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**ISOTHERMAL TRANSPORT PROCESSES
IN MOLTEN SALTS BINARY SYSTEMS**

by

A. BERLIN*, S. FORCHERI, B. LANGEVIN* and V. WAGNER****

* Stable Isotope Department, C.E.N. Saclay

** Euratom

1966



Joint Nuclear Research Center
Ispra Establishment - Italy

Materials Department
High Temperature Chemistry

Paper presented at the 16th CITCE Meeting,
Budapest, September 5 - 10, 1965

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The inert support was provided by a thin layer of fritted porous ceramic oxides (Al_2O_3 , MgO or ZrO_2) fixed on strips of sintered ceramic oxides (Al_2O_3 or ZrO_2) with zero open porosity.

In both the systems $(\text{Cs-Ag})\text{NO}_3$ and $(\text{Na-Tl})\text{NO}_3$ the measured transport numbers vary in a non-linear way with composition, indicating that ionic mobilities are not constant.

From the transport parameters liquid junctions potentials were calculated. These values never exceed 8 mV $(\text{Cs-Ag})\text{NO}_3$, and 3 mV $(\text{Na-Tl})\text{NO}_3$.

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Summary

Transport numbers determinations in the molten systems (Cs-Ag)NO₃ at T=240°C, (Na-Tl)NO₃ at T=320°C and in CsNO₃ rich region of (Na-Cs)NO₃ system at T=440°C, were carried out by means of an ionophoretic technique.

The inert support was provided by a thin layer of fritted porous ceramic oxides (Al₂O₃, MgO or ZrO₂) fixed on strips of sintered ceramic oxides (Al₂O₃ or ZrO₂) with zero open porosity.

In both the systems (Cs-Ag)NO₃ and (Na-Tl)NO₃, the measured transport numbers vary in a non-linear way with composition, indicating that ionic mobilities are not constant.

From the transport parameters liquid junction potentials were calculated. These values never exceed 8 mV (Cs-Ag)NO₃, and 3 mV (Na-Tl)NO₃.

Introduction

The determination of the transport numbers in a molten binary mixture with the classical porous plug method (1,2), presents the disadvantage that the precision of the measurement for a given species depends upon its concentration in the melt. Thus the determination of mobility of an extraneous ion in a molten salt in which its concentration is vanishingly small is impossible.

The ionophoretic method coupled with the use of radioactive isotopes overcomes this difficulty, the precision of the determination being principally a function of the precision with which the displacement of the labelled zone is measured.

The ionophoretic method in fused salts utilizes, in general, as inert support, asbestos (3) and borosilicate glass fibers (4,5). We have preferred the use of porous thin layers of fritted ceramic oxides (Al_2O_3 , MgO or ZrO_2) fixed on salt proof strips of sintered ceramic oxides (Al_2O_3 or ZrO_2), for the following reasons:

- Possibility of varying the thickness of the thin layer. This permits to vary the quantity of salt per unit of area and to choose the optimum work conditions for the system under investigation.
- Refractory and chemical compatibility characteristics of the strips. These can be used with corrosive salts and to high temperature.
- The high temperature of the preparation procedure guarantees, at some extent, an inactive state of the support surface.

Exchange reactions (6) or chemisorption with the molten system cannot take place. Besides the specific area of the

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support surface is small.

- Possibility of using the same strip many times permits to work with constant cell characteristics.

In this work this ionophoretic method was used in order to carry out some determinations of transport numbers and ionic mobilities in molten binary nitrate mixtures.

The knowledge of the ionic transport parameters of the molten binary systems, which is at present poor (1,2, 7,8,9) is helpful for understanding the mechanism of ionic migration in melts, and it permits the evaluation of the liquid junction potential.

Experimental

Chemical Reagents

All the reagents were pure for analysis Merck Co. products. The radioisotopes Na^{22} and Tl^{204} have been supplied by the Radiochemical Centre Amersham (England). Ag^{110} and $\text{Cs}^{134\text{m}}$ were prepared directly in the EL3 reactor at Saclay (France).

Preparation of the fritted strips

The alumina and zirconia strips (Al-23 and Zr-23) were expressly prepared by the firm Degussa (Frankfurt/M. Germany).

The strip (cm. $0.6-2 \times 10^{-30}$) is first sanded and then the molten ceramic oxide is spread on the sanded surface with a flame spray gun. (Apparatus Flame Spray and Plasma Jet Metco). The thickness of the fritted layers thus obtained varies from 5 to 40 mg/cm^2 .

Electromigration procedure

The strip is connected to the reservoirs by means of two small pieces of likewise treated strips, and conditioned with molten salt by impregnation through capillary action.

The ratio of the quantity of salt to the fritted ceramic oxide varies normally from 0.3 to 2 depending on the preparation procedure. The electromigration cell is placed in a controlled atmosphere furnace in which the temperature is maintained constant to $\pm 2^\circ\text{C}$ over a length of forty centimeters.

The electrophoresis experiment is performed by placing the radioactive tracer ($\text{Na}^{22}\text{NO}_3$, $\text{Ag}^{110}\text{NO}_3$, $\text{Tl}^{204}\text{NO}_3$ and $\text{Cs}^{134\text{m}}\text{NO}_3$) on the strip and applying an electrical gradient of $3-10 \text{ V cm}^{-1}$. The electrolytic current is maintained below certain limits so that the Joule heat dispersion does not cause temperature inhomogeneities of more than 2°C . After an electrolysis of 0.5 to 4 hours, the migration of the radioactive zone is determined by scanning the strip with a radiometric method.

An example of an ionophoretic migration can be seen in Fig. 1. The radioactive isotopes Ag^{110} and $\text{Cs}^{134\text{m}}$ have been used. This latter has an half life of 2.7 hours permitting thus a good determination of the migration of Ag after several hours (fig. 1).

Calculation of the transport parameters

The displacement l_i of a radioactive zone of a species i , in a molten mixture of m salts on a porous support, is

referred to its ionic absolute mobility, (frame of reference - walls of the cell) in the most general case by the equation:

$$u_i = K \frac{l_i}{t} \cdot \frac{h}{\phi} \quad (1)$$

where:

t is the time of electrolysis;

ϕ the potential difference at the ends of the strip;

h the length of the strip;

K is a factor which takes in account the influence of the porous support on the observed displacement (tortuous path of the ion, interactions with the melt).

If the porous wall does not interact selectively with the components of the melt, K can be expressed as the inverse of the obstructive factor as defined by Edward (10) for paper electrophoresis and it is a constant for all the ions.

$$K = \frac{R_p}{R} \quad (2)$$

where R_p is the electrical resistance of the strip and R the calculated resistance from the geometrical dimensions of the strip and the quantity of salt. Then the equation (1) becomes:

$$u_i = \frac{X}{d} \cdot \frac{p \cdot l_i}{q} \quad (3)$$

in which X is the specific conductivity of the mixture;

d the density;

p the weight of salt per centimeter length of strip;

q the quantity of electricity passed through the cell.

Now, if the following equations are considered:

$$t_i = \frac{f_i u_i F}{\Lambda} \quad (4)$$

$$\Lambda = X \cdot V \quad (5)$$

$$V = \frac{1}{d} \cdot \sum_{j=1}^m f_j \cdot Me_j \quad (6)$$

where:

F is the Faraday constant;

f_i the equivalent fraction of the i species;

V the equivalent volume of the mixture;

Me_j the equivalent weight of the j salt;

f_j the equivalent fraction of the j salt,

the transport number of the i species becomes:

$$t_i = \frac{p \cdot l_i}{z} \frac{r_i \cdot v_i}{\sum_{j=1}^m n_j \cdot M_j} \quad (7)$$

where: Λ is the equivalent conductivity of the mixture;
z is the number of Faraday passed through the cell;

r_i the number of gram-ions of the i species;

v_i the valence of the i species;

n_j the number of gram-mole of j salt;

M_j the molecular weight of the j salt.

The derivation of the equations (5) and (7) is based on the assumption expressed in equation (2), which is equivalent to the hypothesis of the absence of electroosmosis due to a selective wall effect (*).

(*) In a transport experiment in an ionic molten system there do not exist the possibility to put directly in evidence an electrosmotic phenomenon due to the porous walls of the apparatus, as in aqueous solution. In the most general case

The K values are 1.6 ± 1.9 .

The ionic mobilities or the transport numbers were calculated from equation (3) and (7) respectively: r_i is determined by dissolving the salt, drying, and analyzing the weighed residue; r or q was determined coulometrically.

Results and Discussion

Data relative to the two systems $(\text{Ag-Cs})\text{NO}_3$ and $(\text{Tl-Na})\text{NO}_3$, which are extensively studied, and some preliminary data for $(\text{Cs-Na})\text{NO}_3$ system, are reported.

As the lack of available conductivity data prevented the evaluation of absolute ionic mobilities, the experimental results are reported in form of transport numbers or external mobility ratio. Fig. 2 shows the transport numbers vs the composition in the $(\text{Cs-Ag})\text{NO}_3$ system at $T=240^\circ\text{C}$. The 0-50 mole per cent of CsNO_3 range was investigated. This range corresponds, at this temperature, nearly to the whole liquid zone (13). Thermal decomposition of AgNO_3 prevents the investigation at higher temperatures. Ag and Cs transport numbers have been calculated from eq. (7); nitrate transport numbers from the equation:

$$t_{\text{NO}_3} = 1 - t_{\text{Ag}} - t_{\text{Cs}}$$

the experimental transport number is the sum of the electrical transport number of the salt plus a "wall" transport number (11, 12). For the systems molten nitrate-porous fritted ceramic oxides, there is some evidence that the "wall" influence, if it exists, is small. No chemical corrosion of the support, or exchange reaction or chemisorption occur; the size of the migration channels is of the order of ten microns. It is noteworthy that chromatographic experiments on these

From the non-linear variations of the measured transport numbers vs composition (fig. 3), it appears that ionic mobilities can vary appreciably in the investigated range.

Fig. 3 shows the transport numbers of the ionic species in (Na-Tl)NO₃ system at T=320°C. Transport numbers of thallium and sodium species were calculated from equation (7). The nitrate transport number from equation:

$$t_{\text{NO}_3^-} = 1 - t_{\text{Na}} - t_{\text{Tl}}$$

In the diagram one can observe deviations from linearity of the transport numbers vs composition curves; the ionic mobilities vary with changes in the composition.

In fig. 4 the external mobility ratio, as obtained directly from experiments, is presented. The variation of this ratio is particularly pronounced in NaNO₃ rich region. It is likely that the addition of small quantities of TlNO₃ to the pure NaNO₃ decreases appreciably the equivalent conductivity of the melt.

For the (Cs-Na)NO₃ system some preliminary results seem to indicate that in the CsNO₃ rich region the mobility of cesium species is larger than the sodium one. In particular in pure CsNO₃ a Cs/Na ratio of about 1,35 was found, as compared with a ratio of about 8 previously reported in literature (4).

support in (Cs-Ag)NO₃ and (Na-Tl)NO₃ point out that the adsorptior behaviour on the fritted material of the Cs and Ag species in the former, and of the Na and Tl in the latter is the same; all the species migrate near the solvent front.

This abnormal large value can be explained, in our opinion, by an exchange reaction taking place between the glass support used and the sodium ions present in trace in molten CsNO_3 .

The plot of liquid junction potentials versus concentration for the cell $\text{AgNO}_3/\text{AgNO}_3\text{-CsNO}_3$ is also reported in fig.3(*). At 30 mole per cent of CsNO_3 the value of liquid junction potentials is 5 mV, as compared with 6.5 mV determined by Ketelaar from concentration and formation cell (14). From the data relative to the system $(\text{Na-Tl})\text{NO}_3$ one can expect a value of the liquid junction potential non exceeding 3 mV.

One can observe that the liquid junction potential is a rather insensitive function of the variation of the transport parameters ; therefore from liquid junction potential measurements only qualitative information about the relative mobilities may be obtained.

The knowledge of the transport parameters, on the contrary, can be useful for evaluating the diffusive contribution to the EMF values of concentration cells with transport.

(*) The Klemm equation (15) has been used:

$$\mathcal{E}_L = - \frac{RT}{F} \ln \frac{C_1^{II} b_{12} + C_3 b_{23}}{C_1^I b_{12} + C_3 b_{23}}$$

where b_{12} is the difference between the cationic mobilities, b_{23} the mobility with respect to the common anion; C_1^I and C_1^{II} the cationic fraction of cation 1 on the two sides of the liquid junction. Instead of the constant mobility assumption made by Klemm, graphically integrated values were used. The conductivity data for the utilization of the equation (3), necessary for evaluating the b values, were roughly estimated from the diagram presented by Protsenko and Popovskaya (13); density were interpolated from data of pure salts (16).

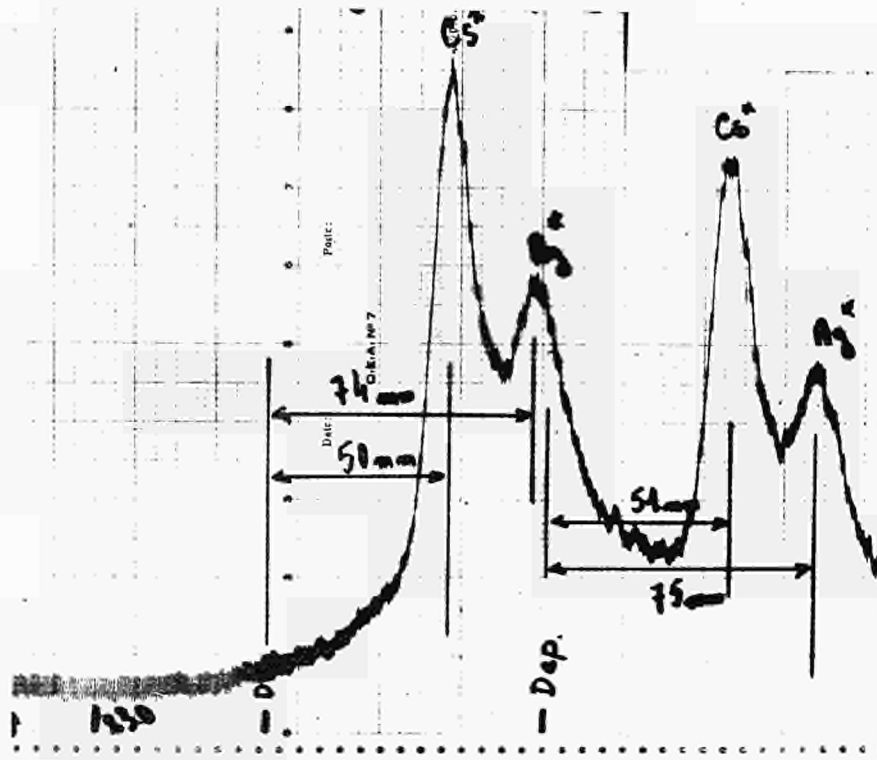
Bibliography

- 1) F.R. Duke, R.W. Laity, B. Owens.-
J. Electrochem.Soc. 104, 299 (1957)
- 2) F.R. Duke, B. Owens.-
J. Electrochem. Soc. 105, 476 (1958)
- 3) H.J.Arnikaar, M.Chemla.-
Radioisotopes in Scientific Research. Vol. II, 421
Pergamon Press - London (1958)
- 4) J.A.A.Ketelaar, E.P. Honig.-
J. Phys. Chem. 67, 1566 (1963)
- 5) G.Alberti, G.Grassini, R.Trucco.-
J. Electroanal. Chem. 3, 283 (1962)
- 6) S.J. Gregg.-
Surface Chemistry of Solids, p.318 fl1, Chapman and
Hall Ltd London (1961)
- 7) F.R. Duke, R.A. Fleming.-
J. Electrochem. Soc. 106, 130 (1959)
- 8) F.Lantelme, M.Chemla.-
Bull.Soc.Chim.France 2200 (1963)
- 9) F.Lantelme, M.Chemla.-
Electrochimica Acta 10, 663 (1965)
- 10) J.T. Edward.-
J. Chromat. 1, 446 (1958)
- 11) A. Lunden.-
J. Electrochem. Soc. 109, 260 (1962)
- 12) S. Forcheri, V. Wagner.-
Annali di Chimica - In Press.
- 13) P.I.Protsenko, N.P. Popovskaya.-
Russian J. Phys. Chem. 35, 424 (1961)
- 14) J.A.A. Ketelaar.-
J.Chim. Phys. 61, 44 (1964)
- 15) A.Klemm.-
Molten Salt Chemistry, p. 554, Edited by M.Blander.
Interscience Publishers, London (1964)
- 16) C.J.Smithells.-
Metal Reference Book, p. 662 - Edited by Butterworths,
London (1962).

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(a)



b)

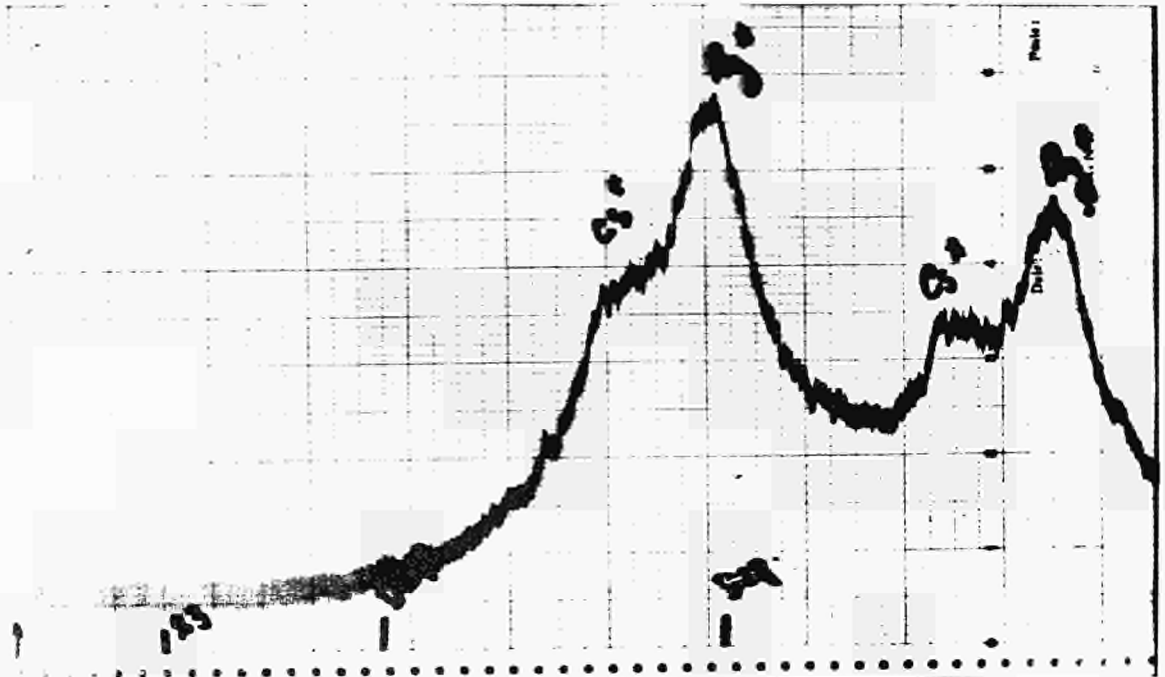


FIG. 1

Electropherogram of Cs-134 m NO_3 and Ag-110 NO_3 in the molten system $(\text{Cs-Ag})\text{NO}_3$ at 48 mole per cent of AgNO_3 at $T=240^\circ\text{C}$.

- Scanning carried out immediately after the experiment;
- Scanning carried out several hours after the experiment.

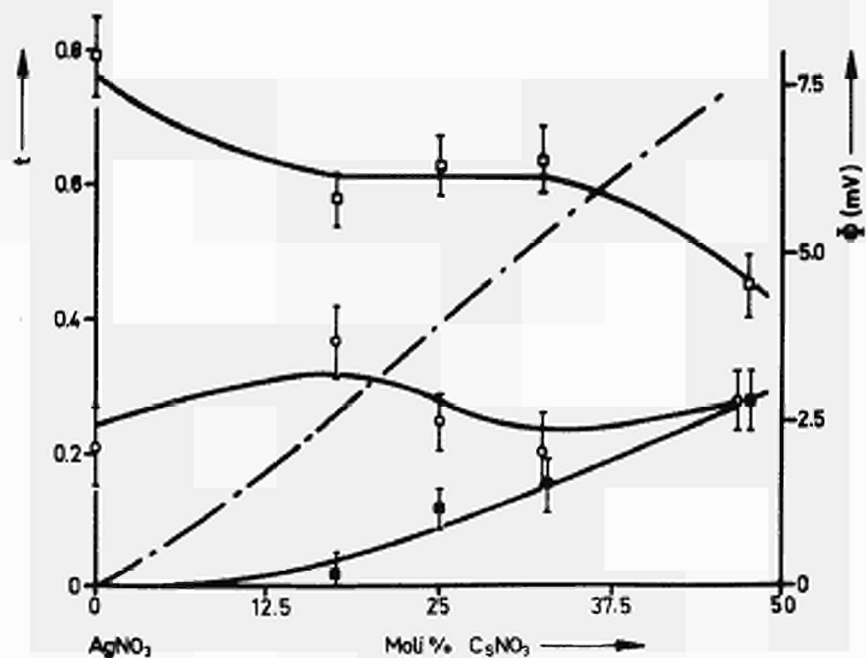


FIG. 2

Transport numbers in the (Cs-Ag)NO₃ system.

■ Cs

□ Ag

○ NO₃

--- liquid junction potentials vs concentration for the cell AgNO₃/AgNO₃-CsNO₃
T = 240°C.

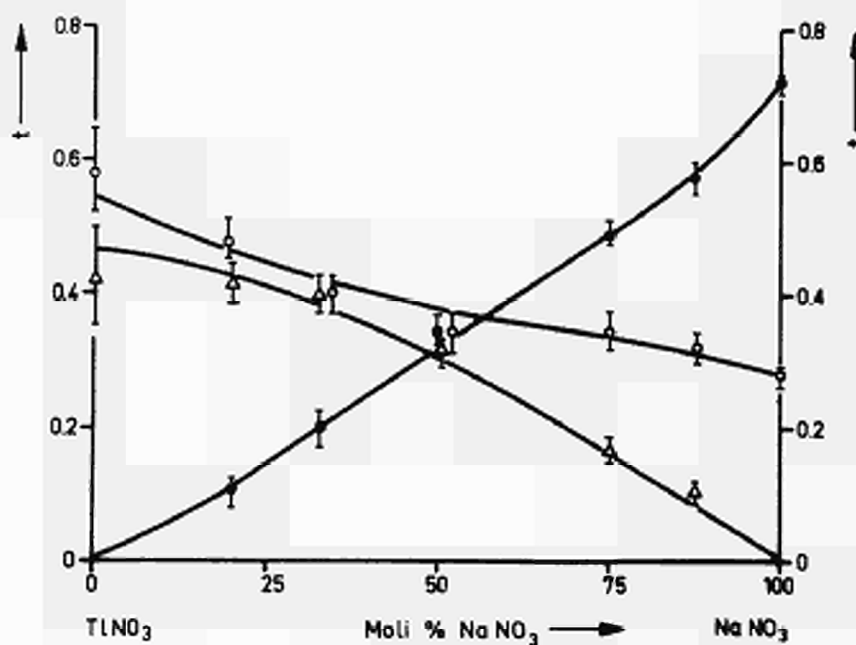


FIG. 3

Transport numbers in the (Na-Tl)NO₃ system.

● Na

△ Tl

○ NO₃

T = 320°C.

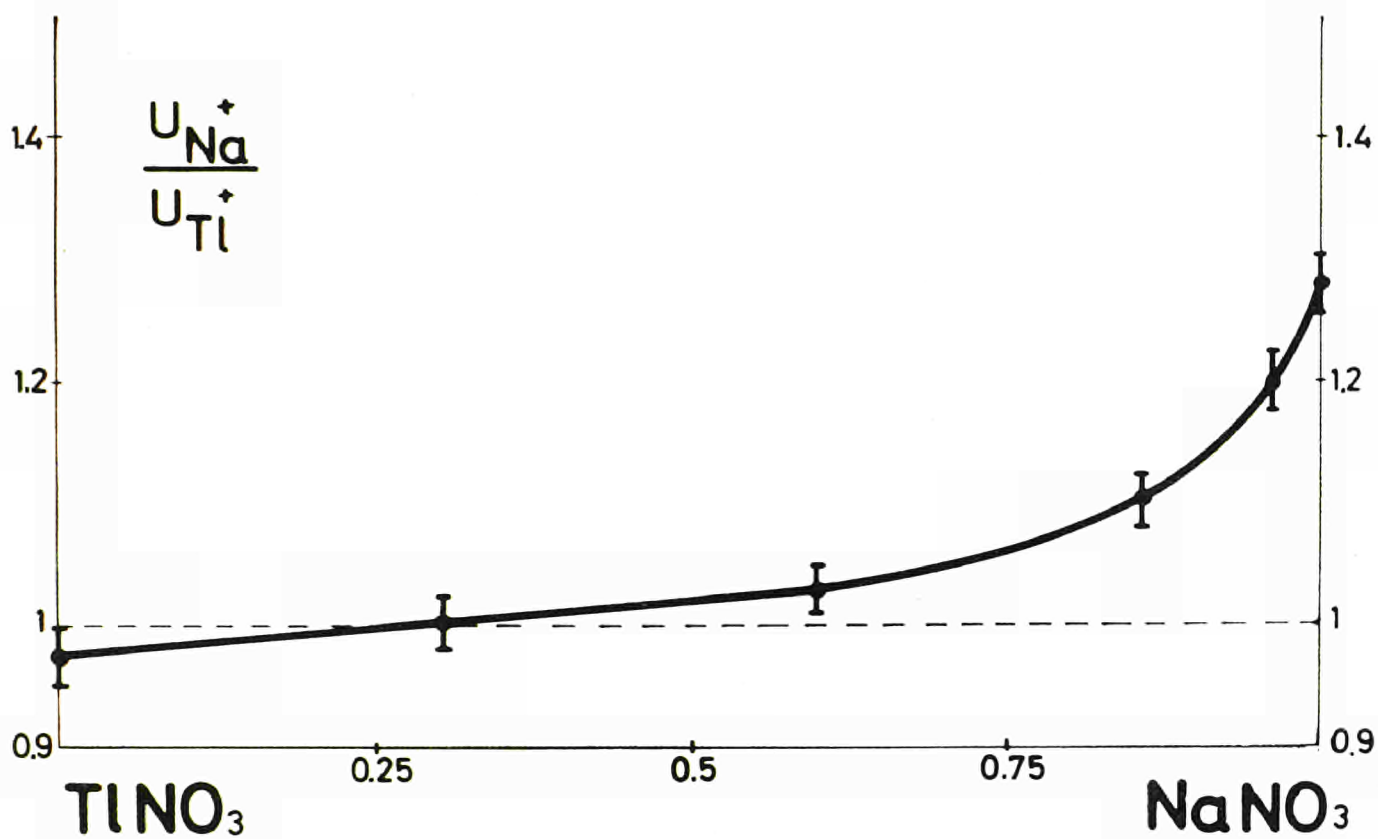


FIG. 4

Mobility ratio $\frac{U_{Na}}{U_{Tl}}$ in the
 $(Na-Tl)NO_3$ system.
 $T = 320^\circ C.$

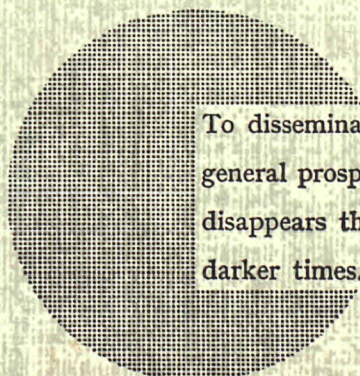
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To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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