PRELIMINARY NOTE

On the O_2 –O_2^- –O_2^{2-} – equilibrium in molten alkali nitrates with a graphite electrode

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In a current study on the possibility of an electrochemical separation of oxygen and nitrogen from air, involving the use of molten nitrate electrolytes, discrepancies were found in literature data concerning the superoxide/peroxide/oxygen disproportionation reaction in the fused sodium–potassium eutectic mixture (MNO_3):

$$2O_2^- \rightleftharpoons O_2^{2-} + O_2 ; \text{ in } MNO_3 \text{ liq.} \tag{1}$$

For the dilute solutions involved, the equilibrium constant K_m of (1) can be written:

$$K_m = [P] [O_2]/[S]^2 \tag{2}$$

where P is the peroxide ion O_2^{2-}; S the superoxide ion O_2^- and where [ ] are molalities (mol kg^{-1}).
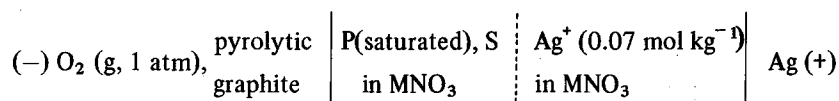
The value of K_m at 502–503 K was first reported by Zambonin and Jordan[1] as the result of a voltammetric study with a rotating disc electrode (RDE). Later on, Zambonin[2] gave a more accurate value on basis of a combined potentiometric and RDE study. Schlegel and Priore[3] used a completely independent, manometric technique in order to check the previous results.

The data on K_m are collected in Table 1 and a considerable discrepancy, involving a factor 180, is seen to occur between the results of ref.2 and ref. 3. It can be shown, however, (see Appendix) that the discrepancy stems for a great deal from the (unnecessary) use of Henry constants $k(O_2)$ with regard to the solubility of oxygen in the MNO_3 melt. Both in the electrochemical[2] and manometric[3] experiments the pressure $p(O_2)$ of gaseous oxygen rather than its molality $[O_2]$ was primarily known. Moreover, the authors of ref. 3, owing to the lack of relevant data for $k(O_2)$, used Henry constants $k(N_2)$ instead, so as to estimate oxygen molalities from corresponding pressures.

Since $[O_2] = kp(O_2)$, a shift of the standard state to oxygen of 1 atm yields

$$K_p = K_m/k(O_2) = \frac{[P]}{[S]^2}\, p(O_2)\quad \text{kg atm mol}^{-1} \tag{3}$$

The re-interpretation of the respective measurements[2,3] in terms of $p(O_2)$ yields the tabulated K_p values which show a clearly better agreement. A somewhat unexpected confirmation about the proper order of magnitude of K_p resulted from e.m.f. measurement of the present authors on the cell with an equilibrated, peroxide saturated, nitrate melt obtained by addition of excess Na_2O_2 to the solvent

$$(-)\, O_2\ (g,\ 1\ atm),\ \begin{array}{c}\text{pyrolytic}\\\text{graphite}\end{array}\ \left|\ \begin{array}{c}\text{P(saturated), S}\\\text{in MNO}_3\end{array}\ \right|\ \begin{array}{c}\text{Ag}^+\ (0.07\ \text{mol kg}^{-1})\\\text{in MNO}_3\end{array}\ \left|\ \text{Ag}\ (+)\right.$$

The Ag^+/Ag reference electrode was similar to the one used by Zambonin[2]. Around 500 K the graphite electrode proved very stable, no CO_2 evolution and weight loss of the graphite could be observed.

Moreover, a Pt electrode in stead of graphite yielded similar e.m.f. data within $\pm$ 5mV. At 502 K, the e.m.f. of the cell was -1.135V, at an analytically determined peroxide concentration[4] 5×10^{-3} mol kg^{-1}. Combination of our e.m.f. and solubility data with Zambonin's[2] e.m.f. results yields the value $Kp = 5 \times 10^{-2}$ kg atm mol^{-1} given in Table 1. Details are given in the Appendix.

With the aid of the recently determined[5] Henry constants $k(O_2)$ in molten MNO_3:

$$\log(k(O_2)/\text{mol kg}^{-1}\ \text{atm}^{-1}) = -(918/T) - 3.55 \tag{4}$$
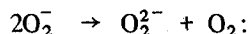
the values of K_p in the table can be "reconverted" into corresponding K_m values as shown in the 4th column of the table. Moreover, the temperature dependence of K_p follows directly from the manometric results[3]:

$$\log(K_p/\text{kg atm mol}^{-1}) = + (2786/T) - 5.40 \tag{5}$$

From (3), (4) and (5):

$$\log K_m = +(1866/T) - 8.95 \tag{6}$$

The latter result corresponds to a standard free enthalpy equation for the reaction (standard states for all species 1 mol kg^{-1})

$$2O_2^- \;\rightarrow\; O_2^{2-} + O_2:$$

$$\Delta G^\circ(\text{kcal})^* = -8.54 + 41 \times 10^{-3}\, T$$

i.e. $\Delta H^\circ = -8.54$ kcal; $\Delta S^\circ = -41$ cal K^{-1} mol^{-1}

As noted already by Schlegel and Priore[3] the exothermic character of the superoxide dis-

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*1kcal $\equiv$ 4.184 kJ.

proportionation reaction is probably due to the gain in solvation energy upon formation of the doubly charged peroxide ions. Though a negative value of $\Delta S°$ is consistent with this phenomenon, the extremely large *magnitude* of $\Delta S°$ (corresponding to typical entropy values of diatomic gases) casts some doubt on the accuracy of the manometric experiments[3], which at the higher temperatures ($\sim$550 K) show a considerable scatter.
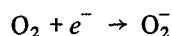
TABLE I

EQUILIBRIUM CONSTANTS OF THE OXYGEN–PEROXIDE–SUPEROXIDE REACTIONS IN (Na–K)NO$_3$ EUTECTIC MELTS AT 503 K

Authors	K_m	K_p/atm kg mol^{-1}	$K_m{}^1$	Method
Zambonin–Jordan[1]	35×10^{-7}	–		RDE voltammetry
Zambonin[2]	5×10^{-7}	0.15	6.3×10^{-7}	RDE + e.m.f.
Schlegel–Priore	930×10^{-7}	1.39	$58 \ \times 10^{-7}$	manometric
Present authors		0.05	2.1×10^{-7}	e.m.f. + peroxide solubility

Appendix

In the subsequent text all potential values (E) are given relative to the Ag$^+$ 0.07 mol kg^{-1}, MNO$_3$/Ag reference electrode used by Zambonin *et al.*[1,2]. The temperature is 503 K.
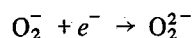
(A) Value of K_p from electrochemical experiments. The processes of interest are:

$$O_2 + e^- \rightarrow O_2^-$$

for which

$$E_a = E_a° + (RT/F \ln p(O_2)/[S] \tag{a}$$

and

$$O_2^- + e^- \rightarrow O_2^{2-}$$

for which

$$E_b = E_b° (RT/F) \ln [S]/[P] \tag{b}$$

At equilibrium, $E_a = E_b$, and therefore:

$$(RT/F) \ln K_p = E_b° - E_a° \tag{c}$$

Since the potential $E_a°$ involves *gaseous* oxygen of 1 atm as standard state, its value is readily obtained from Zambonin's[2] data. At $p(O_2) = 1$ atm and $[S] = 10^{-2}$ mol kg^{-1}, $E_a = -0.985$V. This yields $E_a° = -1.185$V.

The standard potential $E_b°$ is not explicitly given in Zambonin's paper[2], but it is

related to the RDE polarographic half wave value[1] E_b $(\frac{1}{2}) = -1.28V$ by the expression:

$$E_b\ (\tfrac{1}{2}) = E_b^\circ + (RT/F)\ \ln\ [D_P/D_S]^{\,2/3} \tag{d}$$

where $D_P = 3.1 \times 10^{-6}\ cm^2\,s^{-1}$ and $D_S = 4.75 \times 10^{-6}\ cm^2\,s^{-1}$ are the diffusion coefficients[1] of peroxide and superoxide, respectively. From (d) we obtain $E_b^\circ = -1.268V$ and finally from (c): $K_p = 0.15\ atm\ kg\ mol^{-1}$.

(B) K_p from manometric experiments[3]. In Fig.1 of ref. 3, the drawn straight line corresponds directly to the equation:

$$\log(K_p/kg\ atm\ mol^{-1}) = (2786/T) - 2.515 - \log 760;\ (528\text{--}553\ K).$$

Extrapolation to 503 K yields $K_p = 1.39$; *i.e.* less than one order of magnitude greater than Zambonin's value.

(C) Present authors (graphite rod electrode in peroxide saturated (Na–K)NO$_3$ eutectic melt). From the previous equations (a) and (2):

$$E = E_a^\circ + (RT/2F)\ \ln\ \{p(O_2)\,K_p/[P]\ \} \tag{e}$$

Substitution of the observed values $E = -1.135$ V (ref. 6); $p(O_2) = 1$ atm, $[P]_{sat} = 5 \times 10^{-3}\ mol\ kg^{-1}$ (ref. 4) and adoption of Zambonin's[2] potentiometric result $E_a^\circ = -1.185V$ yields $K_p = 0.05\ kg\ atm\ mol^{-1}$.

The observed relation[6] between cell potential and partial pressure of oxygen $dE/d\log p(O_2) = 50$ mV shows that the (Na–K)NO$_3$ melt is indeed a peroxide saturated melt, since $2.303RT/2F = 0.050$ V at the working temperature.

This was confirmed by X-ray analysis of the insoluble suspended particles, obtained by filtration from the melt. The powder diffraction pattern proved that Na_2O_2 rather than K_2O_2 is the solid constituent.

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