The Thermoelectric Power of the Molten Systems $(Ag+Li)NO_3$, $(Ag+Na)NO_3$, and $(Ag+K)NO_3$ *

CESARE SINISTRI

Institute of Physical Chemistry, University of Pavia, Italy

(Z. Naturforschg. **21 a**, 753—755 [1966]; received 7 March 1966)

In a silver electrodes thermocell the thermoelectric power ε_0 at zero time of the molten salt mixtures $(Ag+Li)NO_3$ and $(Ag+Na)NO_3$ at the mean temperature of 340 °C, and of $(Ag+K)NO_3$ at the mean temperature of 360 °C has been measured.

On the basis of these data the transport heats of lithium, sodium and potassium ions in their respective pure nitrates have been roughly evaluated. Moreover a thermodynamical ideal model for the molten salt mixtures in respect to the transport properties is suggested.

The study of the thermoelectric power of systems with variable composition has shown interesting results in the case of water solutions [1]. In molten salt mixtures only the thermoelectric power of the system $(Ag+Na)NO_3$ has been studied. Already in 1890 POINCARÉ [2] mentioned that the thermal emf increases as the silver nitrate concentration diminishes. Recently [3–4] measurements at 310 °C have been made on the same system.

In the present work the thermoelectric power of the $(Ag+Li)NO_3$ and $(Ag+Na)NO_3$ binary mixtures has been measured at the mean temperature of 340 °C and of $(Ag+K)NO_3$ mixtures at the mean temperature of 360 °C, by the use of the thermocell:

$$\text{final stage}\ \Big|\ \underset{T_1}{Ag_{(s)}}\ \Big|\ (Ag+X)NO_3\ \Big|\ \underset{T_2}{Ag_{(s)}}\ \Big|\ \text{final stage} \qquad (1)$$

$(X = Li,\ Na,\ K)$.

The thermal emf was measured at zero time to eliminate every effect of thermodiffusion.

Experimental

The measuring cell, made of pyrex, was similar to the one already used for pure $AgNO_3$ [5]. A small vertical tube was inserted between the two arms of the cell. By means of an external pressure it was thus possible to separate the melt of the warm arm from that of the cold arm. In order to avoid thermodiffusion effects, the melts have been contacted during the actual emf-measurement only.

Special care has been taken in the case of mixtures containing $LiNO_3$ to prevent thermal decomposition: some ε_0 values for these mixtures have been obtained by extrapolation to 340 °C, starting from measurements taken at lower temperature.

The salts employed (C. Erba products), were carefully dried before use. The silver electrodes were made of a wire (0.4 mm ⌀) of at least 99.99% purity.

Results and Discussion

The experimental results are shown in Table 1, where x_{AgNO_3} = molar fraction and $\varepsilon_0 \equiv \Delta\Phi_0/\Delta T$. The function ψ is defined later on (see Eq. 5). The same data are also reported in Fig. 1. In every case the dilution of the solutions has never been carried on below $x_{AgNO_3} = 0.005$, as the ε_0 values in this area become hardly reproducible.

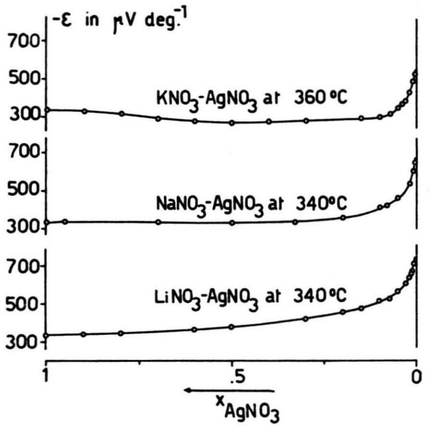

Fig. 1. Values ε_0 (μV degree^{-1}) as function of x_{AgNO_3}.

---

* Work carried out with the aid of the Consiglio Nazionale delle Ricerche (Rome).

[1] See e. g. R. HAASE, Thermodynamik der irreversiblen Prozesse, Steinkopff Verlag, Darmstadt 1963; p. 424.

[2] L. POINCARÉ, Ann. Chim. Phys. (6) **21**, 289 [1890].

[3] R. SCHNEEBAUM and B. R. SUNDHEIM, Disc. Faraday Soc. **32**, 197 [1961].

[4] B. R. SUNDHEIM and J. D. KELLNER, J. Phys. Chem. **69**, 1204 [1965].

[5] C. SINISTRI, Z. Naturforschg. **20 a**, 1045 [1965].

System $LiNO_3 + AgNO_3$ at 340 °C			System $NaNO_3 + AgNO_3$ at 340 °C			System $KNO_3 + AgNO_3$ at 360 °C		
x_{AgNO_3}	$-\varepsilon_0$ (μV deg.$^{-1}$)	ψ (cal deg.$^{-1}$ · mole^{-1})	x_{AgNO_3}	$-\varepsilon_0$ (μV deg.$^{-1}$)	ψ (cal deg.$^{-1}$ · mole^{-1})	x_{AgNO_3}	$-\varepsilon_0$ (μV deg.$^{-1}$)	ψ (cal deg.$^{-1}$) · mole^{-1})
1,00	330	0,00	1,00	330	0,00	1,00	332	0,00
0,90	339 ± 1	+ 0,02	0,95	337 ± 1	− 0,07	0,90	325 ± 2	+ 0,39
0,80	344 ± 2	+ 0,14	0,70	333 ± 1	+ 0,62	0,80	313 ± 2	+ 0,90
0,60	365 ± 2	+ 0,20	0,50	330 ± 1	+ 1,37	0,70	289 ± 3	+ 1,68
0,50	378 ± 3	+ 0,26	0,33	336 ± 2	+ 2,06	0,60	276 ± 3	+ 2,30
0,30	419 ± 2	+ 0,33	0,20	360 ± 2	+ 2,51	0,50	268 ± 3	+ 2,85
0,20	458 ± 4	+ 0,25	0,10	414 ± 3	+ 2,64	0,40	273 ± 3	+ 3,19
0,15	470 ± 4	+ 0,52	0,080	424 ± 2	+ 2,86	0,30	279 ± 4	+ 3,60
0,10	513 ± 5	+ 0,36	0,050	462 ± 4	+ 2,90	0,15	297 ± 5	+ 4,56
0,070	526 ± 4	+ 0,74	0,020	539 ± 5	+ 2,96	0,10	303 ± 4	+ 5,25
0,050	562 ± 5	+ 0,60	0,010	602 ± 5	+ 2,88	0,070	317 ± 3	+ 5,61
0,030	604 ± 3	+ 0,64	0,005	649 ± 12	+ 3,16	0,050	349 ± 3	+ 5,56
0,020	632 ± 3	+ 0,81				0,040	369 ± 5	+ 5,56
0,0136	656 ± 5	+ 1,02				0,030	383 ± 4	+ 5,78
0,0117	668 ± 7	+ 1,04				0,020	430 ± 6	+ 5,52
0,0068	710 ± 6	+ 1,15				0,010	490 ± 8	+ 5,51
						0,005	524 ± 10	+ 6,09

Table 1. Values of the thermoelectric power ε_0 and of the parameter ψ for the systems (Li, Na, K)NO_3+AgNO_3.

The data reported here for the system $(Ag + Na)NO_3$ agree satisfactorily with the results of SCHNEEBAUM and SUNDHEIM [3] obtained at the mean temperature of 310 °C.

On the basis of the thermodynamics of irreversible processes it has already been shown in previous papers [6, 7], that the temperature coefficient of the initial thermal emf $\Delta\Phi_0$ for the thermocell (1) and for ΔT sufficiently small, is given by:

$$\varepsilon_0 \equiv \frac{\Delta\Phi_0}{\Delta T} = \frac{1}{F}\left(S_{Ag} - S_{Ag^+} - S_e{}^* - t_{Ag^+}\frac{Q^*_{Ag^+}}{T} - t_{X^+}\frac{Q^*_{X^+}}{T}\right) \tag{2}$$

In this equation ΔT is the difference of temperature between the two electrodes and $\Delta\Phi_0$ the correspondent thermal emf at zero time; F is FARADAY's constant; S_{Ag} the entropy of metallic silver; S_{Ag^+} the partial molar entropy of the silver ion [8] in the melt; $S_e{}^*$ the entropy of transport of the electron in the metallic silver; t_{Ag^+} and t_{X^+} are HITTORF's transport numbers of the silver and X^+ ions, both referred to the velocity of NO_3^-; T the average temperature of the system; $Q^*_{Ag^+}$ and $Q^*_{X^+}$ the heats of transport of the silver and alkaline ions.

Eq. (2), for $x_{AgNO_3} \to 1$ (in these conditions [9] $t_{Ag^+} \to 1$ and $t_{X^+} \to 0$) becomes:

$$\begin{aligned}\varepsilon_{AgNO_3} &= (1/F)\ (S_{Ag} - {}^0S_{Ag^+} - {}^0Q^*_{Ag^+}/T - S_e{}^*)\\ &= (1/F)\,(S_{Ag} - {}^0S^*_{Ag^+} - S^*_e)\end{aligned} \tag{3}$$

which, obviously, is the equation for pure salts [5–7]. The quantities ${}^0S$ and ${}^0Q$ are referred to pure salt.

For the molar entropy S_{Ag^+} of the silver ion in a mixture

$$S_{Ag^+} = {}^0S_{Ag^+} - R\ln x_{Ag^+} + s^e_{Ag^+}. \tag{4}$$

Here $-R\ln x_{Ag^+}$ represents the configurational contribution to the entropy, $s^e_{Ag^+}$ represents the excess entropy terms in comparison with configurational terms ($s^e_{Ag^+} = 0$ for $x_{Ag^+} = 1$). It must be pointed out that, using the TEMKIN model for the molten salt mixtures, x_{Ag^+} represents the cationic fraction of the silver ions, equal to x_{AgNO_3}, in this particular case.

By subtracting Eq. (3) from Eq. (2) and using Eq. (4), one obtains

$$\begin{aligned}\psi &\equiv F(\varepsilon_0 - \varepsilon_{AgNO_3}) - R\ln x_{Ag^+}\\ &= \frac{{}^0Q^*_{Ag^+}}{T} - \frac{Q^*_{Ag^+}}{T} + T_{X^+}\left(\frac{Q^*_{Ag^+} - Q^*_{X^+}}{T}\right) - s^e_{Ag^+}.\end{aligned} \tag{5}$$

The new function ψ, defined by Eq. (5), contains only directly measurable quantities (ε_0, ε_{AgNO_3} and x_{Ag^+}). This function becomes zero for $x_{AgNO_3} \to 1$, while for $x_{AgNO_3} \to 0$ it tends to the finite value ψ_0:

$$\psi_0 = ({}^0Q^*_{Ag^+} - {}^0Q^*_{X^+})/T - (s^e_{Ag^+})_{AgNO_3=0}. \tag{6}$$

The behaviour of the functions $\psi(x_{AgNO_3})$ for the binary mixtures studied is shown in Fig. 2. By extrapolation for $x_{AgNO_3} = 0$ the following values have been obtained: for $(Ag + Li)NO_3$ at 340 °C $\psi_0 = 1.3$;

---

[6] C. SINISTRI, Ric. Sci., Teil II-A, **32**, 492 [1962].

[7] H. SCHÖNERT and C. SINISTRI, Z. Elektrochem. **66**, 413 [1962].

[8] The word "ion" must be understood in the sense of "ion constituent" as already discussed previously [6, 7].

[9] C. SINISTRI, J. Phys. Chem. **66**, 1600 [1962].

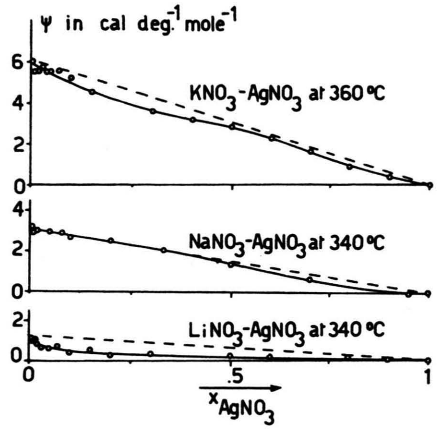

Fig. 2. Values of ψ (cal·degree^{-1}·mole^{-1}) as function of x_{AgNO_3}. Dashed lines represent the ideal behaviour of these systems.

for $(\text{Ag}+\text{Na})\text{NO}_3$ at 340 °C $\psi_0=3.1$ and for $(\text{Ag}+\text{K})\text{NO}_3$ at 360 °C $\psi_0=6.0$ cal·degree^{-1} ·mole^{-1}. So if the values of the quantities $(s^{\text{e}}_{\text{Ag}^+})_{\text{AgNO}_3=0}$ are known, from (6), a relative evaluation of the heats of transport of the ions studied is possible.

In previous works [10] the excess entropies of mixtures at the temperature of solid-liquid equilibrium have been estimated for some AgNO_3+alkali nitrate systems. The excess entropy has proved, as expected from UBBELOHDE's [11] theories, to be almost always positive. A rough evaluation of $(s^{\text{e}}_{\text{Ag}^+})_{\text{AgNO}_3=0}$ in the $(\text{Ag}+\text{Li})\text{NO}_3$ mixture gives $0.5-0.6$ cal·degree^{-1} ·mole^{-1} for the melting temperature of LiNO_3 (253.1 °C), and a value of about $0.2-0.3$ for the $(\text{Ag}+\text{K})\text{NO}_3$ mixture at the melting temperature of KNO_3 (333.9 °C). In accordance with UBBELOHDE's theories, these excess entropies decrease rapidly with increasing temperature. For the system $(\text{Ag}+\text{Na})\text{NO}_3$, measurements taken at 320 °C show that the mixture entropy is about ideal [12]. Finally, according to KETELAAR [13], the excess entropy is practically zero in the $(\text{Ag}+\text{X})\text{NO}_3$ (X = Li, Na, K, Rb, Cs) molten mixtures at 337 °C.

As we have no other available data, the quantities $T\psi_0$ can be assumed as rough approximations for the heats of transport of lithium, sodium and potassium ions in pure nitrates, referred to ${}^0Q^*_{\text{Ag}^+}=0$. One finds: ${}^0Q^*_{\text{Li}^+}=-0.8$, ${}^0Q^*_{\text{Na}^+}=-1.9$, ${}^0Q^*_{\text{K}^+}=-3.8$ kcal·mole^{-1}.

It is now possible to suggest the following thermodynamic model of ideal behaviour of binary mixtures with a common ion, in regard to transport processes. Assuming that in an ideal mixture, the three following conditions are valid: a) the excess entropic terms are zero in the whole concentration field; b) the heats of transport of the single ions are constant and independent from concentration; c) the HITTORF transport numbers of the two cations are equal to the respective ionic fractions (i. e. $t_{\text{Ag}^+}=x_{\text{Ag}^+}$ and $t_{\text{X}^+}=x_{\text{X}^+}$); then the function $\psi_{\text{id.}}$ is given, according to (5) by:

$$\psi_{\text{id.}}=\frac{{}^0Q^*_{\text{Ag}^+}-{}^0Q^*_{\text{X}^+}}{T}\,(1-x_{\text{AgNO}_3}). \qquad (7)$$

Therefore the function $\psi_{\text{id.}}(x_{\text{AgNO}_3})$ can be represented by a straight line with a slope equal to

$$-({}^0Q^*_{\text{Ag}^+}-{}^0Q^*_{\text{X}^+})/T.$$

In Fig. 2 the behaviour of (7) is shown by a dashed line. It is interesting to observe in Fig. 2 how all three systems are not too far from the ideal law expressed by Eq. (7), the negative deviations beeing rather limited for the $(\text{Ag}+\text{Na})\text{NO}_3$ and $(\text{Ag}+\text{K})\text{NO}_3$ systems and more considerable for the $(\text{Ag}+\text{Li})\text{NO}_3$ system. Of course it cannot be excluded that this behaviour results from internal compensations of parameters rather than the adaptation of the ideal conditions suggested.

---

[10] C. SINISTRI and P. FRANZOSINI, Ric. Sci., Teil II-A, **33**, 419 and 439 [1963].

[11] W. J. DAVIS, S. E. ROGERS and A. R. UBBELOHDE, Proc. Roy. Soc. London **A 220**, 14 [1953].

[12] C. SINISTRI, Ric. Sci., Teil II-A, **31**, 56 [1961].

[13] J. A. A. KETELAAR, J. Chim. Phys. **61**, 44 [1964].