

CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DEPARTMENT,  
UNIVERSITY OF SYDNEY, SYDNEY, NEW SOUTH WALES 2006, AUSTRALIA

## The Solubility of Metallic Oxides and the Free Energy of Solvation of Oxide Ion in Molten Alkali Metal Nitrates

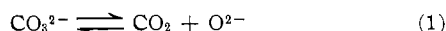
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Received March 4, 1971

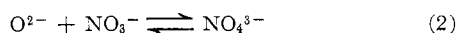
A reversible oxygen electrode has been established in an equimolar NaNO<sub>3</sub>-KNO<sub>3</sub> melt over the temperature range 250–350° and has been used to measure the solubility of CuO, ZnO, PbO, and MgO. By combining these results with lattice free energies calculated by using Born-Haber cycles and the Sackur-Tetrode equation, the free energies of solvation have been determined for these oxides. Making certain assumptions it has proved possible to estimate the absolute free energy of solvation of O<sup>2-</sup> ion in the melt. The value of -422 kcal mol<sup>-1</sup> obtained has been compared to the value calculated by the Born equation which is based on purely electrostatic considerations.

### Introduction

Kust<sup>1</sup> found the dissociation constant of carbonate ion (eq 1) to be much higher in a molten alkali metal



nitrate solvent than the known thermal stability of alkali metal carbonates might suggest. He put forward the tentative suggestion that this dissociation might be favored by solvation of the oxide ion, perhaps to form orthonitrate



It seemed to us that in view of this hypothesis it would be interesting to try to estimate the free energy of solvation of O<sup>2-</sup> in a nitrate melt.

The solubility of simple metallic oxides that dissolve in a molten nitrate to form metal ions and oxide ions can be measured if we can establish a reversible oxygen electrode in the melt. Having done so, it can be used to measure the solubilities of metallic oxides at various temperatures and from this to determine their free energies of solution in the melt. Combining these results with a value of the lattice free energy calculated from a Born-Haber cycle and the Sackur-Tetrode equation, it is possible to estimate the free energy of solvation of the oxides. Solvation energies for ions dissolved in molten nitrates do not appear to have been obtained previously except for the silver halides.<sup>2</sup> By making certain assumptions, a value for the absolute free energy of solvation of the O<sup>2-</sup> ion can be estimated.

### Experimental Section

The potassium and sodium nitrates were purified by being recrystallized after boiling for 2–3 hr in water adjusted to pH 4.5 with HNO<sub>3</sub>. The crystals were dried at 200° for 24 hr and cooled and stored under continuous vacuum.

The cell was a Pyrex tube 40 cm long by 7.5 cm in diameter, fitted with a 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 made of 99.999% pure Ag wire immersed in a 1.0 *m* solution of AgNO<sub>3</sub> in the equimolar NaNO<sub>3</sub>-KNO<sub>3</sub> eutectic melt. The junction was a thin Pyrex membrane, whose dc resistance was approximately 1 megohm.

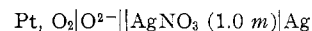
Gas pressures were measured with butyl phthalate manometers and the gases were mixed by passing them through an 8-mm spiral of 6-mm glass tubing.

Potentials were measured with a Type 8687 Leeds and Northrup potentiometer. For the micropolarization tests a Fluke

galvanometer, Type 841, was used to measure the out-of-balance current. The temperature was controlled to 0.25° with a solid-state proportional controller.

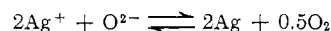
### Results

The electrochemical cell studied was



(NaNO<sub>3</sub>-KNO<sub>3</sub> melt, Pyrex membrane, NaNO<sub>3</sub>-KNO<sub>3</sub> melt)

for which the cell reaction is



If the cell is reversible, the emf should be given by the Nernst equation

$$E = E^{\circ'} - \frac{RT}{2F} \ln \frac{p_{\text{O}_2}^{1/2}}{[\text{O}^{2-}]}$$

to the degree of approximation allowed by substituting concentrations for the unknown activities.  $E^{\circ'}$  contains both the characteristics of the reference electrode and the standard potential  $E^{\circ}$ , which defines the hypothetical state of Ag<sup>+</sup> ions and O<sup>2-</sup> ions at a concentration of 1 *m*, both ions having the properties assigned to an infinitely diluted solution where Henry's law is obeyed.

The applicability of the Nernst equation to the cell was tested by measuring the emf as a function of (a) the partial pressure of oxygen, which was varied by suitably diluting the gas with pure nitrogen, and (b) the oxide ion concentration. The latter was varied by adding the appropriate weight of dry recrystallized Na<sub>2</sub>CO<sub>3</sub> suitably diluted with solvent. This method of adding oxide ion was suggested by Kust,<sup>3</sup> who showed that the CO<sub>2</sub> is totally removed from the melt by the gas stream, so that  $[\text{Na}_2\text{CO}_3]_{\text{added}} = [\text{O}^{2-}]$  in the melt. It should be noted that the decomposition of the carbonate was very slow under the conditions used here and required at least 12 hr for completion, as shown by the time necessary to reach a steady emf after each addition of carbonate. The reversibility of the cell reaction was tested by off-setting the potentiometer on both sides of the balance point and measuring the out-of-balance current from 0, to 20 nA, to -20 nA, and back to 0 using the Fluke galvanometer. The results of these tests on the cell are shown in Figures 1 and 2 and Tables I and II.

At an oxide ion concentration of approximately 10<sup>-5</sup> *m*, the partial pressure of oxygen ( $p_{\text{O}_2}$ ) was varied by

(1) R. N. Kust, *Inorg. Chem.*, **3**, 1035 (1964).(2) S. N. Flengas and E. Rideal, *Proc. Roy. Soc., Ser. A*, **233**, 443 (1956).(3) R. N. Kust, *J. Phys. Chem.*, **69**, 3662 (1965).

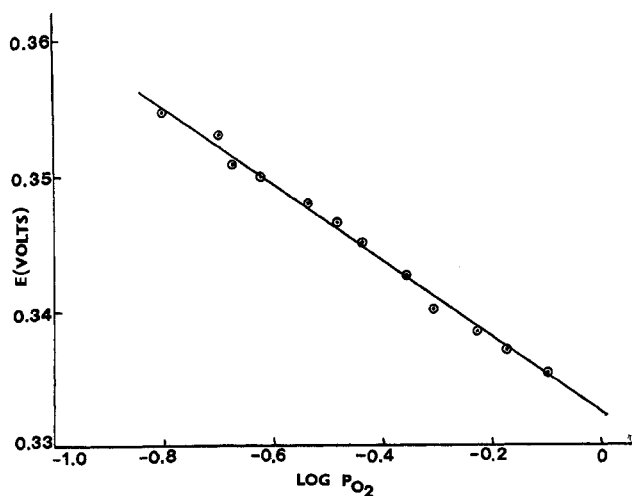


Figure 1.—Variation of cell potential vs. log of partial pressure of oxygen at 300°; oxide ion concentration  $10^{-5} m$ .

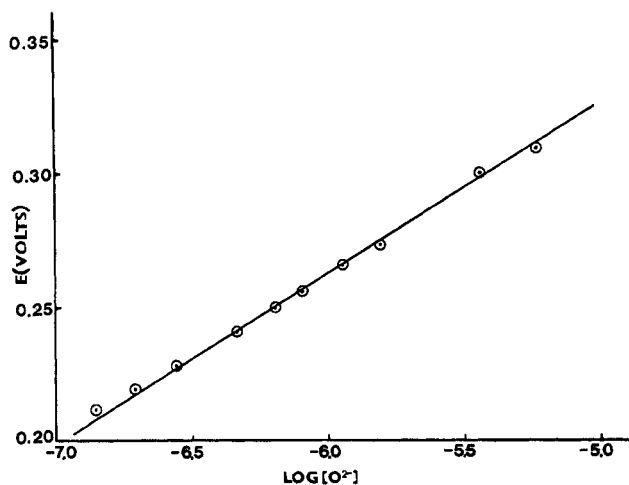


Figure 2.—Variation of cell potential vs. log  $[O^{2-}]$  at 350°; oxygen partial pressure 1 atm.

dilution with pure dry nitrogen. The plot of the cell potential ( $E$ ) vs.  $\log p_{O_2}$  at 300° is shown in Figure 1. The experimental slope, calculated by the method of least squares, is  $-0.0294 \pm 0.0008$  V, which should be compared to a theoretical slope of  $-0.0284$  V.

The oxide ion concentration was varied from  $10^{-8}$  to  $10^{-5} m$  at an oxygen pressure of 1 atm and measurements were made at intervals of 10° between 290 and 320°. The plot of  $\log [CO_3^{2-}]_{total}$  vs.  $E$  should have a slope of  $2.303RT/2F$ , the intercept giving  $E^{\circ}$ . The results for the four different temperatures are given in Table I, those for 320° being shown in Figure 2. The

TABLE I  
COMPARISON OF THEORETICAL AND EXPERIMENTAL SLOPES  
FOR CELL VOLTAGE PLOTTED AS A FUNCTION OF LOG  
 $[CO_3^{2-}]$  AT FOUR DIFFERENT TEMPERATURES

Temp, °C	Exptl intercept $E^{\circ}$ , V	Slope, V		% dev from the theory
		Theoret	Exptl	
290	$0.6191 \pm 0.0039$	0.05586	$0.0563 \pm 0.0007$	0.7
300	$0.6173 \pm 0.0020$	0.05686	$0.0555 \pm 0.0003$	2.4
310	$0.6147 \pm 0.0022$	0.05785	$0.0576 \pm 0.0004$	0.4
320	$0.6121 \pm 0.0028$	0.05884	$0.0583 \pm 0.0004$	0.9

slopes and intercepts were computed by the method of least squares, using an appropriate computer program.

TABLE II  
RELATION BETWEEN OUT-OF-BALANCE CURRENT AND  
VOLTAGE AS A TEST OF CELL REVERSIBILITY

Current, <sup>b</sup>		Current, <sup>b</sup>		Current, <sup>b</sup>	
$E,^a$ V	nA	$E,^a$ V	nA	$E,^a$ V	nA
0.2190	0	0.2204	10	0.2165	-20
0.2205	10	0.2192	0	0.2176	-10
0.2213	20	0.2182	-10	0.2188	0

<sup>a</sup> Deviation  $\pm 0.0001$ . <sup>b</sup> Deviation  $\pm 2$  nA.

Table II shows the relation between the galvanometer deflection and out-of-balance current. As can be seen, the readings were repeatable within the very small error of 0.2% with no appreciable hysteresis.

From these results it can be seen that the cell reaction is reversible, the Nernst equation is applicable, and little error is introduced by the use of concentrations in place of activities. The cell was then used to measure the solubility product of some metallic oxides over a range of temperatures.

**Solubility of Metal Oxides in Molten Nitrates.**—Many sparingly soluble metal oxides MO can, with reasonable certainty, be taken to dissociate completely in the melt into  $M^{2+}$  and  $O^{2-}$  ions.

If the solution is dilute, we can write  $K_{sp} = [M^{2+}] \cdot [O^{2-}]$  and  $\Delta G^{\circ}_{soln} = RT \ln K_{sp}$ . By measuring  $[O^{2-}]$  at various temperatures we can find  $K_{sp}$ ,  $\Delta G^{\circ}_{soln}$ , and  $\Delta H^{\circ}_{soln}$  from the temperature dependence of  $K_{sp}$ .

These quantities ( $\Delta G^{\circ}_{soln}$ ,  $\Delta H^{\circ}_{soln}$ ) refer to the solution of 1 mol of oxide in its standard state to form a hypothetical 1  $m$  solution. If there is no appreciable heat of dilution (and this can be assumed to be so if there is close agreement between the experimental and theoretical Nernst slopes), then these values will be equal to those at infinite dilution and the activity coefficients will be unity. From these results  $\Delta S^{\circ}_{soln}$  can be calculated for the temperature range studied. These results are all given in Table III.

TABLE III  
SOLUBILITY PRODUCTS AND THERMODYNAMIC QUANTITIES FOR  
CuO, ZnO, PbO, AND MgO IN MOLTEN  
NaNO<sub>3</sub>-KNO<sub>3</sub> EUTECTIC

Temp, °K	$K_{sp}$	$\Delta G^{\circ}_{soln}$ , kcal mol <sup>-1</sup>	$\Delta S^{\circ}_{soln}$ , cal deg <sup>-1</sup> mol <sup>-1</sup>
CuO			
563	$2.24 \times 10^{-13}$	32.61	125.38
573	$8.75 \times 10^{-13}$	31.61	124.94
581	$4.26 \times 10^{-13}$	30.35	124.96
593	$2.33 \times 10^{-13}$	28.93	125.24
ZnO			
563	$2.2 \times 10^{-13}$	32.61	16.86
573	$4.12 \times 10^{-13}$	32.47	16.81
583	$7.05 \times 10^{-13}$	32.42	16.60
593	$1.5 \times 10^{-13}$	32.09	16.88
MgO			
563	$2.16 \times 10^{-14}$	35.21	0.87
573	$3.52 \times 10^{-14}$	35.28	0.73
583	$5.93 \times 10^{-14}$	35.29	0.70
593	$12.51 \times 10^{-14}$	35.01	1.16
PbO			
563	$4.34 \times 10^{-12}$	29.27	30.60
573	$7.86 \times 10^{-12}$	29.12	30.33
583	$21.8 \times 10^{-12}$	28.44	30.98
593	$56 \times 10^{-12}$	27.82	31.50

The standard free energy of solution  $\Delta G^{\circ}_{soln}$  can be regarded as the sum of the standard free energy of the

lattice  $\Delta G^\circ_{\text{lattice}}$  plus the standard free energy of solvation  $\Delta G^\circ_{\text{solv}}$ . Since  $\Delta G^\circ_{\text{lattice}}$  can be calculated using an appropriate Born-Haber cycle to find  $\Delta H^\circ_{\text{lattice}}$  and the Sackur-Tetrode equation to calculate  $\Delta S^\circ_{\text{lattice}}$ , we have a method for estimating  $\Delta G^\circ_{\text{solv}}$  from the solubility data. These data have not previously been available.

We recalculated lattice free energies for the oxides using thermodynamic data taken from the compilations by Kubaschewski and Evans<sup>4</sup> and by Dasent.<sup>5</sup> The latter gives 168 kcal mol<sup>-1</sup> as the most up to date figure for the electron affinity for O<sup>2-</sup>. The value used for the dissociation energy of gaseous oxygen was 118.95 kcal mol<sup>-1</sup>.<sup>6</sup> The values of the lattice free energies and solvation energies obtained are given in Table IV.

TABLE IV  
LATTICE FREE ENERGIES AND FREE ENERGIES OF SOLVATION FOR CuO, ZnO, PbO, AND MgO DISSOLVED IN MOLTEN NaNO<sub>3</sub>-KNO<sub>3</sub> EUTECTIC<sup>a</sup>

Oxide	$\Delta H^\circ_{\text{soln}}$	$\Delta G^\circ_{\text{soln}}$	$\Delta G^\circ_{\text{lattice}}$	$\Delta G^\circ_{\text{solv}}$
CuO	103.2	31.61	961	-930
ZnO	42.1	32.47	943	-911
MgO	35.7	35.28	898	-862
PbO	55.4	29.12	817	-788

<sup>a</sup> Values in kcal mol<sup>-1</sup>.

### Discussion

Flengas and Rideal<sup>2</sup> have shown that the solvation energies for AgCl, AgBr, and AgI in molten (Na,K)-NO<sub>3</sub> eutectic at 250° are within 1% of the solvation energies in water at 25°. They commented that this implies that the neutralization of the electric fields of the ions is about the same in both solvents.

Although no other data for solvation energies in the melt have been published, if we assume that this conclusion is correct, we could apply to our melt the data that are already available for solvation energies in water and use them to calculate  $\Delta G^\circ_{\text{solv}}$  for O<sup>2-</sup>. Benjamin and Gold<sup>7</sup> and Dasent<sup>5</sup> have given tables of values of  $\Delta G^\circ_{\text{solv}}$  for individual ions in water relative to  $\Delta G^\circ_{\text{solv}}(\text{H}^+) = 0$ .

Such an empirical procedure could only be justified if it were to yield similar values for  $\Delta G^\circ_{\text{solv}}(\text{O}^{2-})$  from solubility measurements on different oxides.

Table V, column 4, gives the values so obtained: in view of the assumptions made the close agreement is remarkable.

(4) O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, London, 1965.

(5) W. E. Dasent, "Inorganic Energetics," Penguin Education Press, London, 1970.

(6) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, Van Nostrand, Princeton, N. J., 1950.

(7) L. Benjamin and V. Gold, *Trans. Faraday Soc.*, **50**, 797 (1954).

TABLE V  
FREE ENERGY OF SOLVATION FOR OXIDE ION (KCAL MOL<sup>-1</sup>)

Oxide	$\Delta G^\circ_{\text{solv}}$ (MO)	$\Delta G^\circ_{\text{solv}}$ (M <sup>2+</sup> ) <sup>a</sup>	$\Delta G^\circ_{\text{solv}}$ (O <sup>2-</sup> )	$\Delta G^\circ_{\text{solv}}$ (M <sup>2+</sup> ) <sup>a</sup> (abs)	$\Delta G^\circ_{\text{solv}}(\text{O}^{2-})$ (abs)
		([H <sup>+</sup> ] = 0)	([H <sup>+</sup> ] = 0)		
CuO	-930	24	-954	-502	-428
ZnO	-911	36	-947	-489	-422
MgO	-862	65	-927	-460	-402
PbO	-788	163	-951	-354	-434
					Av -422

<sup>a</sup> Values from ref 5.

We might note that Benjamin and Gold gave a value for only one divalent anion S<sup>2-</sup>. This is a large ion ( $r(\text{S}^{2-}) = 1.80 \text{ \AA}$ ;  $r(\text{O}^{2-}) = 1.40 \text{ \AA}$ ); the value given for  $\Delta G^\circ_{\text{solv}}(\text{S}^{2-})$  in water is -825 kcal mol<sup>-1</sup>. Considering the relative ionic radii alone we would then expect  $\Delta G^\circ_{\text{solv}}(\text{O}^{2-})$  to be  $(-825 \times 1.8)/1.4 = -1060$  kcal mol<sup>-1</sup> on the same scale. This is only about 10% greater than our estimated value, which again is surprisingly close agreement.

According to Halliwell and Nyburg,<sup>8</sup> there is considerable evidence that the absolute value for  $\Delta H^\circ_{\text{solv}}$  for H<sup>+</sup> in water is -260 kcal mol<sup>-1</sup> at 25°, while according to Noyes,<sup>9</sup>  $\Delta S^\circ_{\text{solv}}$  for H<sup>+</sup> is nearly zero. If these two statements are correct, the absolute value for  $\Delta G^\circ_{\text{solv}}(\text{H}^+)$  in water will be very close to -260 kcal mol<sup>-1</sup>, and on the basis of our previous assumption that the free energies of solvation for individual ions are the same in the two solvents, we can now assign an absolute value to the free energy of solvation of O<sup>2-</sup> in our melt. The values obtained are given in the last column of Table V, the average value being -422 kcal mol<sup>-1</sup>.

It is of interest to compare this estimate with the value calculated from an expression given by Born,<sup>10</sup> which gives the change in the free energy of a gaseous ion of charge  $z$  and radius  $r$  when immersed in a medium of dielectric constant  $D$ . The Born expression is

$$\Delta G^\circ_{\text{solv}} = -2.39 \times 10^{-11} \frac{N(Ze)^2}{2r} \left(1 - \frac{1}{D}\right) \text{ kcal mol}^{-1}$$

where  $N$  is the Avogadro number and  $e = 4.8 \times 10^{-11}$  statcoulomb. Taking the radius of O<sup>2-</sup> to be 1.40 Å and putting  $D = 5.97$ , which is the average of three values obtained for this melt by Flengas and Rideal,<sup>2</sup> we obtain the figure of -395 kcal mol<sup>-1</sup>. In view of the assumptions involved, it is interesting that the experimental and calculated solvation energies are within about 7% of one another.

(8) H. F. Halliwell and S. C. Nyburg, *ibid.*, **59**, 1126 (1963).

(9) R. M. Noyes, *J. Amer. Chem. Soc.*, **84**, 513 (1962).

(10) M. Born, *Z. Phys.*, **1**, 45 (1920); G. Kortüm, "Treatise on Electrochemistry," 2nd ed, Elsevier, New York, N. Y., 1965, p 119.