Is the Nernst Equation Applicable to Silver(I) Concentration Cells in Fused Nitrate Medium?

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Further improvements of a previously described high-temperature thermostat for potentiometric measurements in molten salt media are described. From measurements of the emf of cells

$$\text{Ag} \left| \begin{array}{c} C \text{ AgNO}_3 \\ (\text{K,Na})\text{NO}_3 \end{array} \right| \left| \begin{array}{c} C^0 \text{ AgNO}_3 \\ (\text{K,Na})\text{NO}_3 \end{array} \right| \text{Ag}$$

at 280°C it is safely concluded that the activity factor for silver ion remains constant in the range 10^{-4} mol kg^{-1} $\leq C \leq 1$ mol kg^{-1}. The deviations from Nernst's equation at very high and very low C are discussed. For $C < 10^{-4}$ mol kg^{-1} the deviations may be attributed to an increment in the silver ion content of the melt, mainly by corrosion.

Concentrations, in mol fractions or in molality units, of solute species, have frequently been used for activities in studies on, e.g., silver(I) complexation in nitrate melts. This is often justified by an experimental verification of the approximate applicability of the Nernst equation in the form

$$E = E_0 - RTF^{-1} \ln 10 \log C \qquad (1)$$

for the emf, E, of concentration cells of the general type

$$\text{Ag} \left| \begin{array}{c} C \text{ AgNO}_3 \\ \text{MNO}_3(\text{l}) \end{array} \right| \left| \begin{array}{c} C^0 \text{ AgNO}_3 \\ \text{MNO}_3(\text{l}) \end{array} \right| \text{Ag}$$

(cf. Ref. 1 and references quoted therein). M stands for an alkali metal or an alkaline earth metal or a mixture of two or more of them.

The measurements are often said to be described by Nernst's equation e.g. to within 1 mV. In cases when the experimental value of RTF^{-1} ln 10 has been given explicitly by an author, this value is, however, as a rule somewhat smaller than the theoretical one. For instance, in (K,Na)NO$_3$(l) Flengas and Rideal[2] found 102.8 mV at 250°C (theoretical: 103.4 mV), Duke and Garfinkel[3] found 124 mV at 366°C (theoretical: 126 mV), Cigén and Mannerstrand[4] found 108.1 mV at 280°C (theoretical: 109.7 mV) and Holmberg[1] later found (109.2 ± 0.2) mV at the same temperature with a different design of the thermostat. Actually, there seem to be no accurate measurements on this cell in equimolar (K,Na)NO$_3$(l), which have confirmed that Nernst's equation in the simple form (1) can perfectly describe the results over a very wide concentration range.

Deviations of about 1 % are often considered to be of minor importance in studies on complex formation in melts, but they are, from a general thermodynamic point of view, very unsatisfactory. This is so because the deviations from the theoretical values are of a systematic nature and are as a rule outside the limits of uncertainty as predicted from the estimated random errors in the measurements. A linear relationship between E and log C is generally taken as a proof for constancy of the activity factor for silver ions. The linearity in itself does not prove, however, that the activity factor is constant. It may change in a way that can be expressed by the equation

$$\ln \gamma = \left(\frac{kF}{RT \ln 10} - 1 \right) \ln C + constant \qquad (2)$$

within the range of linearity. (γ stands for the activity factor and k is the experimentally obtained slope for E vs. log C.)

Hence, if the linearity persists when C is varied over four powers of ten, a deviation of 1 % from the theoretical value of the slope

might have its origin in a change of γ by about 10 % over this concentration range, provided the liquid junction potentials are negligible. If eqn. (2) is used to explain the non-theoretical value of k, it means that the melts are significantly non-ideal. This conclusion is most disturbing for the calculation of complexity constants — and even so for deciding which complex species exist in the melts — since these calculations presuppose ideal solutions.

From previous studies [1,4,5] at this laboratory it has become evident that heat leakage through the electrode wires will give rise to systematic errors in the Nernst slope, simply caused by too low a temperature at the electrode surface. The high precision and reproducibility in the measurements, which is necessary if one wishes to make confident statements on the constancy of activity factors over a very wide concentration range, requires a very careful control of the temperature. In this paper further improvements of a new furnace construction are described, and measurements of the emf of the concentration cell mentioned above are reported. From these measurements more definite conclusions about the ideal behaviour of the liquid system $AgNO_3 - (K,Na)NO_3$ may be drawn.

EXPERIMENTAL

Chemicals used. Potassium nitrate and sodium nitrate (Merck, *p.a.*) were powdered, ground together and dried at 120°C. Selected crystals of silver nitrate (Merck, *p.a.*) were used.

Apparatus. The same kind of electrodes, reference half-cells, and thermostating system as previously described [1] were used, except for two important modifications.

Firstly, the temperature was controlled by a fast cycling, overshoot-free creep controller, type CR/DHS/PID/SCR, from EUROTHERM, Worthing, England. The temperature calibration was carried out by the use of a standard platinum resistance thermometer, immersed in the test melt under operating conditions. During the experiments the test melt temperature was 280.08°C (IPTS — 68) with maximum over-all short-time variations of ± 0.01°C in the bulk melt.

Secondly, the electrode compartment of the asbestos lid was furnished with cylindrical aluminium blocks, embedding the upper part of the electrodes. The blocks were electrically heated to the same temperature as the test melt by means of a separate variable transformer. These electrical heating circuits were temporarily switched off at the very moment of the emf

reading, in order to avoid induction in the electrode wires from the closely situated windings of the heating elements.

The emf was read to 0.1 mV by means of a digital instrument, PHM 52, from Radiometer, Copenhagen.

Procedure. The measurements were performed as titrations. The cell was set up with 250.00 g equimolar $(K,Na)NO_3$ and kept at 280°C without $AgNO_3$ in the test melt for at least 24 h (sometimes 70 h) before the measurements were started. Weighed amounts of $AgNO_3$ or solidified stock melts of $AgNO_3$ in equimolar $(K,Na)NO_3$ were successively added to the test melt. After stabilization of the temperature a stable emf could as a rule be read within 1 min. Repeated series were made with $C^0 = 1$, 0.1, 0.01 or 0.001 mol kg^{-1} in the approximate range 4×10^{-5} mol $kg^{-1} \leq C \leq 3$ mol kg^{-1}.

Analyses. The silver content of the $AgNO_3$ preparations, stock melts, reference melts and the test melt at the end of a series were checked by electroanalytical precipitation of silver on a rotating platinum cathode from hot cyanide solutions.

RESULTS AND DISCUSSION

The electrodes. It is generally recognized [6] that silver wires in electrodes become very brittle even after a rather short exposure to a salt melt at elevated temperature. Sometimes, in rather primitive experimental arrangements, migration of silver on the wire can be observed. These phenomena are obviously due to a recrystallization process, which is probably enhanced by temperature differences in the electrodes and in a melt layer close to the electrode metal surface.
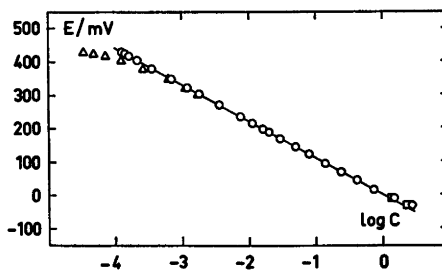
With the experimental arrangement described

Fig. 1. E versus log *C*. Data from a series with a large $\bar{d}$-value. Symbols: uncorrected concentrations, $C_{i,\text{add}}$ ($\triangle$); corrected values according to eqn. (5) (O); concentrations C' according to eqn. (6) ($\square$).

in this paper, temperature differences in the silver electrodes seem to be eliminated. The same electrodes were used throughout all the experiments, and they were exposed to the melt at 280°C for more than seven weeks with occasional periods of *ca* 4 h at room temperature between the measurement series. No change in the mechanical properties of the silver wires could be detected.

The measurements. Fig. 1 gives an example of a plot of E *vs.* log C in a series with $C^0 = 1$ mol kg^{-1}. In the range 10^{-4} mol kg^{-1} $\leq C \leq$ 1 mol kg^{-1} the data of all series fit to linear relationships

$$E = E_0 - k \log C$$

At very low silver(I) concentrations, as calculated from the added amounts of AgNO$_3$, a pronounced deviation from linearity always occurs. In series when the cell was allowed to stand for only about 24 h before the measurements were started, a decrease in the emf with time was observed at the very smallest C-values (*viz.* in the first two or three experimental points). In other cases, when the cell was allowed to stand for *ca.* 70 h before the measurements started, a time-independent, stable emf could be read, even when no addition of AgNO$_3$ to the test melt had been made. (The further calculations and the data of Fig. 1 and Table 1 refer only to stable emf readings.)

The deviation from linearity at low silver(I) concentrations might be due either to the presence of additional redox systems in minor concentrations, causing a mixed electrode potential, or to the fact that the true C is larger than that calculated from the added amount of AgNO$_3$.

The above mentioned time-dependence of the emf could of course mean that the oxidant of the additional redox system corrodes the silver wires, so that an extra amount of silver(I) is introduced into the test melt. Such a small increase in C might also be brought about in other ways, *e.g.* by leakage of reference melt into the test melt through the asbestos fibre connecting the half-cells or by "back exchange" of silver ions for sodium ions between the Pyrex glass equipment and the melt, if the glass had been exposed to melts concentrated in silver(I) in previous experiments. The last explanation is ruled out, however, by the observation that results from experiments performed with fresh Pyrex glass apparatus, do not differ from those where the same glass equipment was used in repeated experimental series.

The magnitude of the deviation seems to be somewhat dependent on C^0 (*cf.* Table 1), which may suggest some contribution by diffusion from the melt in the reference compartment, but probably some type of corrosion of the silver wires [7-9] makes the main contribution to the extra amount of silver(I) present in the test melt.

The silver(I) concentration may be written as

$$C_i = C_{i,\text{add}} + d_i \qquad (3)$$

where i refers to a cell with the emf E_i. $C_{i,\text{add}}$ stands for the concentration, calculated from the added amount of AgNO$_3$, and d_i stands for the extra contribution to the silver(I) concentration. After E_0 and k were determined from the linear part of E_i *vs.* log $C_{i,\text{add}}$, it was assumed that d_i could be calculated from the relation

Table 1. Results from some typical runs.

C^0/(mol kg^{-1})	n_d	$\bar{d} \times 10^5$ mol kg^{-1}	$\overline{\Delta d} \times 10^5$ mol kg^{-1}	n	E_0/mV	$\sigma(E_0)$/mV	k/mV	$\sigma(k)$/mV	$k \log C^0$/mV
1.021	4	8.59	0.07	19	− 0.33	0.09	109.80	0.04	0.99
1.021	4	8.12	0.04	20	− 0.80	0.11	109.69	0.04	0.99
1.021	6	9.02	0.03	20	− 0.19	0.12	109.69	0.05	0.99
0.0994	6	5.17	0.06	20	− 110.04	0.12	109.80	0.05	− 110.08
0.0994	7	6.04	0.09	20	− 109.79	0.10	109.58	0.04	− 109.86
0.01000	5	4.31	0.03	20	− 218.54	0.09	109.52	0.04	− 219.04
0.01000	7	4.56	0.09	19	− 219.03	0.08	109.77	0.03	− 219.54
0.001001	5	4.22	0.02	20	− 329.22	0.14	109.98	0.05	− 329.90
						Average:	109.73	0.04	

$$E_i = E_0 - k \log (C_{i,\text{add}} + d_i) \qquad (4)$$

in the range where an appreciable deviation from linearity is found.

It appeared that the d-values were remarkably constant within a series, but differed significantly between different series. This behaviour suggests that once the emf is stabilized, the melt has got an additional contribution of silver ions, which is not changed when further additions of $AgNO_3$ are made. Therefore, the average value

$$\overline{d} = \frac{1}{n_d} \sum_i d_i$$

was calculated for each series. n_d stands for the number of experimental points used in the calculation of the d_i-values. The total amount of data within each series was then corrected according to

$$C_{\text{corr}} = C_{\text{add}} + \overline{d} \qquad (5)$$

This correction brings about a small change in the values of E_0 and k. The calculations were therefore iterated until the parameters remained constant within the limits of experimental uncertainty.

Fig. 1 shows E vs. $\log C$ for the series with the largest $\overline{d}$ found (9×10^{-5} mol kg^{-1}). The results from some representative series are collected in Table 1. The parameters E_0 and k and the standard deviations $\sigma(E_0)$ and $\sigma(k)$ are computed from least-squares treatments of n experimental points according to $E = E_0 - k \times \log C_{\text{corr}}$ in the concentration range $-4 \leq \log C_{\text{corr}} \leq 0$. The constancy of the d_i-values may be judged from $\overline{\Delta d}$, calculated as

$$\overline{\Delta d} = \frac{1}{n_d} \sum_i \left| \overline{d} - d_i \right|$$

The view that the extra amount of silver ions in the melt remains constant once the emf is stabilized, is supported by the fact that $\sigma(E_0)$, $\sigma(k)$ and $\overline{\Delta d}$ as a rule took their minimum values simultaneously, i.e. when the final corrections of Table 1 were applied, yielding values of k very close to $RTF^{-1} \ln 10$.

The following features of Table 1 should be noticed:

1. The d-value cannot be well reproduced in different series. d ranged between 4×10^{-5} mol kg^{-1} and 9×10^{-5} mol kg^{-1}. An increment in C of this order of magnitude will generally not

influence the results obtained in complex formation studies.

2. There is some decrease in $\overline{d}$ with decreasing C^0, suggesting some influence of the reference half-cell melt on $\overline{d}$.

3. In some experiments, when the cell was allowed to stand for more than 70 h before any $AgNO_3$ had been added to the test melt, a stable emf could be read, corresponding to a small silver(I) concentration in the test melt. This concentration was found to coincide very well with the value of $\overline{d}$ for the actual series.

4. Series with the same value of C^0 give somewhat different E_0-values. The maximum differences amount to about 0.6 mV, whereas $3\sigma(E_0)$ amounts to about 0.3 mV as a rule. These numbers reflect the difficulty in reproducing the properties of the junction between the half-cells.

5. The differences between $k \log C^0$ and E_0 are of the same order of magnitude as those between the E_0-values referring to the same C^0, except for $C^0 = 1$ mol kg^{-1}, where the experimental E_0 is about 1.2 to 1.8 mV smaller than $k \log C^0$. This is expected, since a small deviation from linearity at high values of C starts just around $C = 1$ mol kg^{-1} (vide Fig. 1).

6. The variations in k between different series are small (≈ 0.2 mV). The experimental values are closely gathered around the theoretical $RTF^{-1} \ln 10 = 109.75$ mV.

7. The standard deviations $\sigma(E_0)$ and $\sigma(k)$ are remarkably small, indicating very small random errors in the measurements. This, as well as the coincidence between the experimental and the theoretical value of k, is evidently a consequence of the work on improving the temperature uniformity in the system.

From the results discussed above, it is obvious that concentrations on the molality scale can be used for activities for silver(I) in the range $-4 \leq \log C \leq 0$ in the $AgNO_3 - (K,Na)NO_3(l)$ system. In this range the simple Nernst equation (1) describes the results from emf measurements, provided that the thermostating of the system is good enough.

In more concentrated solutions a weak deviation from the ideal curve occurs. These deviations may be reduced if another concentration unit is used, viz.

$$C' = C \times 10.747/(C + 10.747) \qquad (6)$$

where C is expressed in molality units. C' is proportional to mol fractions and coincides with C at small values of C. Still, however, a weak deviation remains (*cf.* Fig. 1). This behaviour might be due to a change in the activity factor, γ for silver ions, and to increased liquid junction potentials. The junction potentials may be roughly estimated and corrected for as done by Boxall and Johnsson,[9] according to Klemm's [10] method, leaving a remaining deviation from the straight line of 1 to 5 mV at $C = 2$ mol kg^{-1}. If this effect is thought to be caused exclusively by a change in γ on increasing C from 1 mol kg^{-1}, this change would amount to some five percent. (At concentrations below 1 mol kg^{-1} the junction potentials, as estimated in this way, are on the whole negligible.)

Obviously no safer conclusion about the thermodynamics of these more concentrated melts can be drawn from measurements of this kind, but the deviations from ideality that may occur at values of C around 2 mol kg^{-1} are certainly not very large.

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