Relative Determination of the Soret Coefficients of Electrolytes. V

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The Soret coefficients of aqueous solutions of some transition metal chlorides were determined by use of combined thermocells. The following values (in 10^{-3} K^{-1}) were obtained in 0.005 M solutions at 25 °C: -7.01 for $MnCl_2$, -4.61 for $CoCl_2$, -2.67 for $NiCl_2$, and -3.43 for $CuCl_2$. It was concluded that ion paramagnetism does not affect thermal diffusion.

The combined thermocell method[1,2] was proved to be as useful as the most sensitive conductometric method improved by Snowdon and Turner[3] in yielding reasonable values for the Soret coefficients of a number of electrolytes. However, only a few data are reliable for the Soret coefficients so far reported of divalent salts.[2,4] Accurate Soret data are required for a great number of divalent salts. In the present work, the Soret coefficients of a series of the transition metal chlorides, MCl_2, in aqueous solutions were determined by the combined thermocell method, special interest being taken to see whether paramagnetic ions of these salts have any influence upon thermal diffusion. Combined thermocells (a cell system of a back to back combination of two thermocells consisting of common electrodes and different electrolytes without liquid junctions) of the following type were used:

$$\underset{T}{\text{Hg-HgCl}},\ \text{LiCl}(m),\ \underset{T+\Delta T}{\text{HgCl-Hg-HgCl}},$$

$$\text{MCl}_2\left(\frac{m}{2}\right),\ \underset{T}{\text{HgCl-Hg}} \qquad (1)$$

where the concentrations of the chloride ions in the left and right halves of the cell are taken to be equivalent to each other. Lithium chloride was taken as a standard since it shows a very slight Soret effect. The Soret coefficient, σ^{MCl_2}, for MCl_2 can be calculated in terms of the σ^{LiCl} for LiCl from the resulting initial thermoelectric power, $(dE/dT)_0$, of the cell (1) by using the following approximate equation,[2] ignoring terms of the transported entropies of the chloride ion:

$$\sigma^{MCl_2} = [4t_{Li^+}^{LiCl}B^{LiCl}\sigma^{LiCl} + 2F(dE/dT)_0/RT]/3t_{M^{2+}}^{MCl_2}B^{MCl_2} \qquad (2)$$

where t is the ionic transport number of ionic species indicated by the subscripts in the solution phases indicated by the superscripts. B is defined by

$$B = (1+d\ln\gamma_\pm/d\ln m)_{T,P}$$

where $\gamma_\pm$ is the mean activity coefficient in the molality scale at a molality m, F, R, T and P having their usual meanings.

Results and Discussion

All the solutions of four transition metal chlorides, $MnCl_2$, $CoCl_2$, $NiCl_2$, and $CuCl_2$, were prepared by guaranteed reagent grade chemicals (99.8% purity, Wakō Pure Chemical Industries, Ltd.) and adjusted to a concentration of 0.01 mol dm^{-3} with respect to the chloride ions. Experimental equipments and methods are entirely the same as those reported.[2] The range of ΔT was about 10 K around a mean temperature 25 °C, while the temperature T on the terminal electroldes was kept constant at 25 °C.

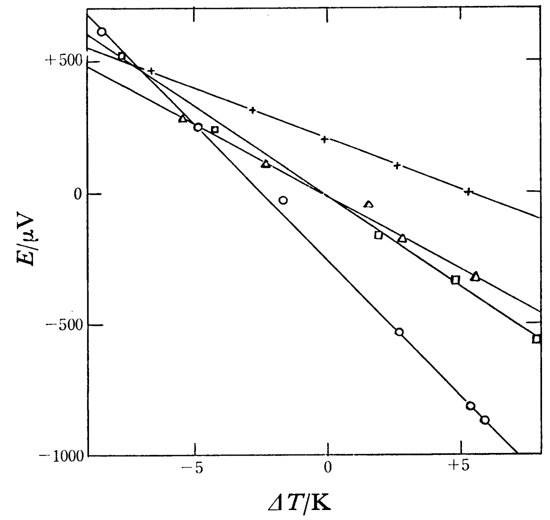

Fig. 1. Emf-plots of the combined thermocells (1) against temperature differences, ΔT: ○ for $MnCl_2$, □ for $CoCl_2$, + for $NiCl_2$, △ for $CuCl_2$.

Some typical results are shown in Fig. 1. The values of the resulting initial thermoelectric power, $(dE/dT)_0$, averaged over 10—20 observations, are given in Table 1. The values of $(dE/dT)_0$ observed in the present work are accompanied by fluctuations several times larger than those ever seen in a similar work. The reason is not clear. The Soret coefficients found for the transition metal chlorides are relatively large for their small cation sizes as compared with those of the alkali and alkaline earth chlorides[2,4] which yield cations of a relatively large size. This is the reverse of the general tendency of the Soret coefficients known since the larger (the smaller) the cation size, the larger (the smaller) the Soret coefficients, and hence the stronger the ion hydration, the weaker the Soret effect. This rule seems to hold roughly so far as the elements of the same family are concerned. On the other hand, all the salts studied here are paramagnetic, and in fact the manganese chloride, which has the highest magnetic moment, showed the most predominant Soret effect, and so paramagnetism seems to have some influence on the Soret coefficient. However, this assumption might not be appropriate, since the Soret coefficients we found are not always parallel with the magnetic moments because of the one exception of cupric chloride which showed a considerable Soret effect despite the fact that the

Table 1. Soret coefficients, σ, and the molar heats of transfer, Q_m of some transition metal chlorides at 0.005 M and 25 °C

Chloride	$\frac{m}{\text{mol kg}^{-1}}$	t_+[a]	B[b]	$\frac{(dE/dT)_0}{\mu\text{V K}^{-1}}$	$\frac{-10^3\sigma}{\text{K}^{-1}}$	$\frac{Q_m}{\text{cal mol}^{-1}}$
LiCl	0.01004	0.3289	0.969	—	(−0.01)[c]	−4
$MnCl_2$	0.00502	0.4120	0.906	−101.0±7.2	7.0_1	3340
$CoCl_2$	0.00498	0.4143	0.906	−64.4±5.7	4.6_1	2210
$NiCl_2$	0.00497	0.4143	0.908	−38.8±4.8	2.6_7	1280
$CuCl_2$	0.00501	0.4231	0.894	−50.1±5.3	3.4_3	1620

a) Estimated from the limiting ionic conductances. b) Graphical determination using the data obtained from Landolt-Boernstein, "Physikalische Chemische Tabellen," Erg. Bd. II (1931) and III (1936). c) The standard Snowdon and Turner's value (*Trans. Faraday Soc.*, **56**, 1409 (1960)) adjusted to the 25 °C.

magnetic moment is the smallest in this family. Thus it seems that ion paramagnetism does not affect the thermal diffusion.

References

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4) A. D. Payton and J. C. R. Turner, *ibid.*, **58**, 55 (1962).