

Abb. 7. Mittleres molares Zusatzvolumen des Systems Benzol-Diphenylmethan.

Dichte der Mischungen Benzol-Diphenylmethan bei 35 °C (Tab. 8)

Da die Theorien auch Aussagen über die Volumenänderung beim Mischen geben können, wurden bei diesem System bei 35 °C die Dichten gemessen. Das damit berechnete Exzeßvolumen ist in Abb. 7 dargestellt.

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The Thermoelectric Power in Molten and Solid Silver Nitrate*

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In a silver electrodes thermocell the thermoelectric power ε of solid β and liquid silver nitrate is measured. The following values are obtained (t_m is the average temperature of the system in centigrade):

solid (from 160 to 209,4 °C): $\varepsilon = -237 \mu\text{V degree}^{-1}$,
liquid (from 209,4 to 350 °C): $\varepsilon = (-304 - 0,077 t_m) \mu\text{V degree}^{-1}$.

The entropies of transport of the silver and nitrate ions in silver nitrate have been calculated at different temperatures.

As part of a larger program, it has been necessary to take measurements on the thermocell:

final stage $|\text{Ag}_{(s)}|_{T_1} \text{AgNO}_{3(l)o(s)} |_{T_2} \text{Ag}_{(s)}|$ final stage (1)

in the temperature range from 160 to 350 °C, covering thus the solid β phase of the AgNO_3 from 160 to 209,4 °C and the liquid phase from the latter temperature upwards.

Apart from an indicative value supplied by POINCARÉ¹ in 1890 and some data reported by HOLTAN² in graph form, values of the thermal emf of this thermocell, limited to the liquid state, have been furnished by SUNDHEIM et al. for four distinct temperatures comprised between 240 and 307 °C in a first report³ and for 310 °C in a second report⁴.

Experimental

The measuring cell, made of pyrex, was of a tubular squared $\square$ shape, with one arm covered by a glass sleeve. In the interspace between that arm of the cell

and the sleeve are located resistances with anti-inductive coils connected through a Variac to a voltage stabilizer. The cell was located in an aluminium block made of three pieces, and the whole was placed in a thermostat oven of high capacity. Two electrode holders, fixed by asbestos plugs, held the chromel-alumel thermocouples and the silver electrodes. The latter were constructed in such a way that the contact with the silver nitrate was located at the small areas where the thermocouples measured the temperature. Differences of temperature, comprised between approximately 5 and 40 °C, were created between the two electrodes. The potential difference $\Delta\Phi$, measured at zero current, showed strict proportionality to ΔT .

Stationary conditions were reached in about 15–20 minutes. Each group of measurements comprised about 7–9 determinations, each of these being the average of at least four readings. The measurements were made in the sense of both heating and cooling. Each loading of the thermocell was used for only one group of determinations.

In the measurements on solid β phase AgNO_3 (160 to 209,4 °C) the technique adopted was that of melting the salt within the cell and then leaving the whole to cool to the temperature at which one wished to take

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

¹ L. POINCARÉ, Ann. chim. phys. [6] 21, 289 [1890].

² H. HOLTAN, Dissertation, Utrecht 1953.

³ B. R. SUNDHEIM and J. ROSENSTREICH, J. Phys. Chem. 63, 419 [1959].

⁴ R. SCHNEEBAUM and B. R. SUNDHEIM, Discussions Faraday Soc. 32, 197 [1961].



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the measurement. By this procedure perfectly reproducible values were obtained.

In order to determine the emf a potentiometer of the K-3 type was used in junction with an electronic D-C null detector (Leeds & Northrup). The silver nitrate used was a C. Erba product. The silver electrodes were made of a wire (0.4 mm ϕ) of at least 99.99% purity.

Results and Discussion

The experimental results obtained for the thermopile (1) are reported in Table 1 where are shown, for the two phases investigated, the values of ε ($\equiv \Delta\Phi/\Delta T$) and the corresponding temperature

	$-\varepsilon \mu\text{Vdeg.}^{-1}$	Field of t_m ($^{\circ}\text{C}$)
AgNO_3 phase β from 160 to 209,4 $^{\circ}\text{C}$	237 ± 2	168–185
	237 ± 3	193–200
	238 ± 2	170–200
	237 ± 1	174–194
Mean value	237 ± 2	
AgNO_3 liquid from 209,4 to 350 $^{\circ}\text{C}$	322 ± 2	215–235
	323 ± 2	232–248
	324 ± 2	247–263
	325 ± 2	271–287
	327 ± 1	287–302
	327 ± 2	289–313
	328 ± 2	306–320
	331 ± 2	329–347
$\varepsilon = -304 - 0,077 \cdot t_m$ (t_m in $^{\circ}\text{C}$, ε in $\mu\text{Vdeg.}^{-1}$)		

Table 1. Values of ε for the thermocell $\text{Ag}/\text{AgNO}_3/\text{Ag}$.

ranges (t_m is the average temperature between the two electrodes). At the foot of the table appears the equation of the straight line which interpolates the experimental data for the liquid phase according to the method of least squares.

All results are represented in Fig. 1 where the experimental values reported by SUNDHEIM et al.^{3,4} appear also.

In previous works it has been shown how one can develop a simple theory of thermocells with fused salts on the basis of the thermodynamics of the irreversible processes, should one adopt the HITTORF system of reference^{5,6}. With the assumption that the hotter electrode is positive, for the thermocell

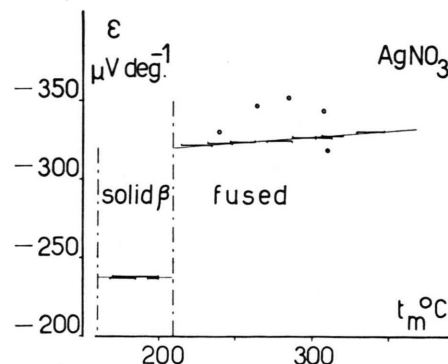


Fig. 1. Thermoelectric power of solid and fused AgNO_3 . $\square$ present work; $\circ$ SUNDHEIM and ROSENSTREICH³; $\bullet$ SCHNEEBaum and SUNDHEIM⁴.

(1) the following relation is valid:

$$\mathcal{F}\varepsilon = S_{\text{Ag}} - S_{\text{Ag}^+}^* - S_e^* \quad (\text{for } T_m = T_1 + \Delta T/2) \quad (2)$$

where $\mathcal{F}$ is the FARADAY'S constant; ε ($\equiv \Delta\Phi/\Delta T$) is the coefficient of temperature of the thermal emf $\Delta\Phi$; S_{Ag} is the entropy of metallic silver; $S_{\text{Ag}^+}^*$ is the entropy of transport of the silver ion⁷ defined by: $S_{\text{Ag}^+}^* \equiv Q_{\text{Ag}^+}^*/T + S_{\text{Ag}^+}$ as a function of the heat of transport $Q_{\text{Ag}^+}^*$ and of the entropy S_{Ag^+} of the silver ion; S_e^* is the entropy of transport of the electron.

Since the simple relation

$$S_{\text{Ag}^+}^* + S_{\text{NO}_3^-}^* = S_{\text{AgNO}_3} \quad (3)$$

is valid^{5,6} (S_{AgNO_3} is the entropy of the AgNO_3 salt), from (2) and (3) it is possible to evaluate $S_{\text{Ag}^+}^*$ and $S_{\text{NO}_3^-}^*$ at different temperatures when ε is measured and the quantities S_e^* , S_{Ag} and S_{AgNO_3} are known.

SUNDHEIM³ has calculated S_e^* to be equal to 0.03 u. e. for silver at 500 $^{\circ}\text{K}$. The term S_e^* has therefore been neglected as certainly inferior to the experimental errors. The value of S_{Ag} can be obtained from the experimental specific heat data of MEADS et al.⁸ up to 25 $^{\circ}\text{C}$ and of JAEGER et al.⁹ and of LYASHENKO¹⁰ for higher temperatures. The entropy S_{AgNO_3} has been evaluated from the measurements of SMITH et al.¹¹ up to room temperature, and from the recent determinations made by JANZ and KELLY¹² for higher temperatures.

⁵ H. SCHÖNERT and C. SINISTRI, Z. Elektrochem. **66**, 413 [1962].

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

⁷ In the following the word "ion" is understood in the sense of "ion constituent" as already discussed previously^{5,6}.

⁸ P. F. MEADS, W. R. FORSYTHE, and W. F. GIAUQUE, J. Amer. Chem. Soc. **63**, 1902 [1941].

⁹ F. M. JAEGER, E. ROSENBOHM, and W. A. VEENSTRA, Proc. Koninkl. Ned. Akad. Wetenschap. **36**, 291 [1933].

¹⁰ Values reported by D. R. STULL and G. C. SINKE, Thermodynamic Properties of the Elements, Ed. Amer. Chem. Soc. 1956, p. 185.

¹¹ W. V. SMITH, O. L. I. BROWN, and K. S. PITZER, J. Amer. Chem. Soc. **59**, 1213 [1937].

¹² G. J. JANZ and F. J. KELLY, J. Phys. Chem. **67**, 2848 [1963].

t °C	$S_{\text{Ag}^+}^*$	$S_{\text{NO}_3^-}^*$
160	18,0	25,8
180	18,2	26,5
200	18,5	27,1
220	20,7	32,1
240	21,0	32,9
260	21,3	33,7
280	21,5	34,5
300	21,8	35,2
320	22,1	35,9
340	22,3	36,6

Table 2. Values of the entropies of transport (in cal/mole deg.) of the silver and nitrate ions in AgNO_3 at different temperatures.

The results obtained for the values of $S_{\text{Ag}^+}^*$ and $S_{\text{NO}_3^-}^*$ as functions of the temperature are schematically shown in Table 2.

The values regarding the solid phase of silver nitrate have been calculated, still holding valid the measurements of TUBAND and EGGERT¹³, who conclude that silver nitrate is an ionic conductor.

¹³ C. TUBAND and S. EGGERT, Z. Anorg. Chem. **110**, 196 [1920].

Eine Methode zur Herstellung dünner Schichten anorganischer Salze

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Die Methode (Sandwich-Methode) besteht darin, daß zwischen zwei Folien verdünnte Salzlösungen präpariert werden. Aus diesen Flüssigkeitslamellen kristallisieren die Salze vorwiegend als dünne Plättchen, da die Wachstumsrichtung in der dritten Dimension weitgehend unterdrückt wird. Alkali- und Ammoniumhalogenide lassen sich danach leicht in Form dünner, im Elektronenmikroskop durchstrahlbarer Folien herstellen. Bei CsCl und den Ammoniumhalogeniden treten stärkere Abweichungen in den Kristallgitterdimensionen auf, die durch die spezielle Präparationsmethode bedingt sind.

Für die Herstellung dünner, im Elektronenmikroskop durchstrahlbarer Folien anorganischer Verbindungen gibt es kein so allgemeines Verfahren, wie es z. B. das Elektropolieren für Metalle darstellt. Es sind bisher mehrere zum Teil recht unterschiedliche Präparationsmethoden für dünne Schichten anorganischer Salze bekannt geworden, die jedoch oft in ihrer Anwendung auf einige wenige Verbindungen beschränkt sind. So konnte MÖLLENSTEDT¹ durch chemische Reaktion zwischen KJ- und $\text{Pb}(\text{NO}_3)_2$ -Lösung PbJ_2 in Form einkristalliner Plättchen erhalten. SCHÜLLER und AMELINCKX² stellten durch Abätzen dünner CaF_2 -Plättchen durchstrahlbare Folien her. YAGI und HONJO³ berichteten kürzlich über dünne NaCl-Kristalle, die durch starke Elektronenbestrahlung dickerer Kristalle im Elektronenmikro-

skop erzeugt wurden. Auch die Ultramikrotomie ist als Präparationsverfahren bekannt geworden⁴. Universeller anwendbar sind die Verfahren, die auf der Kristallisation aus wäßrigen Lösungen beruhen. KOMODA und SAKATA⁵ erhielten durch Aufspritzen von gelatinehaltigen verdünnten Salzlösungen auf Trägerfolien durchstrahlbare Kristallfolien, die sich zwischen Trägerfolie und Gelatine bildeten. Gute Ergebnisse lieferte auch die Methode der Vakuumtrocknung nach HIBI und YADA⁶. Nach MÖLLENSTEDT, GRAFF und SPEIDEL⁷ kristallisieren dünne Schichten von KCl aus einem Film verdünnter Lösung aus, der sich zwischen zwei aufeinandergepreßten, vorher mit Kohle bedampften Glasträgern ausbildet. Weitere spezielle Verfahren sind in⁸ und⁹ angegeben.

* Neue Anschrift: BBC, Abt. ZFL, Heidelberg.

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¹ G. MÖLLENSTEDT, Optik **10**, 72 [1953].

² E. SCHÜLLER u. S. AMELINCKX, Naturwiss. **47**, 491 [1960].

³ K. YAGI u. G. HONJO, J. Phys. Soc. Japan **19**, 1892 [1964].

⁴ G. HAASE, F. GRANZER u. F. ZÖRGIEBEL, Z. Angew. Phys. **18**, 120 [1964].

⁵ T. KOMODA u. S. SAKATA, J. Electronmicroscopy (Tokyo) **7**, 27 [1959].

⁶ T. HIBI u. K. YADA, J. Electronmicroscopy (Tokyo) **9**, 101 [1960].

⁷ G. MÖLLENSTEDT, K. GRAFF u. R. SPEIDEL, Z. Phys. **167**, 367 [1962].

⁸ H. M. MONTAGU-POLLOCK, Proc. Roy. Soc., Lond. **269**, 219 [1962].

⁹ G. A. BASSETT, A. J. FORTY u. M. R. TUBBS, 5. Intern. Congr. Electron Microscopy, Philadelphia 1962.