

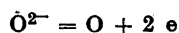
On the Oxygen Electrode in Molten Salts

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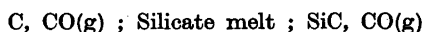
The oxygen ion is one of the chief components of the common salts, glasses and slags. Reactions involving oxides may be described as a transfer of oxygen ions from one state of polarization to another ^{cf. 1}. An acid-base definition based on the oxygen ion ² (analogous to the hydrogen ion in the Brönsted acid-base definition) may therefore give a uniform picture of many different reactions and facilitate the correlation between them. The determination of an acid-base equilibrium in a melt may in principle be regarded as an examination of oxygen ion activities. The experimental determination of oxygen ion activity has therefore recently become the object of considerable interest.

Electrometric determination of oxygen ion activities should be possible by means of an electrode on which the potential is determined by a reaction like



It is the purpose of the present work to examine the question whether such a reversible oxygen electrode can be established in melts.

Several attempts have already been made to measure electromotive forces — EMF — in galvanic cells with molten oxides as electrolytes. Derge and Lo Ching Chang ³ tried to determine the SiO₂-activity in silicate melts by means of EMF-measurements of the cell



They were, however, unable to give a reasonable cell reaction, which could explain the variation of the EMF with the silicate composition, gas pressure etc.

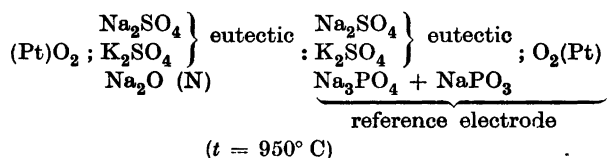
Csaki and Dietzel ⁴ have measured cells like



with electrolytes of fused boric oxide and borates of different alkali ions. Their theoretical considerations are open to severe criticism, and the authors have been unable to give any quantitative evidence as to what kind of reaction is potential determining. It is interesting to note, however, that they claim to have measured well-defined EMF in this type of cells.

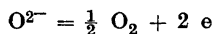
The work of Rose, Davis and Ellingham⁵ on the reducibility of oxides indicates that an oxygen electrode really works reversibly in a melt mainly composed of sodium hydroxide at temperatures from 400 to 700° C. These investigators did not, however, primarily focus their attention on the oxygen electrode, and they therefore did not investigate the EMF as a function of the composition of the melt. (Compare also the overvoltage investigations in fused NaOH by Agar and Bowden⁶).

The investigations of Lux are the only ones which directly aim at establishing an oxygen electrode in a melt, in order to determine the "oxygen ion concentration". We shall here only briefly consider Lux's first paper², on which his later work⁷ is based. Lux tries to establish a cell of the type:



The sodium oxide concentration in the left half cell is varied, and is expected to determine the potential. A weak point in his investigations seems to be that the actual sodium oxide concentration has not been analytically checked, in spite of rapid evaporation of alkali oxide and attack on the alumina crucible during the EMF-measurement. In consequence of the rapid change of EMF with the time, Lux is forced to extrapolate the potential to zero time (that is the point of time when a known amount of sodium oxide was added to the melt).

The result of the measurements is given in a diagram, where this EMF is plotted against the logarithm of the sodium oxide concentration. The curve is very far from linear, and in the middle part a tangent would correspond to the value RT/F . If, however, the electrode process is



then the coefficient should be $RT/2F$.

As an explanation Lux suggests that the potential is determined by the process



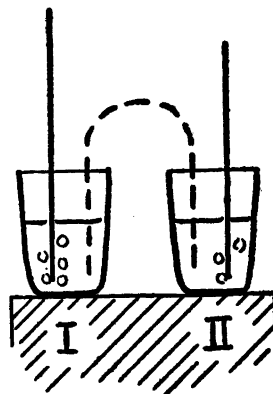
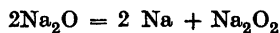


Fig. 1. Type of cell arrangement.

where the sodium is formed by a thermal decomposition of Na_2O according to



A proportionality between $C_{\text{Na}_2\text{O}}$ and C_{Na} , however, demands a constant peroxide concentration independent of $C_{\text{Na}_2\text{O}}$, which is impossible to realize at these temperatures (the oxide is added as peroxide!) On the contrary, the equilibrium



i.e., the thermal decomposition of sodium peroxide, demands a proportionality between the oxide and peroxide concentrations. This brings the theoretical coefficient of EMF back to $RT/2F$.

We are inclined to consider the results as a consequence of an unfavourable cell arrangement combined with a not very fortunate choice of salt system (vaporization of K_2O and no buffer capacity with respect to the oxygen ion).

As a preparation for the present work some investigations on the oxygen overpotential in fused salts were made by Flood and Förland⁸. The results seemed to demonstrate that the overpotential at low current densities was not of the activated type. This indicated that the oxygen electrode would not be hindered in its reversible action.

PRINCIPLES, AND CHOICE OF SALT SYSTEM

Three main factors have to be considered: The type of cell, the salt system and the design of the apparatus.

The galvanic cell. A "formation cell", the type used *e.g.* by Hildebrand and Salstrom^{9,10}, in their electrometric studies of several halogenide mixtures,

has the advantage of not involving any liquid junction potential. To establish a "formation cell" at high temperatures is in general difficult. For this reason we chose instead a concentration cell with transference, introducing no other electrode than the oxygen electrode, but involving an unknown liquid junction potential. The cell, then, in principle should consist of two crucibles with melts of different but fixed oxygen ion activities. In each crucible there is placed an inert electrode (platinum) with oxygen bubbling past it. Between the melts there should be a salt bridge to give electrolytic contact. (Fig. 1).

The liquid junction potential in concentration cells containing fused salts as electrolytes has not been the subject of any extensive treatment in the literature. An attempt at quantitative treatment of transport numbers and liquid junction potential in fused salts has been made by Schwarz¹¹. However, the assumptions on which his treatment rests disagree with the observations subsequently made by Karpachev and Pal'guez¹².

At present it is hard to predict how much the measurements in our cell will be affected by liquid junction potentials. The following extreme cases might give some idea of this. Liquid junction potential does not have to be taken into account if:

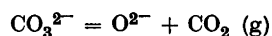
1. The conductivity of the salt bridge in our cell is due to the migration of cations, *i.e.*, the transport number of cations is large compared with that of the anions.

2. The solvent electrolyte alone is responsible for the conductivity of the melt, and there is a considerable excess of the solvent electrolyte.

If one of these conditions is fulfilled, the EMF will be given by the equations derived below, and the transport numbers will not appear in the equations.

The salt system should possess a buffer capacity with respect to the oxygen ion activity, and this activity should preferably vary in a known manner with the composition of the melt. Two salt systems have been dealt with, which were thought to fulfil these requirements.

The first system tried, was fused *sodium sulphate-sodium carbonate mixtures in equilibrium with a constant carbon dioxide pressure*. The sodium carbonate will dissociate into sodium oxide and carbon dioxide. (The corresponding dissociation of the sulphate will at the same temperature be negligible, see below). The dissociation of the carbonate can be written in terms of ions



with the equilibrium constant

$$K = \frac{a_{\text{O}^{2-}} \cdot p_{\text{CO}_2}}{a_{\text{CO}_3^{2-}}} \quad \text{or} \quad a_{\text{O}^{2-}} = K \cdot \frac{a_{\text{CO}_3^{2-}}}{p_{\text{CO}_2}}$$

where a is activity and p gas pressure. The oxygen ion activity is thus fixed by definite carbon dioxide pressure and carbonate activity. Further, investigations of equilibria in sodium borate-carbonate-sulphate-melts¹³ indicated that melts of sodium carbonate-sulphate behaved very close to ideal, *i.e.*, activity equals mole fraction N . (In this system as well as in the chromate-dichromate system the mole fraction equals the ionic fraction as defined by Temkin¹⁴). With a constant partial pressure of carbon dioxide in the atmosphere we thus have

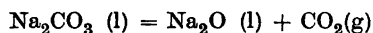
$$a_{\text{O}^{2-}} = \text{const. } N_{\text{Na}_2\text{CO}_3}$$

Hence the electromotive force of the cell should be

$$E = \frac{RT}{2F} \ln \frac{a_{\text{O}^{2-}}(\text{II})}{a_{\text{O}^{2-}}(\text{I})} = \frac{RT}{2F} \ln \frac{N_{\text{II}}}{N_{\text{I}}}$$

where N_{I} and N_{II} denote the mole fraction of carbonate in the crucible I and II respectively.

The equilibrium of the thermal decomposition of sodium carbonate has not yet been properly measured. All previous investigators have measured the "carbon dioxide pressure" at high temperatures, without paying regard to the possibility that the oxide is soluble in the fused carbonate. From thermodynamic data, however, we calculate for the reaction



$$\Delta G^\circ_{1200^\circ \text{K}} = 40 (\pm 5) \text{ kcal}$$

hence

$$N_{\text{Na}_2\text{O}} / N_{\text{Na}_2\text{CO}_3} = 10^{-7} (\pm 1) \text{ at } 900^\circ \text{C} \cdot (p_{\text{CO}_2} = 1 \text{ atm.})$$

From this it is seen that the oxygen ion concentration is very small compared with the carbonate concentration.

For the corresponding thermal dissociation of sodium sulphate we calculate

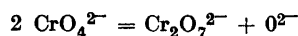
$$\Delta G^\circ_{1200^\circ \text{K}} = 84 (\pm 5) \text{ kcal}$$

Hence we have at 1200° K roughly

$$p_{\text{SO}_2} + p_{\text{SO}_3} / p_{\text{CO}_2} \approx 10^{-8} \cdot N_{\text{Na}_2\text{SO}_4} / N_{\text{Na}_2\text{CO}_3}$$

After it had been confirmed that the oxygen electrode worked satisfactorily in the carbonate-sulphate mixtures, it was of interest to find out whether the electrode would also work reversibly in salt systems with greater acidity. Some experiments were therefore carried out with mixtures of *potassium chromate-*

potassium dichromate. In this system it might be expected that the oxygen ion activity would be determined by the equilibrium



with the equilibrium constant

$$K = \frac{a_{\text{Cr}_2\text{O}_7^{2-}} \cdot a_{\text{O}^{2-}}}{a_{\text{CrO}_4^{2-}}^2}$$

Here again, earlier measurements¹⁵ indicated that the deviation from ideal mixture is comparatively small (though not entirely negligible.) Thus we have

$$a_{\text{O}^{2-}} \cong K \cdot \frac{N_{\text{CrO}_4^{2-}}^2}{N_{\text{Cr}_2\text{O}_7^{2-}}}$$

If we denote chromate by subscript *c* and dichromate by *d*, we have for the electromotive force

$$E = \frac{RT}{2F} \ln \frac{a_{\text{O}^{2-}} \text{ (II)}}{a_{\text{O}^{2-}} \text{ (I)}} \cong \frac{RT}{2F} \ln \frac{N_c^2 \text{ (II)} N_d \text{ (I)}}{N_c^2 \text{ (I)} N_d \text{ (II)}}$$

the liquid junction potential being neglected. The oxygen ion activity in these mixtures is definitely smaller than in the carbonate-CO₂ systems. The ratio of *a*_{O²⁻} in the two systems is estimated to be of the order of magnitude 10⁻⁵. (Entropy data for the alkali chromates are not available).

EXPERIMENTAL

The cell is shown diagrammatically in Fig. 1. the apparatus in Fig. 2.

The salt bridge should consist of a non-conducting, insoluble, porous material, which can act as a sort of wick for the fused, highly conductive salts. For the sulphate-carbonate melts magnesium oxide proved to be a very satisfactory material. For the dichromate-chromate melts sintered alumina worked satisfactorily. In most of the runs the salt bridge and gas tubes were combined, see Fig. 2.

Reliable electric insulation is essential in measurements of this kind. When the temperature is raised to 1 000° C or more, most refractories get perceptible conductivity, this may be still more the case if they are exposed to alkali vapors or the sputtering from fused salts. The ceramic refractories will have the character of electrolytic conductors. Poor insulation between the two crucibles and between the electrodes will therefore not only give a leak current, but may introduce a superimposed EMF on the contact metal-refractory. When carrying out measurements in our apparatus with the salt bridge

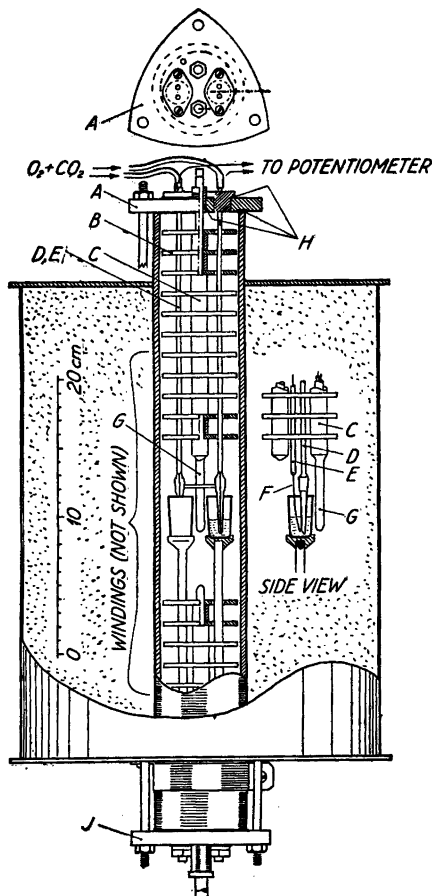


Fig. 2. A: Brass top. B: Alumina radiation shields. C: Mullite rings separating the shields. D: Mullite tubes (3 mm dia.) for gas inlet, prolonged with magnesia or alumina tubes. E: Mullite tubes (3 mm dia.) with internal platinum leads. F: Platinum electrodes. G: Mullite thermocouple sheath. H: Rubber gaskets. J: Brass bottom.

removed, we often found EMF of the order of 1 volt, *i. e.* ten or more times the EMF of the cell (but with definitely smaller sensitivity on the galvanometer).

If E_1 and R_1 represent EMF and internal resistance in the galvanic cell, respectively and E_2 and R_2 the same in the insulation, the error in the EMF measurement will be

$$\Delta E = (E_2 - E_1) \frac{R_1}{R_1 + R_2} \approx E_2 \cdot \frac{R_1}{R_2}$$

If, for instance, $E_2 = 1$ volt, and $R_1/R_2 = 1/1000$, then $\Delta E = 1$ mv. As the measured internal cell resistance R_1 was of the order 10 000 to 1 000 ohms (depending upon temperature *etc.*) the insulation resistance ought then to be at least some megohms.

Proper insulation was ensured by the arrangement shown in Fig. 2. The ceramic tubes supporting the crucibles, as well as the tubes for gas currents and electrode leads, are not in contact with any solid material in the hot zone of the furnace. (During the carbonate runs the insulation between the crucible supporters was not quite so good as indicated in Fig. 2, the measured value being just about $R_1/R_2 = 1/1000$).

The furnace was an ordinary resistance heated vertical tube furnace wound with Kanthal A. The windings were bifilar, and were closer spaced towards the ends of the furnace, to compensate for the extra loss of heat at the ends. A voltage stabilizer was used for the heating current. The furnace tube was internally heat insulated towards the ends by piles of alundum cement discs, with appropriate holes for the internal tubes. In order to get the platinum crucibles in correct position relatively to the electrodes *etc.*, a stable mechanical device was used for lowering and elevating the lower furnace lid. The brass lids were provided with rubber gaskets and were clamped in position by screws to secure a gas-tight sealing. The upper lid was cooled by water. The temperature was measured with a Pt-Pt 10 % Rh thermocouple. The EMF of cell and thermocouple were measured with an Otto Wolff potentiometer.

The atmosphere in the furnace proved to be of major importance. With a more or less uncontrolled atmosphere — *i. e.* the composition of the gas in the furnace differing somewhat from the composition of the gas bubbling on the electrodes, no stable potentials were obtained. The EMF then oscillated in time with each single bubble (a fact which suggests that the time necessary to establish the potential is only a fraction of a second at these high temperatures). Under such conditions the EMF also depended upon the velocity of the gas currents on the electrodes.

The procedure was usually as follows: Prior to the runs, melts of the wanted compositions were mixed, fused in platinum basins, cooled and crushed. (All the reagents were Merck p. a., dried at proper temperatures). Well in advance, the furnace was heated to the proper temperature. About 5 g of the salt mixture were weighed into each of the cell crucibles. These were placed on their refractory supporters, and the lower lid raised to a point about 2 cm from its upper position. After some fifteen minutes the salts were assumed to be fused and the lower lid was fully raised, thus causing the electrodes *etc.* to dip into the melts. From this point onwards readings of temperature and EMF were taken at regular intervals. The lids were tightened by the screws, and the furnace was flushed by a gas current of approx. 1.5 l/min. maintained for half an hour. The gas currents on the electrodes were maintained at 1.5–3 ml/min. (all gas volumes measured at room temperature) *i. e.* approx. 1–2 bubbles per second in the crucibles. Occasionally the electrode gas currents were varied between 1 and 8 ml/min.; this proved to have little or no influence on the EMF.

At the end of the run the lower furnace lid was lowered and the crucibles allowed to cool in a desiccator. The total time of the run varied from 2 to 8 hours.

After being weighed the crucibles were soaked in water, and the contents analysed. The analyses were necessary, because the composition of the melt changed somewhat during a run. This was due in some degree to volatilization of alkali. A more significant cause was the contamination by melts from the previous run, which were left as droplets on the electrodes *etc.* But the dominating factor was that the salt bridge acted as a siphon for the melt. Very frequently there was found a weight loss in one crucible and a corresponding increase in the other. This was difficult to avoid, even when taken into consideration by proper charging of the crucibles. Thus the analyses were indispensable. (It may be mentioned that in run no. 9, where the titrations are lacking, there was as a matter of fact no perceptible siphon action). The titration of carbonate in presence of larger amounts of sulphate has to be performed with an indicator having a pI close to $\text{pH} = 7$ because of the possible co-titration of a fraction of the sulphate. It was found that the best procedure was to titrate with phenol red in constantly boiling liquid (as recommended for the standardization of *N*/100 hydrochloric acid).

Still it proved necessary to apply a correction, especially for the lowest carbonate contents. If the same proportion of the amount of sulphate is cotitrated each time, the correction should take the form of a constant deduction from the total volume of titration, regardless of the magnitude of this volume. By titration of samples with known quantities of sulphate, the value of the correction was found to be -0.048 ml $N/10$ HCl per 5 g sulphate. (Volume of titration about 150 ml).

No free alkali (or acid) could be detected in the pure sulphate, (*i. e.*, less than corresponding to 1 drop $N/100$ HCl = 0.005 ml $N/10$ HCl per 5 g sulphate).

The dichromate-chromate mixtures were analysed by determining the total amount of chromium by means of ordinary iodometric titration. Then the dichromate could be determined by acidimetric titration in the following way: To the water solution an excess of $N/10$ NaOH was added. The solution was heated to boiling, and BaCl_2 was added, whereby the chromate precipitated as BaCrO_4 . The excess of NaOH was then titrated back with $N/10$ HCl.

RESULTS AND DISCUSSION

The system $\text{Na}_2\text{SO}_4\text{--Na}_2\text{CO}_3\text{--CO}_2$

The results from the sulphate — carbonate — carbon dioxide system are shown in Table 1. The values of E_{calc} are calculated from the formula

$$E = \frac{RT}{2F} \ln \frac{N_{\text{II}}}{N_{\text{I}}}$$

where N is the mole per cent of carbonate in the salt mixture as determined by analysis. It is evident that the formula is valid to a high grade of accuracy.

This is also shown in the diagram Fig. 3, where E is plotted against the logarithm of the carbonate mole fraction in the melt. The experimental data are demonstrated in the way that the point for one composition (marked with a vertical bar) has been plotted on a straight line of the theoretical slope $RT/2F$. The other point for the same run (marked with a small circle) is then fixed by the other composition and the observed EMF (adjusted to the temperature of the straight line by multiplying with the factor $T_{\text{obs}}/1223$).

It is evident that the experiments fit the theoretical slope very satisfactorily. This means that the electrode really behaves as an oxygen (oxygen ion) electrode in the melt.

Regarding the difference between the calculated and the observed EMF, $-\Delta E$ in Table 1, — it should be noted that 1 relative per cent error in *one* of the titrations corresponds to an error of 0.5 mV in E_{calc} , and that a number of the titration volumes were very small. For the greater part of the runs the discrepancy thus lies within the analytical uncertainty. The maximum difference (3 mV) between observed and calculated EMF corresponds to 0.02 pO ($\text{pO} = -\log a_{\text{O}^{2-}}$), and the average deviation of observed and calculated pO is less than 0.01.

Table 1. *E.M.F. measurements in concentration cells with the system sodium sulphate — sodium carbonate — carbon dioxide.*

Run No.	Gas	Start		End (analysed)		T_{obs} °K	E_{obs} mV	E_{calc} mV	ΔE mV	Time h
		Mol % Na_2CO_3		Mol % Na_2CO_3						
		N_{I}	N_{II}	N_{I}	N_{II}					
1	B	1	5	1.135	4.595	1227	74.5	73.9	+ 0.6	8
2	B	0.5	5	0.489	4.732	1222	122.3	119.4	+ 2.9	2 ½
3	B	2	10.4	1.937	10.00	1224	86.8	86.5	+ 0.3	4
4	A	2	30	1.954	28.96	1223	144.1	142.0	+ 2.1	5
5	A	2	20	1.966	19.40	1225	121.1	120.8	+ 0.3	5 ½
6	A	2	20	1.967	19.13	1223	120.5	119.8	+ 0.7	5 ½
7	D	2	20	1.992	19.49	1223	120.6	120.1	+ 0.5	5
8	C	2	5	1.990	4.983	1224	48.0	48.4	- 0.3	5 ½
9	C	0.5	2	—	—	1222	73.5	(73.0)	+ 0.5	4
10	C	0.5	2	0.483	2.007	1224	76.0	75.1	+ 0.9	7
11	C	0.00	1	0.0412	0.991	1223	166.8	167.5	- 0.7	3
12	D	5	—	4.879	57.11	1224	131.2	129.8	+ 1.4	4
13	D	2	100	1.953	93.96	1224	206.2	204.2	+ 2.0	2 ½
14	D	0.1	2	0.1374	2.474	1224	154.4	152.4	+ 2.0	3 ½
15	C	2	10.4	1.919	10.089	1324	97.6	94.6	+ 3.0	3
16	C	2	10.4	1.902	9.755	1321	93.1	93.0	+ 0.1	3 ½
17	C	1	5	0.947	4.758	1422	98.0	98.9	- 0.9	2 ½

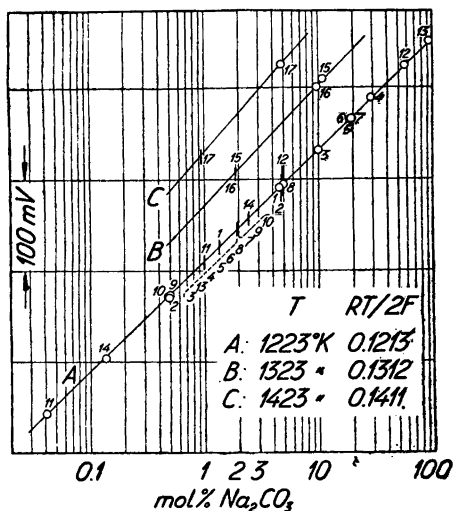
Composition of gas mixtures:

A:	35.6 % CO_2	62.6 % O_2	1.8 % N_2
B:	57 » »		
C:	70.1 » »	29.1 » »	0.8 » »
D:	95.0 » »	4.6 » »	0.4 » »

As the equation above is valid also up to the highest carbonate contents it may be concluded that the system Na_2SO_4 - Na_2CO_3 forms an ideal mixture in the fused state. Further it may be concluded that the liquid junction potential is negligible in a cell containing Na_2SO_4 - Na_2CO_3 mixtures of different compositions.

The two conclusions are obviously reciprocally dependent, but they are reasonable as the simplest explanation to the observations.

Fig. 3. Logarithmic diagram of EMF between oxygen electrodes as a function of the carbonate contents (in mol %) for concentration cells with the system sodium sulphate — sodium carbonate — carbon dioxide.



The system $K_2CrO_4 - K_2Cr_2O_7$

The experiments in the chromate system were of a more preliminary character. Their purpose was to give information about the possibility of using the oxygen electrode in systems with a greater acidity.

The results are given in Table 2. As will be seen from the table, the observed potentials were about 15 % lower than calculated from the theoretical formula

$$E = \frac{RT}{2F} \ln \frac{N_c^{(II)} \cdot N_d^{(I)}}{N_c^{(I)} \cdot N_d^{(II)}}$$

Hence the deviation seems to be proportional to the absolute value of E .

As follows from the equilibrium experiments¹⁵ the deviations from ideality in these mixtures are not of such a magnitude as to explain the observed deviation of EMF. At present it is difficult to give any definite explanation of the deviations. One possibility is that they are due to a liquid junction potential. Compared with the sulphate-carbonate system, in which no liquid junction potential was found, two factors have to be considered. The cation K^+ is larger, and therefore has a lower transport number, than Na^+ . The oxygen ion may contribute considerably to the conductivity on account of a possible relay mechanism, analogous to the H^+ transport in water.

Another possibility must also be taken into account. The chromate-dichromate mixture might have a partial electronic conductivity (compare its dark metallic colour). This would to some extent short-circuit the cell, thus reducing the EMF.

Table 2. *E.M.F. Measurements in concentration cells with the system potassium chromate — potassium dichromate.*

Run No.	Start		End (analysed)		T_{obs} °K	E_{obs} mV	E_{calc} mV		$E_{\text{calc}}/E_{\text{obs}}$
	Mol % $\text{K}_2\text{Cr}_2\text{O}_7$		Mol % $\text{K}_2\text{Cr}_2\text{O}_7$				Start	End	
	N_{d} (I)	N_{d} (II)	N_{d} (I)	N_{d} (II)					
1	20.6	3.9			1265	101	111		1.10
2	20.8	8.4			1257	52	60		1.15
3	20.8	5.1			1263	84	97		1.15
4	22.4	9.6			1259	53	63		1.19
5	21.8	9.7			1258	51	60		1.18
6	41.3	5.2			1258	173	197		1.14
7	22.8	10.4			1251	48	56		1.17
8	22.1	10.1			1248	51	57		1.12
9	21.8	9.9	21.3	9.7	1248	51	58	56	1.14 (1.10)
10	45.6	10.6	45.9	11.5	1248	115	131	127	1.14 (1.10)

Gas: 98 % O_2 2 % N_2

Note: In the chemical analysis of runs 1–8, the method employed (after addition of BaCl_2 direct titration of dichromate with $N/10$ NaOH) was found to give uncertain values, due to occlusion phenomena. As, however, the difference between start- and endpoint compositions seems to be rather unimportant, compared with the relatively large deviations between E_{calc} and E_{obs} , we have laid no stress on reproducing the measurements with correct analysis.

SUMMARY

The investigations deal with the determination of oxygen ion activities in fused salts by means of an oxygen electrode. It is shown that the oxygen ion activity in melts of sodium sulphate-carbonate mixtures in equilibrium with carbon dioxide can be determined very accurately by means of an electrode consisting of platinum in an atmosphere of an oxygen-carbon dioxide-mixture.

In the more acid system, fused chromate — dichromate — mixtures, the measured EMF is about 15 % lower than calculated. Possible reasons for this are discussed.

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