Electrochemical Determination of the Free Energy of Formation of Tantalum Oxide

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As it has been demonstrated by many authors, the determination of the thermodynamic stability of metal-oxygen systems may be performed by electromotive force measurements across all-solid galvanic chains[1]. The electrolyte, consisting of a highly defective solid solution of refractory oxides, must exhibit a pure ionic conductivity in order to avoid the establishment of both junction potentials and irreversible polarization phenomena.

The cell under investigation was:

$$\text{Pt} \mid \text{Ta}+\text{Ta}_2\text{O}_5 \mid \text{ThO}_2(+15\ \text{Mol-\%}\ \text{La}_2\text{O}_3) \mid \text{Fe}+\text{“FeO”} \mid \text{Pt}$$

"FeO" indicating the iron-defective, iron monoxide-wüstite phase in equilibrium with iron.

Provided that the above-mentioned condition be satisfied, the e.m.f. developed at the ends of this cell yields directly, by means of the basic Nernst relationship, the difference between the partial molar free energies of oxygen in equilibrium with the electrode systems.

The virtual electrochemical reactions are:

$$2\,\text{Ta}+5\,\text{O}^{--} \rightleftarrows \text{Ta}_2\text{O}_5+10\,\Theta\,,$$
$$5\,\text{“FeO”}+10\,\Theta \rightleftarrows 5\,\text{Fe}+5\,\text{O}^{--}\,,$$

and the total process is:

$$2\,\text{Ta}+5\,\text{“FeO”} \rightleftarrows 5\text{Fe}+\text{Ta}_2\text{O}_5\,.$$

Neglecting the solubility of oxygen in the metal phases, i. e. considering the metal phases as pure phases, it is possible to write:

$$\mu_{\text{O}_2,\text{Ta}_2\text{O}_5}-\mu_{\text{O}_2,\text{“FeO”}}=\tfrac{2}{5}\,\Delta G^0{}_{f,\text{Ta}_2\text{O}_5}-2\,\Delta G^0{}_{f,\text{“FeO”}}=-4\,F\,E \qquad (1)$$

where μ_{O_2}'s are the partial free energies (Gibbs potentials) of oxygen in equilibrium with metal + metal oxide systems, $\Delta G^0{}_{f,\text{Ta}_2\text{O}_5}$ the standard molar free energy of formation from the elements of Ta_2O_5, $\Delta G^0{}_{f,\text{“FeO”}}$ the standard free energy of formation of wüstite per atom of oxygen and E the e.m.f. values, as measured from the right to the left.

The solid components of the galvanic chain are pellets of 12 mm diameter and 3 – 4 mm thick. They were laid one upon the other in an alumina crucible, placed in a silica tube, as shown in a previous work[2]. Around the crucible a sheet of zirconium was wound in order to getter the residual oxygen surrounding the cell. The measuring and recording apparatus was described previously[2].

The iron + iron oxide pellets were prepared by thoroughly blending very fine powders of Fe and Fe_2O_3 in such a ratio as to get a final composition of about 25 at.-% of oxygen, pressing in a die and then annealing overnight under vacuum at 1000 °C. Analogously, tantalum + tantalum oxide pellets were sintered after blending extremely fine (25 000 mesh/cm^2) component powders in such a ratio as to get a 20 at.-% oxygen composition. The preparation of the intermediate electrolyte pellets was described elsewhere[3].

The experimental results are reported in the following table:

	Run No.	T (°K)	E (mV)
Cell No. 1	1	1275	585,2
	2	1276	586,8
	3	1221	592,2
	4	1183	596,3
	5	1125	600,5
	6	1079	607,7
	7	1098	604,5
	8	1153	598,7
	9	1188	594,7
	10	1241	586,6
	11	1210	591,5
	12	1168	596,7
Cell No. 2	13	1272	585,9
	14	1080	605,2
Cell No. 3	15	1232	587,1

Table 1.

The results are reproducible and the e.m.f. values are stable over many hours. The complete stabilization of the e.m.f. after changing the running temperature takes a time ranging between 10′ and one hour, depending on the temperature itself. Run No. 1 of cell No. 1 was obtained with a non-stationary technique after polarization, a technique developed by the author some years ago[4]. During this run the residual oxygen pressure in the cell was higher than the oxygen pressures of the other runs because the zirconium getter was not placed into the cell. Anyway the e.m.f. value is comparable with the others since the equivalence of the stationary and the non-stationary methods has been demonstrated[2].

The E vs. T function has been approximated by a straight line (reported in Fig. 1), and the following equation has been calculated using the least squares method:

$$E\,(\text{mV}) = 723{,}6 - 0{,}1087\,T\,(^\circ\text{K})\,. \qquad (2)$$

The standard deviation results as ± 1.27 mV.

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[1] An exhaustive review of the entire subject has been done by B. C. H. STEELE, Proc. Symp. Nuffield Res. Group, Imperial College London 1967 (Publ. by the Inst. of Mining and Metallurgy).

[2] G. B. BARBI, Z. Naturforsch. **23 a**, 800 [1968].

[3] G. B. BARBI, Z. Naturforsch. **24 a**, 1580 [1969].

[4] G. B. BARBI, Trans. Faraday Soc. **62**, 1589 [1966].

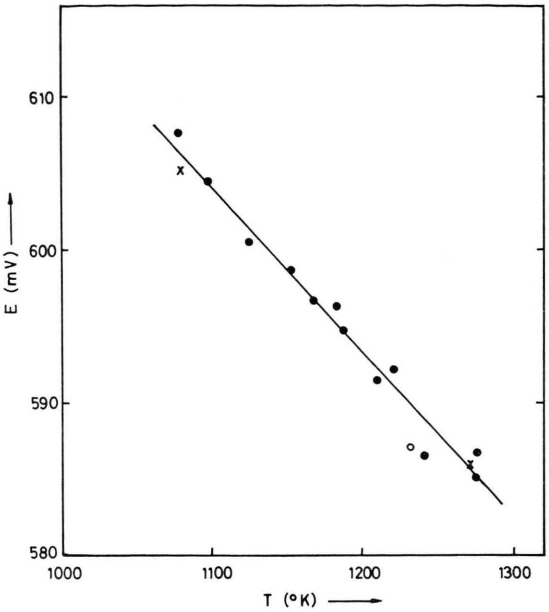

Fig. 1. Electromotive force vs. temperature of the electrochemical cell:

$$\text{Pt} \mid \text{Ta}+\text{Ta}_2\text{O}_5 \mid \text{ThO}_2(+\text{La}_2\text{O}_3) \mid \text{Fe}+\text{“FeO”} \mid \text{Pt}\,.$$

The recently reported JANAF data[5] have been taken into account for calculating the $\Delta G^0{}_{f,\text{“FeO”}}$ vs. T function. This function, in the range 1000 – 1300 °K, may be fairly well approximated by the linear relationship:

$$\Delta G^0{}_{f,\text{“FeO”}} = -63.25 + 15.56 \cdot 10^{-3}\, T \text{ kcal/atom of oxygen.} \qquad (3)$$

Substituting Equations (2) and (3) in Eq. (1), yields ($F = 23.06$ kcal·Volt^{-1}·equiv.$^{-1}$):

$$\frac{\Delta G^0{}_{f,\text{Ta}_2\text{O}_5}}{5} = -96.62 + 20.57 \cdot 10^{-3}\, T \text{ kcal/atom of oxygen.}$$

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[5] JANAF Thermochemical Tables Addendum PB 168 370/1 (Clearinghouse 1966).

The Temperature Dependence of Far Infra-red Absorptions in Non-polar Liquids

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Recent measurements[1] of non-polar liquids in the far infra-red have confirmed the expectations of Poley[2] and Whiffen[3] by showing the presence of a distinct absorption. The possible origins of the absorption have already been discussed[4, 5]. To add some new data we have measured the temperature dependence of the infrared absorption in the range 10 – 100 cm^{-1} for three non-polar liquids: C_6H_6, CS_2 and CCl_4.

All spectra were recorded on a Fourier spectrophotometer with a RIIC variable temperature cell.

The three characteristic features of the measurements are (Figs, 1 – 3 and Table 1):

1. The ratios of the integrated absorption intensities of $C_6H_6 : CS_2 : CCl_4$ are 1 : 0.75 : 0.36.
2. There is an increase of the integrated absorption intensity with the decrease of temperature.
3. The bands shift to higher frequencies with increasing temperature.

The integrated absorption intensities depend on the moments of inertia and the observed trend suggests the rotational origin of these bands. This statement has to

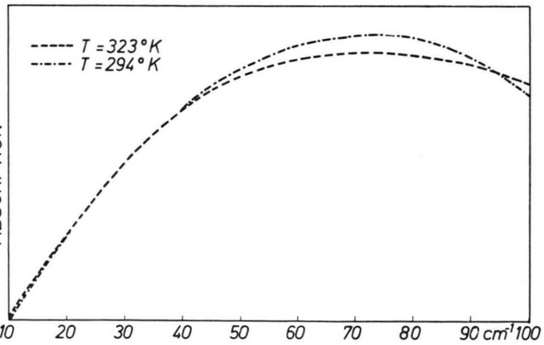

Fig. 1. The effect of the temperature on the absorption of C_6H_6.

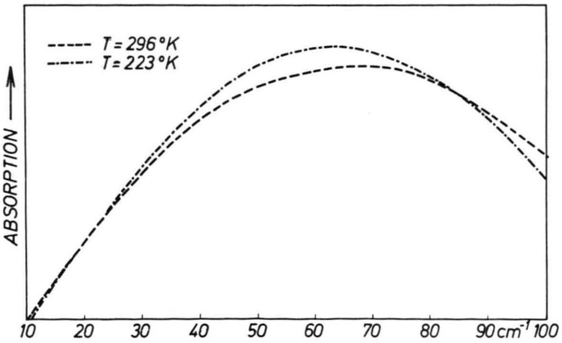

Fig. 2. The effect of the temperature on the absorption of CS_2.

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[1] S. K. Garg, J. E. Bertie, H. Klip, and C. P. Smyth, J. Chem. Phys. **49**, 2551 [1968] and references therein.

[2] J. Ph. Poley, J. Appl. Sci. B **4**, 337 [1955].

[3] D. H. Whiffen, Trans. Faraday Soc. **45**, 124 [1949].

[4] N. E. Hill, Chem. Phys. Letters **2**, 5 [1968].

[5] J. Chamberlain, Chem. Phys. Letters **2**, 464 [1968].