Thermoelectric Properties of Fused Alkali Nitrate–Silver Nitrate Systems *

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(Z. Naturforsch. **23 a**, 1155—1157 [1968]; received 21 May 1968)

In a thermocell with silver electrodes the thermoelectric power ε at zero time of the molten systems $(Ag+Rb)NO_3$ and $(Ag+Cs)NO_3$ at various temperatures has been measured.

These data, combined with previous measurements [1], allow to obtain information about the heat and electricity transport phenomena in the fused systems ($AgNO_3$+alkali nitrates).

In a previous paper [1] we have measured the thermoelectric power of the binary mixtures $(Ag+Li)NO_3$, $(Ag+Na)NO_3$, and $(Ag+K)NO_3$. In order to complete this study, we report in the present work some results obtained on the thermoelectric properties of the mixtures of silver nitrate with rubidium or cesium nitrates.

Experimental

The measuring "U" shaped cell, made of pyrex, was placed in an aluminium block divisible into two pieces. The differential heating of one of the two arms of the cell was obtained by means of Thermocoax resistances (Philips).

All other experimental features had been previously described [1, 2]. The salts employed, $AgNO_3$ (C. Erba RP), $RbNO_3$ (Merck) and $CsNO_3$ (BDH) were carefully dried before use.

Results and Discussion

In Figs. 1 and 2 the results obtained for the two examined mixtures are reported: the values of ε, the thermoelectric power at zero time, are plotted as a function of the mean temperature of the system. For the $(Ag+Rb)NO_3$ system ten different compositions have been studied at temperatures which allow to obtain interpolated values at 360 °C. For the $(Ag+Cs)NO_3$ system nine different compositions have been studied. In this case, owing to the high melting point of $CsNO_3$ (406 °C), the values of ε at 360 °C for mixtures rich in $CsNO_3$ could be obtained only by extrapolations.

In both cases the absolute value of the thermoelectric power increases with temperature: this is also the case for pure $AgNO_3$ (l. c. [2]).

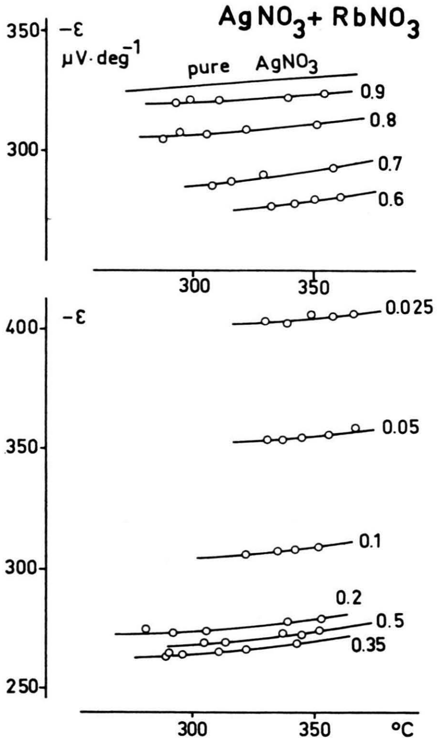

Fig. 1. Values of ε vs. the mean temperature of the thermocell, for the $(Ag+Rb)NO_3$ system. The numbers recorded near the curves represent the molecular fractions of $AgNO_3$.

The ε values for the mean temperature of 360 °C are summarized in Table 1, where, near the compositions of the mixtures, values of Ψ and Ψ' functions [see Eq. (1) and (2)] are also reported. The figure corresponding to $x_{AgNO_3}=0.05$, which is somewhat uncertain for having been obtained by extrapolation, appears in parenthesis.

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* Work carried out with the aid of the "Consiglio Nazionale delle Ricerche".

[1] C. Sinistri, Z. Naturforsch. **21 a**, 753 [1966].

[2] C. Sinistri, Z. Naturforsch. **20 a**, 1045 [1965].

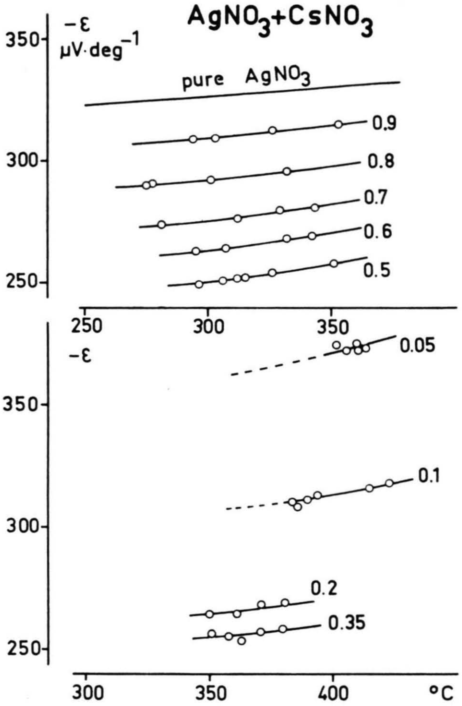

Fig. 2. Values of ε vs. the mean temperature of the thermocell, for the $(Ag+Cs)NO_3$ system. The numbers recorded near the curves represent the molecular fractions of $AgNO_3$.

x_{AgNO_3}	System $(Ag+Rb)NO_3$ $-\varepsilon$	Ψ	Ψ'	System $(Ag+Cs)NO_3$ $-\varepsilon$	Ψ	Ψ'
1.00	332	0.00	0.00	332	0.00	0.00
0.90	324	0.39	0.38	316	0.58	0.57
0.80	313	0.88	0.85	299	1.20	1.18
0.70	294	1.58	1.51	284	1.82	1.81
0.60	281	2.19	2.06	271	2.42	2.32
0.50	275	2.69	2.49	260	3.04	2.89
0.35	271	3.49	3.15	254	3.88	3.62
0.20	280	4.40	3.89	266	4.72	4.33
0.10	311	5.06	4.41	308	5.13	4.64
0.05	356	5.40	4.68	(362)	(5.26)	(4.71)
0.025	405	5.64	4.88	—	—	—

Table 1. Interpolated values of the thermoelectric power ε (μV deg^{-1}) and of the Ψ and Ψ' (cal deg^{-1} mole^{-1}) functions for the systems $(Ag+X)NO_3$ (X=Rb, Cs) at 360 °C.

In Fig. 3 are shown the ε values as a function of the concentration for the five binary systems formed by $AgNO_3$ with the alkali metal nitrates. Data for the systems $Ag+(Li, Na, K)NO_3$ have already been published[1].

The mixtures $(Ag+Li)NO_3$ and $(Ag+Na)NO_3$ show a distinct trend, while the remaining systems behave similarly with partial overlapping of the functions $\varepsilon(x_{AgNO_3})$.

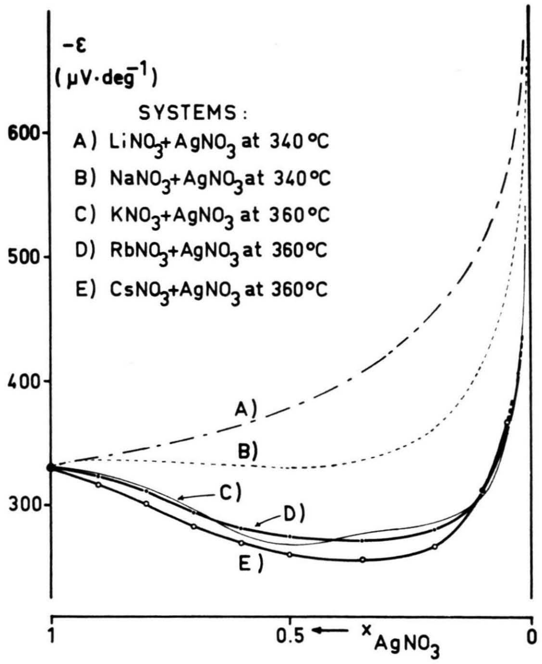

Fig. 3. Values of ε versus composition for the systems $(Ag+Rb)NO_3$ and $(Ag+Cs)NO_3$ at 360 °C. There are also plotted the functions for the systems $(Ag+Li)NO_3$, $(Ag+Na)NO_3$ and $(Ag+K)NO_3$ previously reported[1].

The behaviour of these mixtures in connection with the heat and electricity transport phenomena can be analized by means of the Ψ function defined as[1]:

$$\Psi \equiv \mathcal{F}(\varepsilon - \varepsilon_{AgNO_3}) - R \ln x_{Ag^+} \qquad (1)$$
$$= ({}^0Q^*_{Ag^+} - Q^*_{Ag^+})/T + t_{X^+}(Q^*_{Ag^+} - Q^*_{X^+})/T - s^e_{Ag^+}.$$

In this equation the symbols have the usual meaning[1], and the Hittorf's reference system for velocities ($\boldsymbol{v}_{NO_3^-} = 0$) has been assumed. If the excess entropy terms $s^e_{Ag^+}$ are available, it is possible to define a corrected Ψ' function:

$$\Psi' \equiv \Psi + s^e_{Ag^+}. \qquad (2)$$

For the systems here examined, KETELAAR and DAMMERS-DE KLERK[3], combining electromotive measurements with calorimetric data, have given an estimation of the magnitude of the excess entropy. Employing their data it is possible to evaluate Ψ'.

In Table 1 both these functions are reported, while in Fig. 4 the behaviour of $\Psi'(x_{AgNO_3})$ is shown for the five binary systems investigated. The

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[3] Y. A. A. KETELAAR and A. DAMMERS-DE KLERK, Koninkl. Ned. Akad. Wetenshap., Proc. Ser. B **68**, 169 [1965].

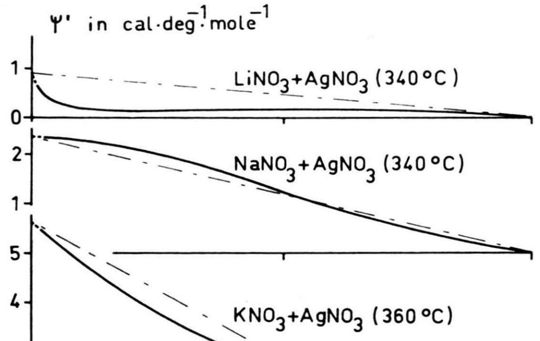

Fig. 4. Behaviour of the Ψ' functions for the systems $AgNO_3$ + Alkali nitrates. Dashed lines represent the ideal behaviour.

excess entropy terms being quite small, the features of the $\Psi(x_{AgNO_3})$ functions are not substantially changed.

Salt	Ψ_0' (cal deg^{-1} mole^{-1})	$^\circ Q^*_{Ag^+} - {}^\circ Q^*_{X^+}$ (kcal/mole)
$LiNO_3$	0.9	0.6
$NaNO_3$	2.5	1.5
KNO_3	5.7	3.6
$RbNO_3$	5.1	3.2
$CsNO_3$	4.8	3.0

Table 2. Values of Ψ_0' (obtained by extrapolation of Ψ' for $x_{AgNO_3}=0$) and relative values of the heats of transport for the five alkali nitrates.

Extrapolated values Ψ_0' (for $x_{AgNO_3}=0$) are reported in Table 2. Only for the system containing lithium nitrate the extrapolation presents some difficulties: the quantities given for this system must therefore be considered as approximated.

The Ψ_0' data are related to the heats of transport of the cations in pure salts ($^0Q^*$), by the equation:

$$\Psi_0' = ({}^0Q^*_{Ag^+} - {}^0Q^*_{X^+})/T\,. \tag{3}$$

Assuming ${}^0Q^*_{Ag^+}=0$, this relation inables to calculate relative values of the heats of transport of the alkali cations in pure nitrates. These data are reported in Table 2.

By means of these heats of transport it is possible to predict the ideal behaviour of the function $\Psi'(x_{AgNO_3})$. Now the conditions for ideality are the following only: a) the heats of transport of the single ions are additive; b) the Hittorf's transport numbers of the two cations are equal to the respective ionic fractions. This ideal behaviour is shown, in Fig. 4, by the dashed lines.

The systems showing the greatest deviations from ideality are those containing the lithium ion and the cesium ion: in these two cases the deviations are opposite. On the contrary the two systems containing the sodium ion and the rubidium ion are very close to the ideal behaviour, while intermediate deviations are presented by the systems containing the potassium ion.

It is interesting to observe that, if we assume as additive the heats of transport only, the ratio Ψ_0'/Ψ' gives directly the value of the Hittorf's transport number of the alkali cation in the mixture.

Some measurements of transference numbers on the mixtures $(Ag+Na)NO_3$ and $(Ag+K)NO_3$ have been reported in literature [4, 5]. Since however these are scanty and somewhat uncertain, no comparison with the present data can be made on a quantitative basis. Nevertheless, particularly for the system containing $NaNO_3$, the Hittorf's transport numbers of the cations are very close to their ionic fractions. It seems therefore, that a least for these two systems, the heats of transport are almost additive.

Careful measurements of transport numbers on all these systems would be highly desirable, in order to verify on a quantitative basis, a possible non additivity of the heats of transport.

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[4] F. R. Duke, R. W. Laity, and B. Owens, J. Electrochem. Soc. **104**, 299 [1957].

[5] F. R. Duke and B. Owens, J. Electrochem. Soc. **105**, 476 [1958].