Redox Chemistry of the System O_2–O_2^-–O_2^{2-}–O^{2-} in Fused Salts[1]

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Abstract: The following equilibria have been substantiated in molten alkali nitrate solvents at 229°: $O^{2-} + NO_3^- = NO_2^- + O_2^{2-}, K \simeq 3$; $O_2^{2-} + 2NO_3^- = 2NO_2^- + 2O_2^-, K = 6.7 \pm 0.5 \times 10^{-11}$; $2O_2^- = O_2 + O_2^{2-}, K = 3.5 \pm 1 \times 10^{-6}$. In terms of basic chemistry, the salient feature is the virtually complete conversion of the ion O_2^- by nitrate, and/or gaseous oxygen, to peroxide (O_2^{2-}) and superoxide (O_2^-). These findings are based on conclusive voltammetric studies at Levich's rotated platinum disk electrode in perfectly dry and silica-free melts. They compel a drastic reappraisal of the role of oxide, hitherto considered a mainstay of acidity concepts in fused-salt chemistry.

The role of the oxide ion, O^{2-}, has been a controversial ghost which has haunted the chemistry of fused nitrates. Results, based on experiments carried out in glass or quartz containers, reported by prominent investigators, reveal puzzling inconsistencies. Some authors[3–5] have adduced evidence suggesting the prevalence of the Lux–Flood acid–base-type equilibrium[6]

$$NO_3^- = NO_2^+ + O^{2-} \qquad (1)$$

while others[7] questioned the very existence of the species NO_2^+. Concomitantly, the nature of the oxygen electrode in fused salt media has been subject of controversy: Nernst slopes corresponding to the *two-electron transfer* equilibrium

$$O^{2-} = {}^1/{}_2O_2 + 2e^- \qquad (2)$$

have been substantiated in some instances,[3,8,9] while in others[8,10] a *one-electron transfer* slope was reported. In previous communications[11] on the voltammetry of peroxide and superoxide in nitrate melts, we have shown that a "one-electron oxygen electrode" is accounted for by the reversible couple O_2^-–O_2. We obtained consistent results in *silica-free* melts (using platinum-lined containers) which had been painstakingly dried. Our preliminary qualitative findings[11] have indicated the prevalence of the equilibria

$$O^{2-} + NO_3^- \rightleftharpoons O_2^{2-} + NO_2^- \qquad (3)$$

$$O_2^{2-} + 2NO_3^- \rightleftharpoons 2NO_2^- + 2O_2^- \qquad (4)$$

Quantitative results, obtained at Levich's rotated platinum disk electrode, are presented and discussed in this paper. Our results are uniquely consistent with the following paradoxical conclusions. Because of reactions 3 and 4, oxide—whose stability in fused nitrates has never been previously questioned[3,4,7–9,12,13]—is *not* capable of existence at appreciable concentration levels. On the other hand, peroxide (O_2^{2-}) and superoxide (O_2^-) are important species, interrelated by the electron transfer and disproportionation equilibria

$$O_2 \overset{e}{\rightleftharpoons} O_2^- \overset{e}{\rightleftharpoons} O_2^{2-} \qquad (5)$$

$$2O_2^- \rightleftharpoons O_2^{2-} + O_2 \qquad (6)$$

Experimental Section

Chemicals. Reagent grade chemicals were used throughout. An equimolar mixture of molten sodium–potassium nitrate served as solvent. Potassium superoxide (supplied by Alfa Inorganics, Beverly, Mass.) was ascertained to assay as >98% KO_2.

Apparatus and Procedures. The platinum-lined electrolysis cell is shown in Figure 1. Details will be presented in a separate communication.[14] Only essential features are outlined in this paper. A so-called "three-electrode system" was used to record dc current–voltage curves at scan rates between 1 and 20 mV/sec with the aid of an electronic polarograph.[11] The indicator electrode, which was rotated at 600 rpm, consisted of a circular platinum surface 0.017 cm² in area, embedded in the middle of a concentric and coplanar circular glass surface. The design of this rotated disk electrode is apparent from Figure 1: it had a perfect cylindrical geometry[15] and an over-all diameter of 7 mm. The reference electrode was a Ag|Ag⁺ half-cell, containing 0.07 *m* silver nitrate in the solvent melt. Electrical contact between the reference half-cell and the bulk electrolyte was maintained *via* the capillary action of an asbestos wick.[16] The potential of the rde was swept linearly *vs.* the reference electrode, from which no appreciable current was drawn at any time. Currents were measured in a circuit consisting of the indicator electrode and a "counter electrode" (a platinum cylinder, 3 cm² in area) separated from the bulk of the electrolyte melt by a fritted borosilicate disk.

Contact between melt and glass surfaces was minimized. The rotated disk surface of the indicator electrode was immersed only for short times (during actual recording of voltammograms). All other glass surfaces were covered with thin platinum foil (perforated when appropriate). Gas inlet f was used to deaerate the electrolyte melt by bubbling with dry argon or to saturate the melt with dry oxygen.

Experiments were performed just above the melting point of the Na–K nitrate solvent. A temperature of 229 ± 1° was maintained with the aid of an aluminum block thermostat, insulated with magnesia, heated electrically, and controlled by a proportional thermoregulator. The choice of the lowest feasible temperature was predicated by the following considerations: comparison with

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[3] R. N. Kust and F. R. Duke, *J. Am. Chem. Soc.*, **85**, 3338 (1963).

[4] F. R. Duke in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, Chapter 7.

[5] G. Delarue, Abstracts, 13th Meeting, Comité International de Thermodynamique et Cinétiques Electrochimiques (CITCE), Rome, Italy, 1962, No. 8.2.

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[8] A. M. Shams el Din, *Electrochim. Acta*, **7**, 285 (1962).

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[10] N. S. Wrench and D. Inman, *J. Electroanal. Chem.*, **7**, 319 (1968).

[11] P. G. Zambonin and J. Jordan, *J. Am. Chem. Soc.*, **89**, 6365 (1967); *Anal. Letters*, **1**, 1 (1967).

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[13] H. S. Swofford and P. G. McCormick, *Anal. Chem.*, **37**, 970 (1965).

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[15] E. Yeager and R. W. Zurilla, Reprints of Papers, Symposium on Electrochemical Processes, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Division of Fuel Chemistry, pp 66–73.

[16] S. N. Flengas, *J. Chem. Soc.*, 534 (1956).

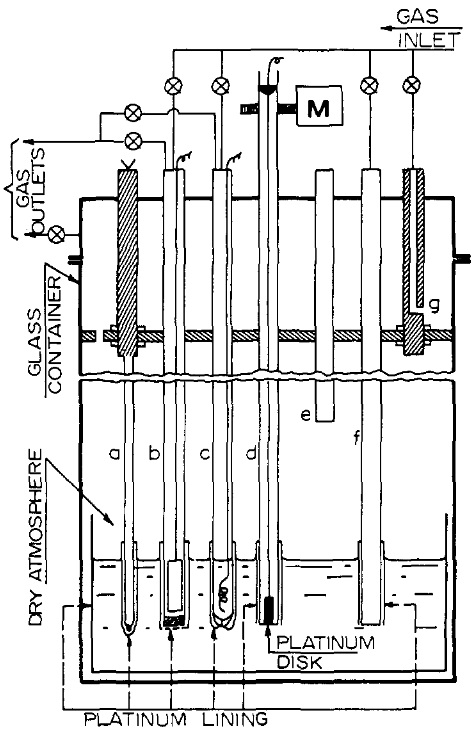

Figure 1. Schematic sketch of electrolysis cell: (a) thermistor or thermocouple; (b) counter electrode; (c) reference electrode Ag| Ag^+ (0.07 *m*); (d) indicator electrode (rotated disk); (e) inlet for solid samples; (f, g) argon (or nitrogen) inlets.

relevant data in literature and optimum resolution of current-voltage waves and residual currents.

Potential assignments are reported in this paper in concordance with the Stockholm IUPAC Convention,[17] *i.e.*, the more cathodic a potential, the more negative its value. However, they are necessarily referred to the $Ag|Ag^+$ half-cell used in this particular investigation rather than to the normal hydrogen electrode.

Results

Freshly prepared, dilute solutions of superoxide in melts containing comparable concentrations of nitrite yielded current–voltage curves which exhibited remarkable changes in shape as function of time. The effect is illustrated in Figure 2, which is a representative example of results obtained in an extended series of experiments performed at concentration levels between 5×10^{-4} and 3×10^{-3} *m*. Significant findings are outlined below with reference to Figure 2.

$t = 0$, **Oxygen-Free Melt, Curve I.** The limiting currents (expressed in amperes) identified in the figure corresponded respectively to the following electrode reactions[11] occurring with Nernstian reversibility

$$O_2^- + e^- = O_2^{2-}$$

$$h_1 = 0.62nFAD_{O_2^-}{}^{2/3}\nu^{-1/6}\omega^{1/2}c_{O_2^-} \tag{7}$$

$$O_2^- = O_2 + e^-$$

$$h_3 = -0.62nFAD_{O_2^-}{}^{2/3}\nu^{-1/6}\omega^{1/2}c_{O_2^-} \tag{8}$$

where the symbols have their usual significance in the Levich equation,[18] *viz.*, *nF* is the number of coulombs per mole and *A* is the area of the indicator electrode (cm^2); *D* and ν denote diffusion coefficients and kinematic viscosity, respectively, both expressed in cm^2/sec; ω is the angular velocity (rads/sec); *c* is the bulk concentration (expressed in moles/cm^3) of the electroactive species identified by subscripts. Assignment of the relevant electrode processes relied on the usual diagnostic criteria, *viz.*, half-wave potentials, mathematical wave analysis, etc.

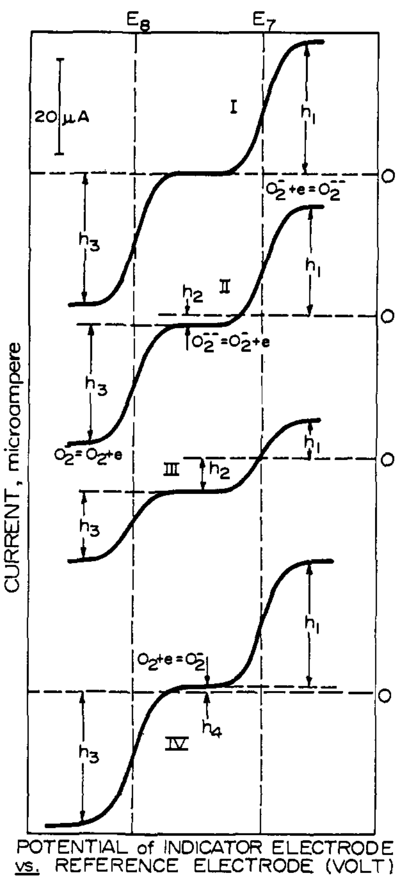

Figure 2. Sequential voltammograms (zero current axis shifted arbitrarily. Initial solution: 5.05×10^{-3} *m* $NaNO_2$ plus 2.92×10^{-3} *m* KO_2, no oxygen. Curves recorded after lapse of specified times: (I) $t = 0$; (II) $t = 150$ min; (III) $t = \infty$ (6 hr). (IV) 30 min after bubbling pure oxygen through III. *E*, half-wave potentials corresponding to electrode reactions identified by subscripts.

$0 < t < \infty$, **Oxygen-Free Melt, Curve II.** The salient feature of curve II is the conversion of the cathodic wave h_1 into a Nernst-reversible composite wave whose anodic component corresponded to

$$O_2^{2-} = O_2^- + e^-$$

$$h_2 = -0.62nFAD_{O_2^{2-}}{}^{2/3}\nu^{-1/6}\omega^{1/2}c_{O_2^{2-}} \tag{9}$$

$t = \infty$, **Oxygen-Free Melt, Curve III.** This voltammogram corresponded to the attainment of an equilibrium situation. The limiting currents h_1, h_2, h_3 exhibited no further transient changes.

$t = \infty$, **Melt Equilibrated with 1 Atm of Oxygen, Curve IV.** This curve shows the effect of oxygen on curve III. Salient features include: disappearance of the peroxide wave, h_2; reconversion of h_3 to its "zero-time value" (as in Curve I); appearance of a distinct, albeit small cathodic wave component, h_4, due to the following electrode reaction.

$$O_2 + e^- = O_2^-$$

$$h_4 = 0.62nFAD_{O_2}{}^{2/3}\nu^{-1/6}\omega^{1/2}c_{O_2} \tag{10}$$

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[17] J. A. Christensen, *J. Am. Chem. Soc.*, 82, 5517 (1960).

[18] V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

In any series of sequential experiments, similar to the sample shown in Figure 2, it was found that the limiting currents h_1 and h_2 were correlated linearly, regardless of whether solutions were equilibrated with oxygen (as in curve IV), or not (as in curves I-III). A plot of h_1 *vs.* h_2 measured at different times during the experiment of Figure 2 is shown in Figure 3.

Half-wave potentials corresponding to reactions 7 and 8 were invariant throughout our experiments as theoretically expected. They had the values shown in Figure 2, *viz.*

$$E_7 = -1.28 \text{ V}; \; E_8 = -0.74 \text{ V} \tag{11}$$

Likewise the quantitative correlations anticipated from eq 7-10 were verified experimentally, *viz.*
In the absence of oxygen

$$|h_3| = |h_2| + |h_1| \tag{12}$$

In the presence of oxygen

$$|h_1| = |h_3| + |h_4| \tag{13}$$

The following diffusion coefficients were evaluated from our experimental data (see Appendix).

$$D_{O_2^-} = 4.75 \times 10^{-6} \text{ cm}^2/\text{sec} \tag{14}$$

$$D_{O_2^{2-}} = 3.1 \times 10^{-6} \text{ cm}^2/\text{sec} \tag{14'}$$

Discussion

Basic Chemistry. The interesting sequence of results exemplified in Figure 2 is accounted for by the following reactions

Curve I → II → III:

$$2O_2^- + 2NO_2^- \longrightarrow 2NO_3^- + O_2^{2-} \tag{4'}$$

Curve III → IV:

$$O_2^{2-} + O_2 \longrightarrow 2O_2^- \tag{6'}$$

The change from curve I ($t = 0$; $O_2^- > 0$; $O_2^{2-} = 0$) to curve III ($t = \infty$; $O_2^- > 0$; $O_2^{2-} > 0$) reflects the gradual conversion of superoxide to peroxide until equilibrium 4 was attained in oxygen-free melts. Subsequently, this situation was rapidly altered by oxygen, owing to reaction 6′. The prevalence of equilibrium 4 has been substantiated previously.[11] Reaction 6′ is an electron-transfer process known to occur[19] between solid Na_2O_2 or K_2O_2, on the one hand, and gaseous oxygen on the other. Our interpretation of Figure 2 in terms of reactions 4′ and 6′ is supported by the following considerations of "internal consistency." A common feature of the two reactions 4′ and 6′ is the stoichiometric correspondence that 2 moles of superoxide yield 1 mole of peroxide or *vice versa*. Consequently for any given time interval, $\Delta t = t_2 - t_1$, the two concentrations must be related by the equation

$$[O_2^-]_{t_2} - [O_2^-]_{t_1} = -2\{[O_2^{2-}]_{t_2} - [O_2^{2-}]_{t_1}\} \tag{15}$$

$$\Delta[O_2^-] = -2[O_2^{2-}] \tag{15'}$$

Substitution of the applicable Levich eq 7 and 9 evidently yields

$$\Delta h_1 = -2\left(\frac{D_{O_2^-}}{D_{O_2^{2-}}}\right)^{2/3} \Delta h_2 \tag{16}$$

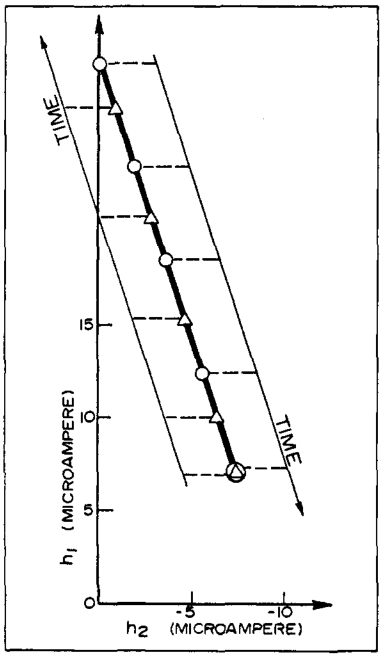

Figure 3. Plot of h_1 *vs.* h_2, measured at different times during the experiment illustrated in Figure 2: (○) in absence of oxygen; (△) in presence of oxygen.

The fact that sequential plots of h_1 *vs.* h_2 fell on the same straight line in the presence as well as in the absence of oxygen (Figure 3) substantiates convincingly that reactions 4′ and 6′ are necessary and sufficient for interpreting our relevant experimental results.

Thermodynamics. From a series of "equilibrium voltammograms" exemplified by Figure 2, curve III, the equilibrium constant (see Appendix) defined by eq 17 was evaluated

$$K_4 = \frac{[O_2^-]_\infty^2[NO_2^-]_\infty^2}{[O_2^{2-}]_\infty[NO_3^-]^2} = 6.7 \pm 0.5 \times 10^{-11} \tag{17}$$

where the square brackets denote molality concentrations. The assignment in eq 17 and the corresponding precision were based on five discrete determinations. Reaction 6′ is a rate process whose converse is reaction 6, *i.e.*, the disproportionation of superoxide to peroxide plus oxygen. We have shown that voltammograms corresponding to the one-electron-transfer processes O_2^--O_2^{2-} and O_2-O_2^- were Nernst reversible. Therefore, the disproportionation constant

$$K_6 = \frac{[O_2][O_2^{2-}]}{[O_2^-]^2} = 3.5 \pm 1 \times 10^{-6} \tag{18}$$

was evalulated accordingly from eq 7, 8, and 11. Pertinent assumptions and approximations are discussed in the Appendix.

It is of interest to obtain a quantitative estimate for the equilibrium constant of reaction 3 (oxide + nitrate = peroxide + nitrite). In the previous paper[11] it was merely found qualitatively that the equilibrium was far to the right. A direct determination of K_3 in a nitrate melt was not feasible. However, we have evaluated K_3 by combining the value of K_4 reported in this paper (eq 17) with the equilibrium constant for the reaction

$$3O_2^{2-} = 2O^{2-} + 2O_2^- \tag{19}$$

estimated from information in literature which had

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(19) For a review see I. I. Vol'nov, "Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals," translated by Z. E. Woroncow, Plenum Publishing Corp., New York, N. Y., 1966.

been obtained in an "inert" (nonoxidizing) solvent.[20] A value of

$$K_{19} = \frac{[O_2^-]^2[O^{2-}]^2}{[O_2^{2-}]^3} \simeq 10^{-11} \qquad (20)$$

was calculated (see Appendix) from the voltammetric data obtained by Goret and Tremillon[20] who studied the electrochemistry of oxide and peroxide in a molten sodium–potassium hydroxide solvent at 227°. Combination of K_4 and K_{19} yielded

$$K_3 = \frac{[NO_2^-][O_2^{2-}]}{[NO_3^-][O^{2-}]} = \sqrt{\frac{K_4}{K_{19}}} \simeq 3 \qquad (21)$$

It is realized, of course, that there was a difference in the solvent anions (nitrate in our work *vs.* hydroxide in ref 20). However, it was assumed that this would not affect the order of magnitude of the equilibrium constants and that an intercomparison of data obtained in the two solvents was reasonable: the species involved in the equilibria (all anions) were unlikely to form ion pairs or solvates with either nitrate or hydroxide; the cations (Na^+, K^+) were the same in both solvent media and the dielectric constants were probably comparable.

The implications of equilibria 3, 4, and 6 are far-reaching. This can be appreciated by realizing that only a small fraction of any oxide dissolved in a nitrate melt or generated *in situ* (*e.g.*, by the dissociation of a Lux–Flood base) can exist as such under equilibrium conditions. The remainder is oxidized to peroxide and superoxide. For instance, if a total of 0.001 mole of Na_2O were added per 1000 g of pure nitrate solvent and if the partial pressure of oxygen in the supernate were negligible, the equilibrated melt would contain only 5×10^{-8} mole of dissolved O^{2-} (0.005% of the oxide added). Naturally, if an appreciable partial pressure of oxygen were maintained (as in curve IV of Figure 2), the percentage of O^{2-} remaining in solution as such would be even smaller. More than 99.9% of it would be converted to superoxide by reactions 3 and 6′ if $P_{O_2} = 1$ atm or $[O_2] \simeq 10^{-5}$ m in the melt. For this reason the "oxygen electrode" in fused nitrates reflects the behavior of the reversible redox couple O_2–O_2^- and exhibits a one-electron Nernst slope.[8,10,11]

Appendix

Determination of Diffusion Coefficients. $D_{O_2^-}$ was evaluated from the limiting currents h_1 or h_3 on the basis of the applicable Levich equation (eq 7 and 8, respectively), using known bulk concentrations of potassium superoxide.

$D_{O_2^{2-}}$ was calculated from eq 16.

Computation of Equilibrium Constants. For evaluating K_4 from eq 17, requisite concentrations were estimated as follows: $[O_2^-]_\infty$ and $[O_2^{2-}]_\infty$ were calculated *via* eq 7 and 9, respectively, from experimental values of h_1 and h_2, determined in appropriate solutions in which genuine equilibrium prevailed; the value of $[NO_2^-]_\infty$ was obtained from the relationship

$$[NO_2^-]_0 - [NO_2^-]_\infty = [O_2^-]_0 - [O_2^-]_\infty \qquad (22)$$

which is an obvious consequence of the stoichiometry of reaction 4.

The equilibrium constant K_6 (eq 6 and 18) was computed from the applicable rigorous correlation

$$K_6 = \exp\left[\frac{nF}{RT}(E^\circ_{O_2^-/O_2^{2-}} - E^\circ_{O_2/O_2^-})\right] \qquad (23)$$

The standard potentials were approximated as follows from the corresponding half-wave potentials E_7 and E_8 (see Figure 2).

$$E^\circ_{O_2^-/O_2^{2-}} \equiv E_7 + \frac{RT}{F}\ln\frac{D_{O_2^-}}{D_{O_2^{2-}}} - \ln\frac{\gamma_{O_2^-}}{\gamma_{O_2^{2-}}} \simeq E_7 \qquad (24)$$

$$E^\circ_{O_2/O_2^-} \equiv E_8 + \frac{RT}{F}\ln\frac{D_{O_2}}{D_{O_2^-}} - \ln\frac{\gamma_{O_2}}{\gamma_{O_2^-}} \simeq E_8 \qquad (25)$$

The order of magnitude of the neglected logarithmic terms is 10 mV. The value of K_{19} (eq 19 and 20) was calculated from the equation

$$K_{19} = \exp\left[\frac{2F}{RT}(E^\circ_{O_2^{2-}/O^{2-}} - E^\circ_{O_2^-/O_2^{2-}})\right] \qquad (26)$$

The requisite standard potentials were estimated from data reported by Goret and Tremillon.[20]

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[20] J. Goret and B. Tremillon, *Bull. Soc. Chim. France*, 67 (1966).