THE EFFECT OF WATER VAPOUR ON THE BEHAVIOUR OF THE OXYGEN ELECTRODE IN MOLTEN NITRATES

By M. Fredericks* and R. B. Temple*

Abstract

Water vapour has been deliberately introduced into an oxygen gas electrode in an equimolar $NaNO_3$–KNO_3 melt at 300°. When this is done the slope of the line obtained for E_{cell} against $\log[O^{2-}]_{Total}$ changes from the $2 \cdot 303RT/2F$ obtained with dry oxygen to almost exactly $2 \cdot 303RT/F$. On discontinuing the passage of water vapour into the melt, the cell reverts to its original condition within 3 hr.

These experimental results are discussed theoretically. The results also yield a value of $3 \cdot 2 \times 10^{-2}$ for the equilibrium constant of the reaction

$$O^{2-} + H_2O = 2\,OH^-$$
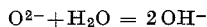
Introduction

In a previous paper,[1] we have demonstrated that in an equimolar $NaNO_3$–KNO_3 melt at 300°C the cell

$$Pt \mid O_2 \mid O^{2-}(melt) \mid Pyrex\ membrane \mid AgNO_3(1 \cdot 0m\ in\ melt) \mid Ag$$
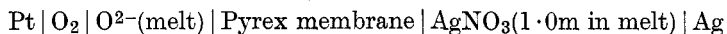
behaves as expected for the cell reaction

$$2Ag^+ + O^{2-} = 2Ag + \tfrac{1}{2}O_2 \tag{1}$$

That is to say, the slopes obtained for the plots of E_{cell} against $\log[O^{2-}]$ and $-\log p(O_2)^{1/2}$ do not differ in any instance by more than $2 \cdot 5\%$ from the value calculated for $2 \cdot 303RT/2F$, as expected from equation (1). The results also indicated that the concentration of O^{2-} produced in the melt by thermal decomposition of the solvent is very much smaller than the amounts of oxide ion added, under the experimental conditions employed.

These results were in complete agreement with those of Kust and Duke,[2] but were at variance with the earlier ones of Shams el Din and Gerges,[3] who reported that when they added KOH, Na_2O_2, or K_2O to a Pt/O_2 gas electrode in molten KNO_3 at 350°C, as a source of oxide ion, the results were indicative of a one-electron transfer at the electrode. For example these authors added Na_2O_2, assuming that the decomposition

$$O_2^{2-} \rightarrow O^{2-} + \tfrac{1}{2}O_2 \tag{2}$$
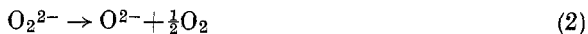
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[1] Fredericks, M., and Temple, R. B., *Inorg. Chem.*, 1972, **11**, 968.

[2] Kust, R. N., and Duke, F. R., *J. Am. chem. Soc.*, 1963, **85**, 3338.

[3] Shams el Din, A. M., and Gerges, A. A. A., Proc. 1st Australian Conf. Electrochem., 1963. (Ed. J. Friend.) (Pergamon: London 1964.)

would be complete. However, the resulting plot of E_{cell} against $\log[O_2^{2-}]_{Total}$ had a slope of $2 \cdot 303RT/F$ instead of the expected $2 \cdot 303RT/2F$. It should be noted that these authors show a figure for E_{cell} against $\log[O^{2-}]$ but the text of their paper makes it quite clear that what was plotted was really E_{cell} against $\log[O_2^{2-}]_{Total}$.

These authors very briefly discussed the possibility that this anomalous slope might be due to the presence of water in the melt, leading to the reaction

$$O^{2-} + H_2O = 2\,OH^- \tag{3}$$

In view of a recent statement,[4] that potentiometric results which appear to agree with the electrode reaction (1) are spurious and "probably caused by contamination reactions with traces of moisture and/or silica from container walls", we decided to examine the effect of deliberately introducing water vapour into our electrochemical cell.

If we make the initial assumption that the oxygen electrode continues to respond only to oxide ion in the presence of dissolved water, it is possible to predict the effect of adding water vapour to the cell.

As before, the expression for the e.m.f. of the cell at a constant partial pressure of oxygen (1 atm) will be

$$E_{cell} = E^{\circ\prime} + (RT/2F)\ln[O^{2-}] \tag{4}$$

where $E^{\circ\prime}$ contains not only the standard e.m.f. (E°), but also a term involving the partial pressure of oxygen. In addition we have the possible reaction

$$O^{2-} + H_2O = 2\,OH^- \tag{5}$$

for which we can write

$$K = [OH^-]^2/([H_2O][O^{2-}]) \tag{6}$$

to the extent at least that we can use concentration terms instead of activities.

From (4) and (6) at constant partial pressure of water vapour we obtain

$$E_{cell} = E^{\circ\prime\prime} - (RT/2F)\ln K + (RT/F)\ln[OH^-] \tag{7}$$

if we add K_2O as a source of oxide ion, we have

$$[O^{2-}]_T = \tfrac{1}{2}[OH^-] + [O^{2-}] \tag{8}$$

for the mass balance, where the subscript $_T$ indicates the total quantity added.

From (7) and (8) we then obtain the corresponding Nernst equation, namely

$$E_{cell} = E^{\circ\prime\prime}(RT/2F)\ln K + (RT/F)\ln 2 + (RT/F)\ln([O^{2-}]_T - [O^{2-}]) \tag{9}$$

and provided the hydroxide is not too greatly dissociated this reduces to

$$E_{cell} = E^{\circ\prime\prime\prime} + (RT/F)\ln[O^{2-}]_T \tag{10}$$

Alternatively, if O_2^{2-} is added as a source of oxide ion this can react according to

$$O_2^{2-} + H_2O = 2\,OH^- + \tfrac{1}{2}O_2 \tag{11}$$
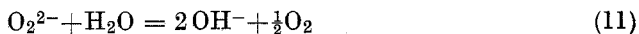
[4] Jordan, J., *J. electroanal. Chem.*, 1971, **29**, 128.

which will be virtually complete if sufficient water is present. In this case we can write for the concentration of hydroxyl ion

$$[OH^-] = \tfrac{1}{2}[O_2^{2-}]_T \tag{12}$$

since the oxygen that enters reaction (11) as H_2O can be regarded as being completely eliminated as molecular oxygen, so that (7) becomes

$$E_{cell} = E^{\circ\prime\prime\prime} + (RT/F)\ln\tfrac{1}{2} + (RT/F)\ln[O_2^{2-}]_T \tag{13}$$

Equations (10) and (13) are seen to be in agreement with the results reported by Shams el Din and Gerges.[3] A very similar result to (10) is obtained if KOH is added as a source of oxide ion. From the foregoing we can predict that if we introduce a sufficient partial pressure of water vapour into the oxygen entering our cell the slope of E_{cell} against $\ln[O^{2-}]_T$ should rise from the value of $RT/2F$, previously found, to double this value.

<div align="center">EXPERIMENTAL</div>

All chemicals used were Analytical Reagent grade. The potassium and sodium nitrates were purified by being recrystallized after boiling for 3 hr in distilled water adjusted to pH 4·5 with nitric acid. The crystals were dried at 190°C for 24 hr and cooled and stored under continuous vacuum.

The cell was a Pyrex tube 40 cm long by 7·5 cm diameter, fitted with water-cooled brass lid carrying the reference electrode, a platinum resistance thermometer, and the gas inlet, which was a glass spiral containing the platinized platinum foil forming the oxygen electrode.

The reference electrode was 99·999% pure Ag wire immersed in a 1·0m solution of $AgNO_3$ in the equimolar $(Na-K)NO_3$ melt. The junction was a thin Pyrex membrane whose d.c. resistance was approximately 1 MΩ. Potentials were measured with a Leeds & Northrup Type 8687 potentiometer. The temperature of the melt was kept at $300\pm0\cdot25°$ by means of a solid state proportional controller.

The oxygen used was carefully dried by being passed through Linde molecular sieve, and all gas-tubing not of glass was Tygon, as rubber and some other synthetic materials are known to be permeable to water vapour.

When required, water vapour was deliberately introduced into the gas stream in two ways. In the first, the previously dried oxygen was passed through a tube containing pink (water saturated) silica gel. In the second it was bubbled through water kept at constant temperature (20°C). In each case the water content of the resulting gas was measured by condensing the water in a trap cooled in alcohol–dry ice and weighing the amount collected over periods up to 5 hr. Both methods appeared to give partial pressures of water which remained reasonably constant when checked over 5 successive days. Using silica gel the calculated partial pressure of water was $(9\cdot9\pm0\cdot4)\times10^{-4}$ atm, while using liquid water it was $(7\cdot8\pm0\cdot1)\times10^{-3}$ atm. In two series of measurements made at these partial pressures, the e.m.f. of the cell was measured when sufficient oxide ion was added to the cell to produce a *total* oxide ion concentration between 6×10^{-7}m and 10^{-5}m. The oxide ion was added in the form of carefully dried Na_2CO_3 as suggested by Kust.[5]

<div align="center">RESULTS AND DISCUSSION</div>

Figure 1 shows the relation which we have observed between E_{cell} and $\log[O^{2-}]_{Total}$ in the presence of 1 atm of dry oxygen. Its slope is $0\cdot0555\pm0\cdot0003$ V, which should be compared to the theoretical value of $0\cdot05686$ V required for

[5] Kust, R. N., *J. chem. Phys.*, 1965, **69**, 3662.

$2 \cdot 303RT/2F$. It will be seen that it is sensibly linear down to about 6×10^{-7}m. We therefore believe that the concentration of residual oxide ion in our melt, produced from whatever cause, is less than this.
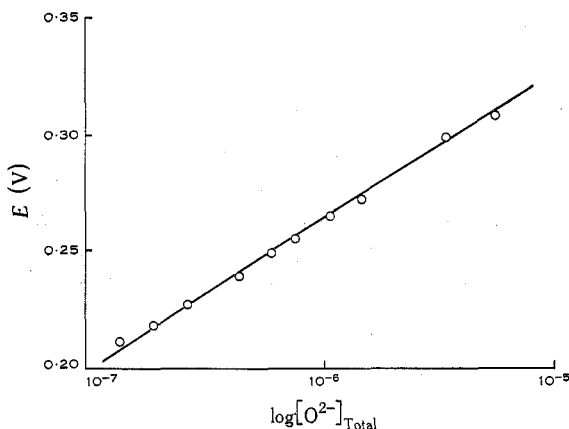

Fig. 1.—E_{cell} against $\log[O^{2-}]_{Total}$ in equimolar $NaNO_3$–KNO_3 at 300°C; $p(O_2)$ 1 atm.

When wet gas was passed into the dry melt, the e.m.f. fell and reached a new equilibrium value after 2–3 hr. If the dry gas was then once more bubbled through the melt, the e.m.f. rose to the initial value within 3 hr. This shows that if OH⁻ is formed according to reaction (5), this reaction is readily and completely reversible.

The results obtained at the two partial pressures are given in Figure 2 which shows E_{cell} plotted against $\log([O^{2-}]_T—[O^{2-}])$ (equation (9)).
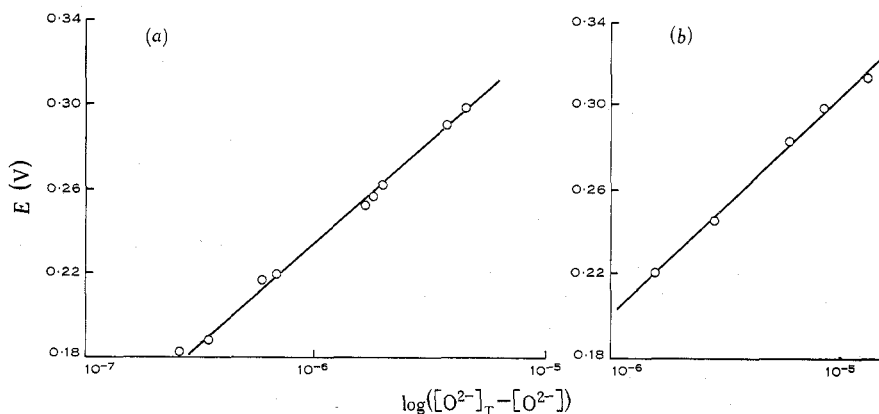

Fig. 2.—E_{cell} against $([O^{2-}]_T—[O^{2-}])$ in equimolar $NaNO_3$–KNO_3 at 300°C. (a) $9 \cdot 9 \times 10^{-4}$ atm H_2O; (b) $7 \cdot 8 \times 10^{-3}$ atm H_2O.

We chose to use this form of presentation since it seemed that K might not be as large as hitherto expected. In computing the logarithmic term we made the reasonable assumption that the equilibrium values of $[O^{2-}]$ present when water vapour is passed into the melt can be read from Figure 1 obtained in the dry melt.

At the lower partial pressure of water vapour, the slope yielded a value of $1 \cdot 22 \pm 0 \cdot 08$ for n in $2 \cdot 303 RT/nF$, while at the higher pressure $n = 1 \cdot 02 \pm 0 \cdot 04$. These values appear to be in satisfactory agreement with the theory developed above, especially at the higher concentration of water in the melt. They afford good support for the view that the unexpectedly high slopes observed by Shams el Din and Gerges[3] were caused by the accidental introduction of water.

At the same time we believe that these results are incompatible with the view that apparent two-electron slopes are caused by contamination with water vapour or silica from the cell walls.[4] It may perhaps be argued that the presence of water vapour will catalyse the decomposition of nitrate ion in the melt:

$$NO_3^- = NO_2^- + \tfrac{1}{2}O_2 \qquad\qquad (14)$$

since it has been noticed that water vapour increases the rate of decomposition of nitrates at temperatures between 560 and 800°C.[6] However, the presence of a catalyst cannot influence the position of an equilibrium such as (14). Furthermore, in the presence of excess oxygen at 1 atm pressure, we believe that this reaction will contribute negligible quantities of O^{2-} at 300°C and the linearity of Figure 1 appears to support this view.

It may also be suggested that the corrosion of the container walls will be increased in the presence of water vapour. We believe this factor also to be insignificant in these experiments because we found that when we ceased to inject water vapour into our melt, the e.m.f. rose within 3 hr to its former value. Any additional oxide ion dissolved from the container must therefore be negligible within experimental error. We might note in passing that it appears to be experimentally impossible to devise a cell in which the melt is completely out of contact with silicate materials. Even in the cell described by Zambonin[7] the melt is in contact with the boundary of the reference electrode.

Our results show how a two-electron slope can be turned into an apparent one-electron slope by the presence of sufficient moisture. We have so far been unable to devise an explanation for the converse effect. That is to say, we have not been able to show how the results of Kust and Duke[2] and of Fredericks and Temple[1] can be reconciled with a single-electron transfer at the electrode such as the reaction $O_2 + e = O_2^-$ proposed by Jordan.[4]

Estimate of K *for Reaction (5)*

It is possible to calculate K for reaction (5) from equation (9). When this is written in expanded form it becomes

$$E_{\text{cell}} = E^{\circ\prime} + (RT/2F)\ln K - (RT/2F)\ln[H_2O] + (RT/F)\ln 2 + (RT/F)\ln([O^{2-}]_T - [O^{2-}]) \quad (15)$$

where K for equation (5) is written in molal terms throughout and $E^{\circ\prime}$ has been published previously for this cell.[1] At 300° $E^{\circ\prime} = 0 \cdot 6173$ V. Using the solubility

[6] Freeman, E. S., *J. phys. Chem.*, 1956, **60**, 1487; *J. Am. chem. Soc.*, 1957, **79**, 838; see also Butkov, K., and Chassovenny, V., *Acta phys.-chim. URSS*, 1936, **5**, 137; Leschewski, K., *Ber. dt. chem. Ges.*, 1939, **72B**, 1763.

[7] Zambonin, P. G., *Analyt. Chem.*, 1969, **41**, 869.

figures for water in the melt given by Frame et al.,[8] it is possible to estimate the Henry's law constant for water vapour as $0 \cdot 368$ mol kg^{-1} atm^{-1}, and using our results for the higher partial pressure of water vapour, the values of K for equation (5) obtained from equation (15) are shown in Table 1.

TABLE 1

VALUES OF K FOR EQUATION (5)

E_{cell} (V)	$10^6([O^{2-}]_T - [O^{2-}])$ (mol kg^{-1})	$10^2 K_{(5)}$
$0 \cdot 2160$	$1 \cdot 506$	$2 \cdot 8$
$0 \cdot 2379$	$2 \cdot 753$	$3 \cdot 9$
$0 \cdot 2803$	$5 \cdot 476$	$2 \cdot 8$
$0 \cdot 2936$	$8 \cdot 117$	$2 \cdot 9$
$0 \cdot 3160$	$13 \cdot 01$	$3 \cdot 7$
		av. $3 \cdot 2$

This value is very much smaller than the value foreshadowed by Jordan et al.[9] but is in line with the unexpectedly high value found for the dissociation of CO_3^{2-} ion in the same melt by Kust.[5] To check the reversibility of equation (5) in our melt, we have in other experiments added OH$^-$ ion to the solvent in macroscopic quantities and have found that, under vacuum, a half-mole of water can be pumped off for each mole of hydroxide added.

[8] Frame, J. P., Rhodes, E., and Ubbelohde, A. R., Trans. Faraday Soc., 1961, 57, 1075.
[9] Jordan, J., McCarthy, W. B., and Zambonin, P. G., in "Molten Salts." (Ed. G. Mamantov.) (Marcel Dekker: New York 1969.)