ between 1050 and 1300° K are shown in Figure 2. The difference in ΔG_f° reflects the homogeneity range of the Nb_2O_5 phase and increases slightly with increasing temperature, perhaps indicating that the homogeneity range is increasing. In the phase diagram for the Nb-O system [22], the homogeneity range of Nb_2O_5 is indicated by dashed lines and is shown increasing with increasing temperature.

4.2 Gibbs Energy of Formation of NbO

Using equations 5, 10, and 13, one obtains the following equation for ΔG_f° of NbO between 1050 and 1300° K:

$$\Delta G_f^\circ \text{ (cal)} = -100,350 + 21.42\ T \tag{14}$$

On the other hand combining equation 10 and 7 yields:

$$\Delta G_f^\circ \text{ (cal)} = -99,920 + 21.58\ T \tag{15}$$

for NbO in the same temperature region.

The thermodynamic stability of NbO calculated from equation 14 is shown in Figure 2, in which it is compared to that given in the critical review of Schick [14]. The values for ΔG_f° calculated from equation 15 would be about 600 calories less negative than those from equation 14, but equation 15 contains the suspected systematic error of equation 7.

Lavrent'ev, et al. [8] measured the Emf of the galvanic cell Fe, $Fe_{0.95}O$ / ThO_2 (La_2O_3) / Nb, NbO. Their experimental data are given by the equation:

$$\Delta G_f^\circ \text{ (cal)} = -34,500 + 3.15\ T \quad (1114 \text{ to } 1346\ ^\circ\text{K}) \tag{16}$$

for the reaction:

$$Nb + Fe_{0.95}O = 0.95\ Fe + NbO \qquad \text{VI}$$

Adding equations 11 and 16, one obtains -97,600 + 18.66 T for ΔG_f° of NbO. The values of ΔG_f° calculated from this equation are 400 to 700 calories more negative than the values obtained from equation 14 of this study. However, Lavrent'ev et al.'s measured Emf values [8] are 20-30 mV higher than those obtained by Steele and Alcock [7] from a similar cell.

Using the high-temperature thermal data of Gel'd and Kusenko [23], values of -101.0 (±2.0) kcal/mole and 10.2 (±1.0) eu. are obtained from equations 14 and 15 for ΔH_{298}° and S_{298}° of NbO respectively. An uncertainty considerably higher than the precision of the experiments has been assigned to these values to reflect the possible shifts in equilibrium composition with temperature of the niobium and niobium oxides. Schick [14] selected a value of -97.7 (±2.0) kcal/mole for ΔH_{298}° of NbO and estimated S_{298}° of NbO to be 12.0 ± 1.5 eu. Schaefer and Liedmeier [25] recently obtained a value of -97.0 (±1.0) kcal/mole for ΔH_{298}° of NbO from combustion calorimetry. The comparison of the value for ΔH_{298}° of NbO obtained in this study with that obtained from calorimetric is not meant to imply equality of accuracy in ΔH_{298}°. However, when it is the Gibbs energy of the equilibrium phases at elevated temperatures that is of primary interest, the values obtained in this study are to be preferred over those deduced from thermochemical measurements.

It should be noted that the value of S_{298}° of NbO obtained in this study was determined by choosing the value which would give the best fit to the data for cells C, D and E. Using Schick's selected value (-97.7 kcal/mole) for ΔH_{298}° of NbO [14], one would calculate enthalpy terms for equations 14 and 15 which are 3.3 to 3.8 kcal less negative than those obtained in this

study. With the calculated enthalpy terms, a value of 13.0 (±0.5) eu. for S°_{298} of NbO would be required to obtain the Gibbs energy of formation values obtained in this study. However, a value of 13.0 eu. for S°_{298} of NbO would require the slopes of the Emf versus temperature lines of cells C, D and E to be opposite from that shown in Figure 1. This discrepancy between the calorimetric and equilibrium data could be caused by composition variations in the equilibrium phases. For example, the composition of NbO in equilibrium with niobium could vary significantly from the stoichiometric one. Although Brauer [9] in 1941 detected no significant homogeneity range in NbO, the VO phase exists between 44.5 and 54.5 atomic % oxygen [10]. The effect of the variation in composition of the niobium in equilibrium with NbO is discussed in section 4.4.

4.3 Gibbs Energy of Formation of Ta_2O_5

Subtracting equation 9 from equation 14, one obtains the following expression for ΔG°_f of Ta_2O_5 per gram atom of oxygen between 1050 and 1300° K:

$$\Delta G^{\circ}_f \text{ (cal)} = -96,320 + 19.44 \ T \tag{17}$$

The agreement between the values calculated from equation 17 and those tabulated in the literature [14, 24] is shown in Figure 2; they are in such excellent agreement that they appear as one line. Because the thermodynamic stability of Ta_2O_5 was obtained using equation 11, the agreement between the thermal and equilibrium data of Ta_2O_5 supports the Gibbs-energy-of-formation equation for NbO obtained in this study.

If one uses equation 15 instead of 14, one obtains values for ΔG°_f of Ta_2O_5 that are about 0.6 kcal per g-atom oxygen less negative than those

calculated from equation 17. However, the thermal data for Ta_2O_5 are well established, and their uncertainty is only ±0.1 kcal per g-atom oxygen. One also would expect excellent agreement between the thermal and high-temperature equilibrium data because the homogeneity range of Ta_2O_5 has been observed to be very limited [13].

4.4 Influence of the Solubility of Oxygen in Niobium and Tantalum

Between 1100 and 1300° K, the saturated-oxygen concentration in niobium varies from approximately 1.4 to 2.3 atomic % respectively [18]. Over the same temperature range, the oxygen concentration in tantalum in equilibrium with Ta_2O_5 increases from approximately 2.5 to 3.0 atomic % [19]. Assuming that the activity of oxygen in the metal obeys Henry's law, calculations were made to correct the measured data of cells D and E. The correction changes both the enthalpy and entropy terms in equations 7 and 9 because the saturated-oxygen concentration varies with temperature. However the correction is quite small. For example, when the correction is applied to the data from cell D, it alters equation 7 to:

$$\Delta G \text{ (cal)} = -14,160 + 4.0\ T \tag{18}$$

At 1200° K this changes the Gibbs energy of reaction III by only 90 calories.

Acknowledgements

The author wishes to express his appreciation to Professors Leo Brewer and Ralph Hultgren for their support and encouragement, and to Raymond Orr and K. K. Kelley for their helpful suggestions. He especially wishes to thank Stanley Ross for his aid in the experimental portion of the study. This work was done under the auspices of the U. S. Atomic Energy Commission.

References

[1] KIUKKOLA, K. and WAGNER, C., J. Electrochem. Soc. 104 (1957) 379/387.

[2] SCHMALZRIED, H., Z. Elektrochem. 66 (1962) 572.

[3] MARKIN, T. L., ROBERTS, L. E. J. and WALTER, A., in Thermodynamics of Nuclear Materials, International Atomic Energy Agency, Vienna (1962) 693-711.

[4] ALCOCK, C. B. and BELFORD, T. N., Trans. Faraday Soc. 60 (1964) 822/835.

[5] BELFORD, T. N. and ALCOCK, C. B., Trans. Faraday Soc. 61 (1965) 443/453.

[6] ALCOCK, C. B. and STEELE, B. C. H., in Science of Ceramics 2 (STEWART, G. H., ed.) The British Ceramic Society (1964) 397-406.

[7] STEELE, B. C. H. and ALCOCK, C. B., presented at the 93rd AIME Annual Meeting, February, 1964; to be published in Trans. Met. Soc. of AIME (1965).

[8] LAVRENT'EV, V. I., GERASIMOV, Y. I., and REZAKHINA, T. N., Dokl. Akad. Nauk SSSR 136 (1961) 1372.

[9] BRAUER, G., Z. Anorg. Chem. 248 (1941) 1/31.

[10] HANSEN, M. and ANDERKO, K., in Constitution of Binary Alloys, McGraw-Hill, New York (1958) 1067-1068.

[11] LAGERGREN, S. and MAGNELI, A., Acta. Chem. Scand. 6 (1952) 444/446.

[12] HOCH, M. and MATHUR, M., J. Am. Ceram. Soc. 45 (1962) 373.

[13] KOFSTAD, P., J. Electrochem. Soc. 109 (1962) 776/781.

[14] SCHICK, H. L., Thermodynamics of Certain Refractory Compounds, Fifth Progress Report, September 15, 1963, RAD-SR-63-183.

[15] KELLEY, K. K. and KING, E. G., U. S. Bur. Mines Bull. 592 (1961).

[16] KELLEY, K. K., U. S. Bur. Mines Bull. 584 (1960).

[17] KING, E. G. and CHRISTENSEN, A. U., U. S. Bur. Mines R. I. 5789 (1961).

[18] GEBHARDT, E. and ROTHENBACHER, R., Z. Metallkde. 54 (1963) 623/630.

[19] GEBHARDT, E. and SEGHEZZI, H. D., Z. Metallkde. 50 (1959) 521/527.

[20] WORRELL, W. L., J. Phys. Chem. 68 (1964) 952/953.

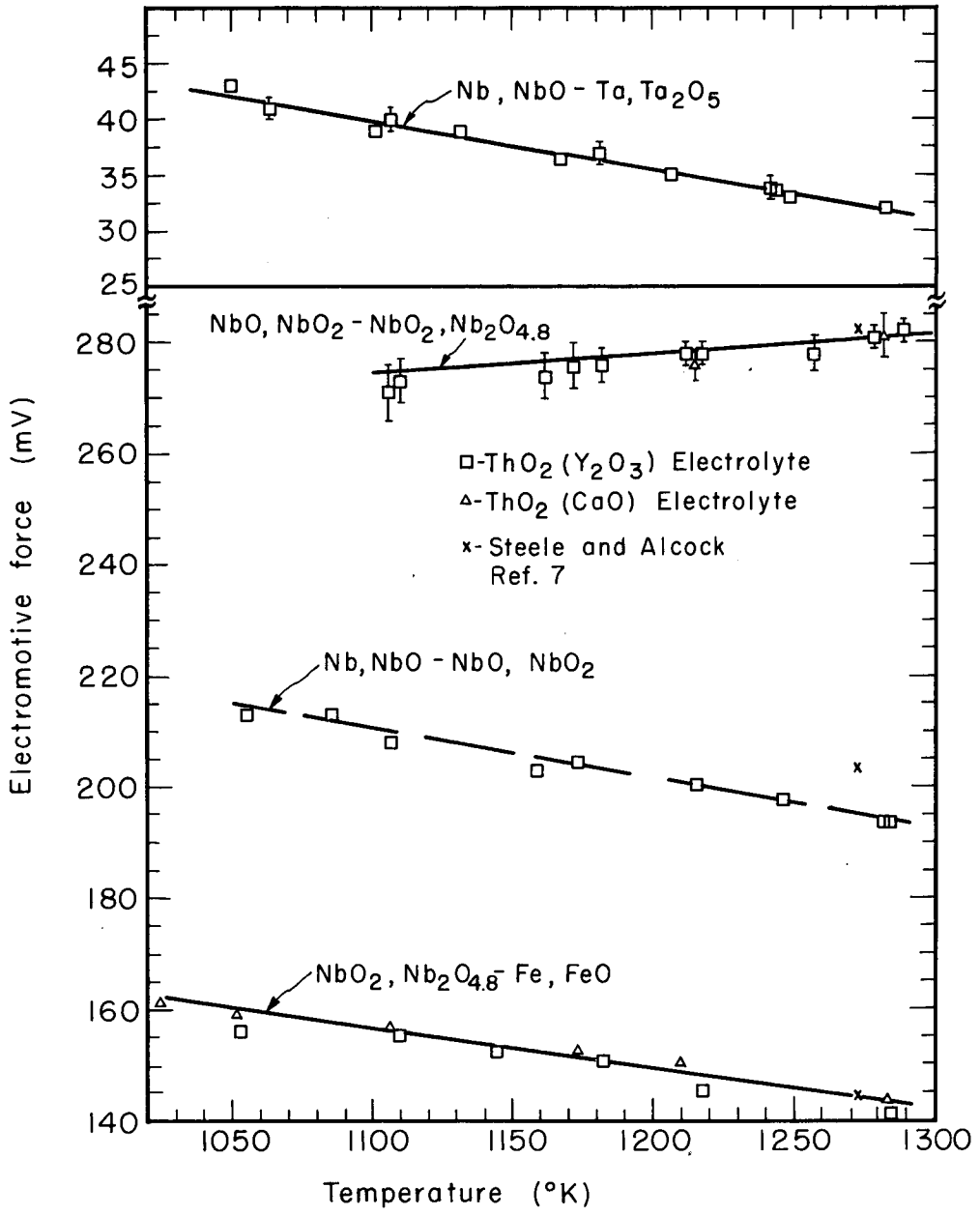
[21] BLUMENTHAL, R. N. and WHITMORE, D. H., J. Am. Ceram. Soc. 44 (1961) 508/512.

[22] ELLIOTT, R. P., Trans. Am. Soc. Metals 52 (1960) 990/1014.

[23] GEL'D, P. V. and KUSENKO, F. G., Izv. Akad. Nauk SSSR O. T. N. Met. i Top., No. 2, (1960) 79/86.

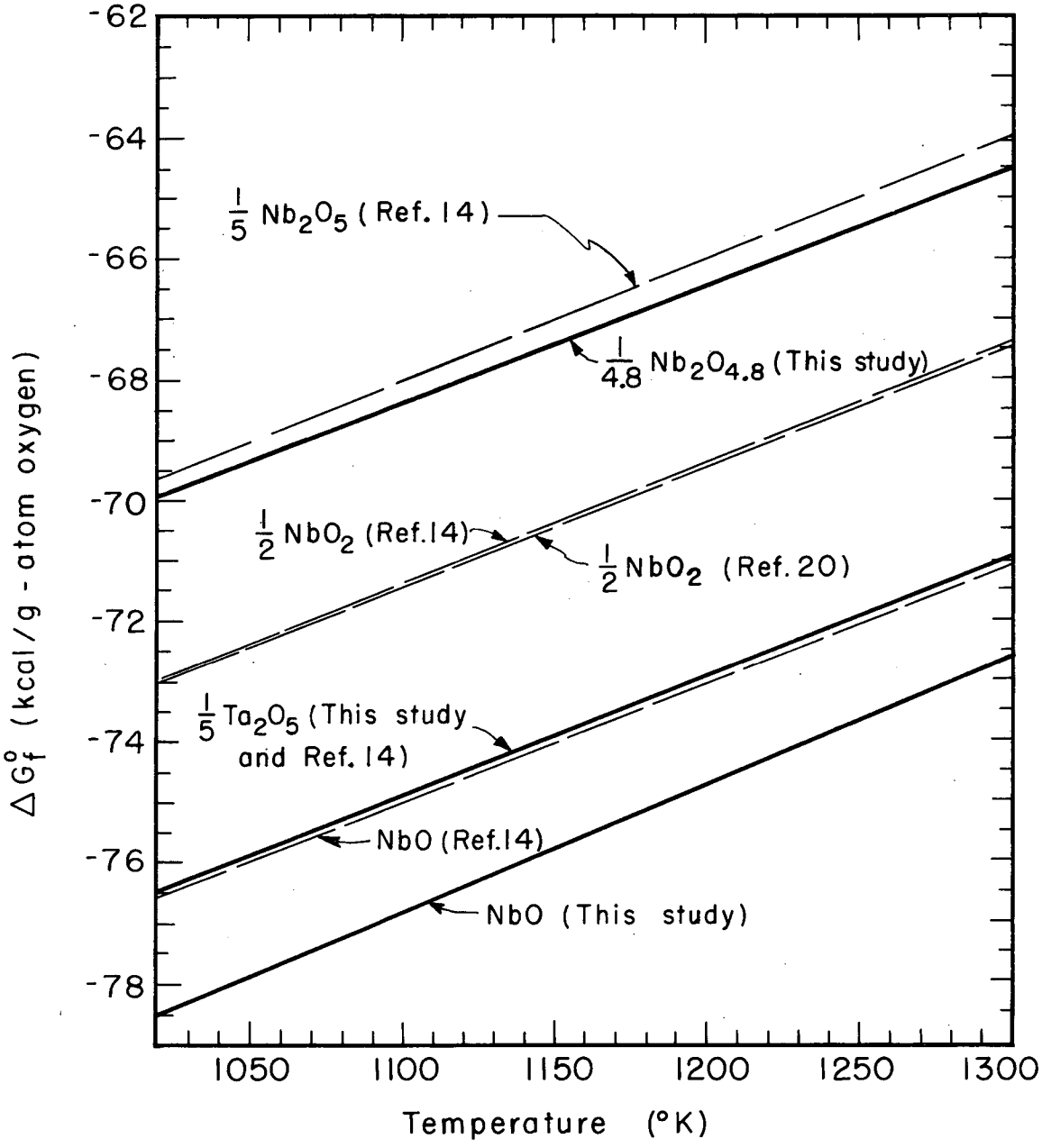
[24] ELLIOTT, J. F. and GLEISER, M. in Thermochemistry for Steelmaking 1, Addison-Wesley, Reading, Mass. (1960) p. 203.

[25] SCHAEFER, H. and LIEDMEIER, F., Z. Anorg. Chem. 329 (1964) 225.



MUB-6660

Figure 1. Temperature Dependence of the Electromotive Force for the Galvanic Cells Investigated.



MUB-6661

Figure 2. Standard Gibbs Energy of Formation of the Niobium and Tantalum Oxides between 1020 and 1300° K.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

For IAEA-Symposium on Thermodynamics -
July 22-27, 1965 in Vienna, Austria

UCRL 11957 Abstra

Measurements of the Thermodynamic Stabilities of the Tantalum, Niobium, and Vanadium Oxides Using a High-Temperature Galvanic Cell

Wayne L. Worrell

Lecturer and Research Metallurgist, Department of Mineral Technology and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California

February 1965

A high-temperature galvanic cell using a thoria-based solid-oxide electrolyte has been constructed to measure the thermodynamic stability of some refractory-metal oxides. The electrolyte is a solid solution of ThO_2 (94 wt %) and Y_2O_3 (6 wt %) which remains an ionic conductor at lower oxygen activities and higher temperatures than the more commonly used zirconia-based electrolyte. Solid mixtures of either Ni-NiO or Fe-FeO have been used as standard electrodes.

Preliminary results with a Ta-Ta_2O_5 electrode suggest that the Gibbs energy of formation of Ta_2O_5 may be one kcal/gm. atom oxygen less negative than the presently accepted values. However, this difference could be attributed to a compositional variation in the Ta_2O_5 phase. The galvanic-cell data apply to the metal-saturated oxide, while the literature values are tabulated for the stoichiometric oxide.

The niobium-oxygen and vanadium-oxygen systems have also been investigated. With Nb-NbO and V-VO electrodes, slight drifts of the Emf with time were observed, indicating the occurrence of electronic conductivity in the thoria-based electrolyte.

The thermodynamic stabilities of the Group Va metal oxides are critically summarized by correlating the galvanic-cell results with previous thermodynamic data and the appropriate phase diagrams.