

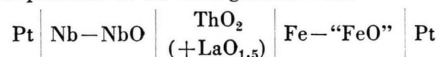
Non-Stationary E. M. F. Measurements after Polarization of Solid Galvanic Cells. The Stability of NbO

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The open-circuit electrical potential of the solid galvanic cell:



was measured between 1000 and 1400 °K.

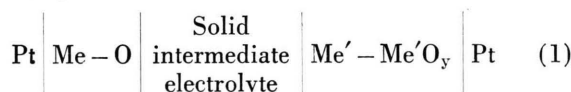
The measurements were carried out both in stationary and in non-stationary conditions after cathodic polarization of the Nb—NbO electrode, recording the e. m. f. decay curves.

A comparison between the two sets of results was made and the conditions which assure the reliability of the tensiometric measurements under non-stationary technique were stated.

The standard free energy of formation of niobium monoxide was then calculated from the experimental data.

The discrepancies with the literature values of the standard enthalpy and entropy of formation were interpreted in terms of a significant homogeneity field of stability of the NbO phase.

In order to determine the oxygen chemical potential of a metal-oxygen system, many Investigators carried out measurements of the open-circuit electrical potential of cells:



where Me'—Me'O_y is a biphasic metal-oxygen system whose oxygen chemical potential is known. The intermediate electrolyte consists of a solid solution of refractory metal oxides of different valence and shows a pure oxygen-ion electrical conductivity¹⁻¹⁰.

Nevertheless, the measurements are affected by some limitations, mainly:

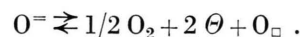
1) It is possible that the actual composition of the metal-oxygen systems at the interfaces with the intermediate electrolyte is different from that of the bulks;

2) The pure ionic conductivity of the electrolyte is assured only within a certain range of oxygen

partial pressure in the cell and, out of this range, mixed conduction occurs.

The first limitation is due to the fact that the cell lies in a gaseous atmosphere having an oxygen pressure different from those corresponding to the thermodynamic equilibrium with the systems; so, a gradient of oxygen activity may exist in these systems between the external surfaces in contact with the gas phase and the bulk. How such gradients affect the measurements was described elsewhere¹¹; in brief, the influence of such surface layer effects on e. m. f. depends on the rates of the interdiffusion processes through the layer.

The second limitation was extensively studied by many authors¹²⁻¹⁵ for several solid solutions of refractory metal oxides. At very low oxygen partial pressure a remarkable electronic conductivity takes place due to the shifting versus the right hand side of the equilibrium:



¹ U. CROATTO and C. BRUNO, Ric. Sci. Ric. **17**, 1998 [1947].

² K. KIVUKKOLA and C. WAGNER, J. Electrochem. Soc. **104**, 379 [1957].

³ K. KIVUKKOLA and C. WAGNER, J. Electrochem. Soc. **104**, 308 [1957].

⁴ S. ARONSON and J. BELLE, J. Chem. Phys. **29**, 151 [1958].

⁵ S. ARONSON and J. C. CLAYTON, J. Chem. Phys. **32**, 749 [1960].

⁶ G. B. BARBI, J. Phys. Chem. **68**, 2912 [1964].

⁷ R. N. BLUMENTHAL and D. H. WHITMORE, J. Amer. Cer. Soc. **44**, 508 [1961].

⁸ T. N. REZUKHINA et al., Zhur. Fiz. Khim. **35**, 1367 [1961].

⁹ H. SCHMALZRIED, Z. Phys. Chem. NF **25**, 178 [1960].

¹⁰ G. B. BARBI, Ann. Chim. **56**, 992 [1966].

¹¹ J. WEISSBART and R. RUKA, Rev. Sci. Instrum. **32**, 593 [1961].

¹² N. J. BRIDGER and W. A. DENNE, AERE-R 4329 [1963].

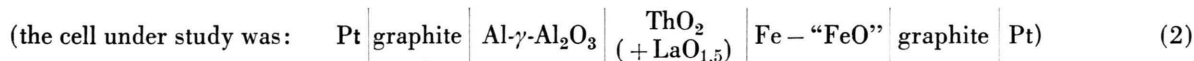
¹³ S. F. PAL'GUEV and A. D. NEUMIN, Trans. Inst. Electrochem. USSR, Vol. 1 (Transl. Cons. Bur. Entrpr.), p. 90—96 [1960].

¹⁴ H. SCHMALZRIED, Z. Electrochem. **66**, 572 [1962].

¹⁵ B. C. STEELE and C. B. ALCOCK, Trans. Met. Soc. AIME **233**, 1359 [1965].



Nevertheless, in a previous work¹⁶, in order to measure the extremely low oxygen pressures in equilibrium with some metals



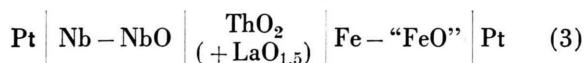
a non-stationary e. m. f. measurement method was developed which allows to work at rather high oxygen partial pressures of the gas phase, well compatible with the anionic conductivity requisite of the electrolyte.

As a matter of fact, the actual residual oxygen pressure is often higher than those in equilibrium with the systems at the ends of the chain; then, if the aforementioned interdiffusion processes are not fast enough, oxidation products grow at the ternary boundaries metallic systems / ceramic electrolyte / gas phase and then diffuse tangentially onto the whole interfaces metallic systems/intermediate electrolyte.

The method consists in removing these oxidation products by means of cathodic reduction; of course, at the anodic interface oxidation products are developed but if the rates of the diffusion processes are high, after the polarizing current has been cut off, the original system is rapidly restored. From this time onwards the counterelectrode starts to behave as oxygen reference electrode and the e. m. f. *E* vs. time curve reflects the situation of the oxygen chemical potential at the other interface. The operating conditions for the cells are better the larger is the difference between the rates of the diffusion processes at the two interfaces.

In short, it is possible to say that in a cell working in nonstationary conditions, the aforesaid limitations may be overcome; moreover, the slowness of the interdiffusion processes at the Me-O electrode surface layer could bring some advantages since it would allow a good separability and characterization of the anodic and cathodic contributions to the trend of the e. m. f. vs. time decay curves.

The e. m. f. of the cell



was measured both in stationary and in nonstationary conditions in order 1) to compare the results

and then to evaluate the reliability of the non-stationary technique and 2) to obtain the thermodynamic functions of NbO, since the values determined by others^{15, 17, 18} are somewhat discordant.

Apparatus and Materials

The solid components of the cell were pellets of 12 mm diameter and 3–4 mm thick. The preparation of the Fe-“FeO” and ThO₂(+LaO_{1.5}) pellets was described elsewhere¹⁶ but, for thorium tablets, the final firing was done at 1600 °C for two hours under vacuum; they were subsequently annealed in air at 1200 °C for 15 hours.

The niobium-niobium monoxide pellets were prepared by sieving niobium and niobium pentoxide powders (purity better than 99.9%) at 25,000 mesh per cm². The powders were thoroughly blended in a ratio corresponding to about 20 mol% of NbO and then pressed at 5 tons/cm². They were heated under vacuum at 1200 °C for one hour, fired at 1600 °C for four hours and slowly cooled. The X-ray diffraction patterns showed the pellets to contain only Nb and NbO.

All the tablets were polished with fine diamond paste and assembled in the cell as shown in Fig. 1.

A device allowed pure oxygen to pass from a reservoir at ≈1 mm Hg pressure into the cell. The adjustment of the oxygen transfer was such that a dynamic vacuum ranging between 5 × 10⁻⁶ and 2 × 10⁻⁴ mm Hg, as indicated by a Penning gauge placed at the upper side of the cell (values corrected for thermal transpiration), was maintained. It is worth while to note that such a gauge can not give any indication of the oxygen pressure on the surroundings of the galvanic chain at the lowest pressures, while at the higher pressures its indications are only very rough.

The pellets were held in contact with one another by the weight of the upper silica electrode holder which contains also the Pt-Rh/Pt thermocouple.

¹⁶ G. B. BARBI, Trans. Faraday Soc. **62**, 1589 [1966].

¹⁷ V. I. LAVRENT'EV and Y. I. GERASSIMOV, Dokl. Akad. Nauk. SSSR **136**, 1372 [1961].

¹⁸ W. L. WORRELL, Symp. on Thermodynamics and Transport Properties in Solids, IAEA Vienna 1965, SM 66/66.

The whole cell was placed in an oxidation-resistant steel tube.

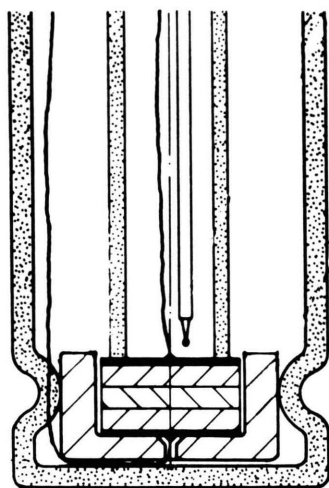


Fig. 1. The electrochemical cell (detail).

The polarizing current was supplied by a Metrohm Mod. E211 constant current generator. After polarization, a switch shifted the cell from the generator to the Keithley Mod. 610R electrometer. An e. m. f. generator can be put in opposition to the cell in order either to permit an expansion of the scale range of the electrometer or to use it as a null detector. This generator was calibrated by a potentiometer and the calibration checked frequently. The e. m. f. E vs. time t curves were recorded.

Results and Discussion

E. m. f. measurements in stationary conditions

In our operative conditions the residual oxygen pressure, even at the highest vacuum, was still so high that it could not be counterbalanced by the niobium diffusion from the bulk to the surface; then, mixed potentials would be measured. So, the method of gettering the residual oxygen in the surroundings of the galvanic cell was adopted, wrapping a zirconium foil around the alumina crucible containing the pellets.

In this way stable and reproducible e. m. f. values were obtained. The straight line equation:

$$E(\text{mV}) = -804.6 + 0.144 T \text{ (}^\circ\text{K)} \quad \text{I}$$

fits well with the experimental data and is plotted in Fig. 2.

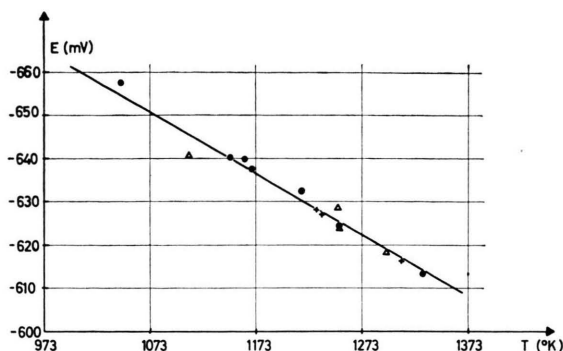
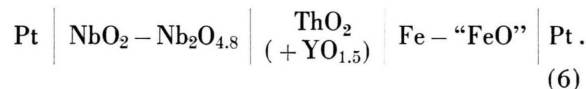
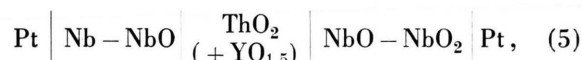
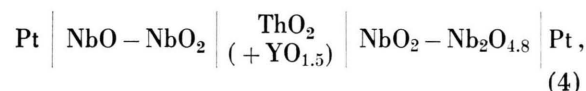


Fig. 2. Measurements in stationary conditions — E. m. f. values at various temperatures for cell [3] (different symbols refer to different runs).

The results agree poorly with those of LAVRENT'EV and coworkers¹⁷, better with those of STEELE and ALCOCK¹⁵. They agree with the WORRELL data¹⁸ as they result from the summation of e. m. f. vs. temperature curves of the cells:



E. m. f. measurements in non-stationary conditions

In this case a current of constant intensity was made to flow through the cell in order to reduce the surface niobium oxidation products. After switching off the current ($t = t_0$), E decay was recorded.

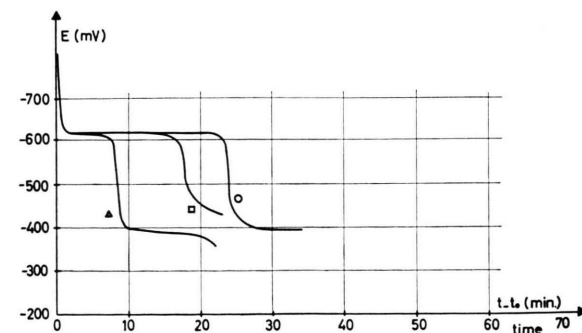


Fig. 3. E. m. f. vs. time decay curves at 1287 °K of one cell after polarization:

- 0.3 mA × 10 sec (measured vacuum 1×10^{-5} mmHg),
- △ 0.3 mA × 10 sec (measured vacuum 1.5×10^{-4} mmHg),
- 0.3 mA × 30 sec (measured vacuum 1.5×10^{-4} mmHg).

The curves (Fig. 3) show, in order of occurrence, a rapid initial decay, a very constant rest-potential followed by a second steep drop. At the flat portion of the curve only the phases Nb and NbO coexist.

In fact, let us hypothesize that the corresponding E value would be a mixed potential due to the presence, at the interface with thoria, of other systems (e.g. NbO–NbO₂ or NbO not in equilibrium with the metal) too. In this case, owing to the uptake of oxygen from the gas, the global oxygen content at the interface increases since it is not completely compensated by the metal diffusion from the bulk, as the curves, after some time, well decay. Hence, the ratio of the interface where the more oxidized systems should be present to that pertaining to the system Nb–NbO should increase. The potential of the semicell is given by the contributions of the local potentials at all points of the interface and thus, increasing the aforementioned ratio, a gradual decrease of e. m. f. should take place.

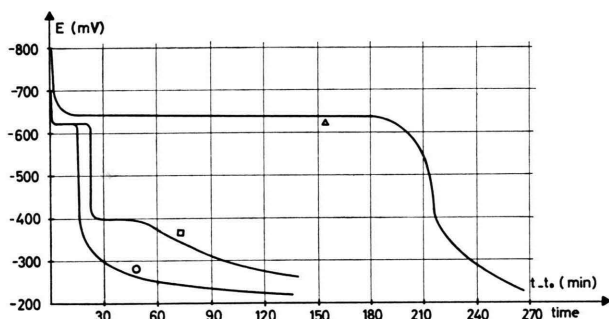


Fig. 4. E. m. f. decay curves of a cell after polarization:

- 0.3 mA × 10 sec; $T = 1287^{\circ}\text{K}$,
- 0.3 mA × 10 sec; $T = 1287^{\circ}\text{K}$,
- △ 0.3 mA × 10 sec; $T = 1127^{\circ}\text{K}$.

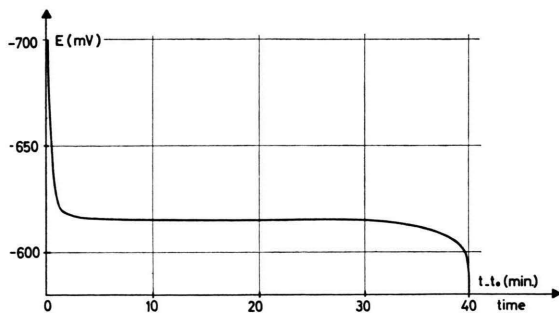


Fig. 5. E. m. f. decay curve of a cell after polarization
1 mA × 30 sec at $T = 1330^{\circ}\text{K}$.

But Fig. 4 and 5 show that this hypothesis is unrealistic since the e. m. f. remained extremely constant also for very long time (in some cases more than two hours within ± 2 mV). It is possible then to infer that, practically, the global process of oxidation of the surface takes place at the expense of the metal phase or, even a higher oxide would form, it rapidly diffuses and is readily reduced by the metal to the lower-oxygen-boundary NbO, so that its stationary amount at the interface remains negligible. This situation lasts as long as metal phase exists at the interface and then E drops rapidly until a second rest-potential, either sharp or ill-defined, is sometimes reached at -380 to -420 mV. The occurrence of this second rest-potential depends on the temperature and the residual pressure in the cell, but the pressure data are too rough to allow a treatment of the subject. It seems probable that it represent the formation of NbO₂ phase¹⁹ and then the presence of the NbO–NbO₂ biphasic system at the thoria interface; the Worrell data for the cells (4) and (6) seem to confirm this supposition.

In Fig. 6 the values of the first rest potential are plotted vs. temperature. They can be expressed by the equation

$$E(\text{mV}) = -797.7 + 0.140 T (^{\circ}\text{K}) \quad \text{II}$$

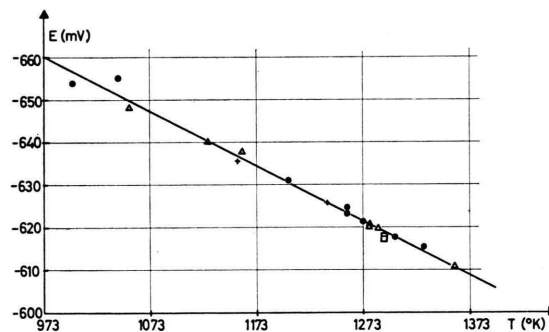


Fig. 6. Measurements in non-stationary conditions. First plateau electrical potential values vs. temperature (different symbols refer to different runs).

The length of the horizontal portion of the decay curves, at constant temperature, measured vacuum and polarization current, was found to be roughly proportional to the polarization time; furthermore, it decreases as the temperature and measured pressure increase²⁰.

¹⁹ H. INOUE, Proc. Symp. Columbium Metallurgy — Metall. Soc. Conf. N° 10 — Interscience Publ., London 1900, p. 649–665.

²⁰ These results refer to the behaviour of a single cell and cannot be compared with other cells since no reproducibility of the contact between Nb–NbO and thoria could be achieved (differences in the apparent surface of contact, in flatness, smoothness etc.).

Both sets of experimental data, as expressed by Eqs. I and II, show a close agreement, in any case better than those obtained by the aforementioned Authors with the same stationary method and allow to consider the non-stationary technique as a reliable tool for the determination of the thermodynamic functions as far as the horizontality of the rest-potential portion of the decay curves is such to exclude the occurrence of mixed potentials.

The stability of NbO

The E vs. T function, averaged from Eqs. I and II:

$$E(\text{mV}) = -800.6 + 0.142 T \text{ (}^\circ\text{K)}$$

may be introduced into the fundamental equation:

$$(\mu_{\text{O}_2, \text{Nb-NbO}} - \mu_{\text{O}_2}^\circ) - (\mu_{\text{O}_2, \text{Fe-FeO}} - \mu_{\text{O}_2}^\circ) = 4FE \quad (4)$$

where μ_{O_2} are the Gibbs chemical potentials of oxygen in equilibrium with the respective systems and $\mu_{\text{O}_2}^\circ$ is the chemical potential of oxygen at 760 mm Hg.

Taking the recent thermodynamic data for the standard (Gibbs) free energy of formation of ferrous oxide²¹ in the interval 1000–1400 $^\circ\text{K}$, we get ($F = 23.060 \text{ kcal} \cdot \text{Volt}^{-1} \cdot \text{g} \cdot \text{equiv}^{-1}$):

$$\mu_{\text{O}_2, \text{Nb-NbO}} - \mu_{\text{O}_2}^\circ \quad (5)$$

$$= -200.47 + 0.04424 T \text{ kcal/mole of oxygen.}$$

Neglecting the oxygen solubility in niobium²², as a first order approximation, the standard molar free energy of formation of NbO results as:

$$\Delta G_{\text{NbO}}^\circ = -100.2 + 0.0221 T \text{ kcal/mole.} \quad (6)$$

Our $\Delta G_{\text{NbO}}^\circ$ values in the range 1000–1400 $^\circ\text{K}$ show a fair agreement with other data²³ but the entropic and enthalpic terms disagree, since our value of the standard entropy of formation results to be about 5 e. u. more negative than that calculated from the standard entropies of the elements and of NbO; correspondingly, the standard enthalpy of

formation at 298 $^\circ\text{K}$ is about 3 kcal higher than the value obtained by others^{23–25}.

In order to explain these discrepancies we have to remind that the entropy of formation of metal oxides of stoichiometric composition generally lies between -42 and $-46 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mole of oxygen}^{-1}$, in close agreement with the present data. But, as the phase has an oxygen-excess homogeneity field of stability, the process of incorporation of oxygen to lead to an oxygen richer composition is accompanied by an increase of valence electronic disorder and configurational defect disorder²⁶; as a consequence, the entropy of formation becomes less negative (as, for instance, the phase wüstite).

All the calorimetric measurements (as, for instance²⁷) and equilibration experiments at different temperatures could be affected by errors due to the fact that they involve dynamic processes whose significant kinetic parameters cannot assure the composition of the oxide to be exactly that corresponding to the lower oxygen boundary and to be the same in the whole system.

On the contrary, when we obtain the entropy of formation by e.m.f. measurements, this value is more reliable because in the *infinitesimal* process at the interface with the intermediate electrolyte the composition and the structure disorder is not changed and a perfect, long-time equilibrium of the oxide phase with the metal is attained²⁸.

From the above considerations we hypothesize:

1) Since the number of vacant sites in both niobium and oxygen sublattices is high, the experimental very negative value of the standard entropy of formation in the whole 1000 to 1400 $^\circ\text{K}$ interval to be accounted for a low oxygen boundary structure with a low valence disorder and in which the defects tend to arrange in ordered substructures;

2) The increase, as temperature increases, of the discrepancies with the literature data of the standard entropy of formation of NbO to be due to a non negligible homogeneity range of the NbO phase.

²¹ JANAF Thermochem. Tabl. Addendum PB 168 370–1 [1966] (Clearinghouse).

²² Oxygen has been found to dissolve in Nb (2.3 at.% at 1300 $^\circ\text{K}$) (E. GEBHART u. R. ROTHENBACHER, Z. Metallk. **54**, 623 [1963]), but the activity coefficient is not known. So, it is not possible to correct the oxygen potential data in order to calculate the exact values of the standard molar free energy of formation of NbO.

²³ A. GLASSNER, ANL 5750.

²⁴ H. L. SCHICK, RAD-SR-63-183 [1963].

²⁵ O. KUBASCHEWSKI and E. LL. EVANS, Metallurgical Thermochemistry, Pergamon Press, London 1958, p. 262.

²⁶ J. M. HONIG, A. F. CLIFFORD, and P. FAETH, Inorg. Chem. **2**, 791 [1963].

²⁷ H. SCHAEFER and F. LIDMEIER, Z. Anorg. Chem. **329**, 225 [1964].

²⁸ Actually the oxide, as soon as it forms by re-oxidation during the flat portion of the curve, could not be perfectly equilibrated with the metal; but if the rate of re-oxidation is small, the oxygen potential is practically determined by the preexisting excess NbO phase. In any case, the rate of the reoxidation, well below those of processes occurring during a calorimetric experiment, seems to justify, although not strictly, this statement.