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SORET CELL DIFFUSION IN TWO ANION–TWO CATION SALT SOLUTIONS

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Abstract—Soret coefficients are reported for salts of Cu, Ni, and Co, with cations of SO_4 and NO_3. Single salt coefficients and two salt coefficients for the cations are reported for 0·5 molal solutions in a 16 degC temperature difference. A cell utilizing diffusion through a cellophane membrane was used.

NOMENCLATURE

D, diffusion coefficient, area/time;
D', thermal diffusion coefficient, area/time-degree;
J_A, diffusion rate, moles/time-area;
T, temperature;
T_1, T_2, temperature of the cold wall and hot wall;
x, point mole fraction of salt;
$\bar{X}_1, \bar{X}_2$, average mole fraction in the cold and hot side cavities;
z, co-ordinate distance;
ρ, density, moles/volume;
σ, Soret coefficient, degrees^{-1}.

THERE are no previous reported results on thermal diffusion of mixed salts with no common ions. This investigation was initiated to determine interaction effects of mixed salts in a Soret cell. The ions Cu^{++}, Ni^{++}, Co^{++}, $SO_4^{=}$ and NO_3^{-} were examined.

EXPERIMENTAL

A Soret cell design first used by Fisher, Prados and Bosanquet [2] was used for the measurements. This design, which is illustrated in Fig. 1, consists of two chambers in a Teflon bar separated by a cellophane membrane. The upper cavity is heated by an electric heater, and the lower cavity is cooled by a refrigerant evaporator. The thermal sources are constructed externally to the cell and are clamped in the slots in the top and bottom. This construction facilitated cell assembly. The cell was constructed of Teflon to prevent any interaction of the salt with the construction material, and to prevent external electric currents caused by the concentration cell of the salts. It was found necessary to use the red sheet rubber gaskets to prevent solution leakage. With this design, each cavity held 17 ml, with a wall-to-wall spacing of 1·25 cm. The cell could be constructed from two Teflon strips with no machining; the cavities could be formed entirely by the gaskets. The surface temperature of the Teflon in contact with the solution was estimated with thermocouples attached to the walls by epoxy resin with distilled water in the solution cavities; temperatures of thermocouples in holes drilled in the Teflon bars were noted, and these indicators were used to estimate the wall temperatures in all runs with salt solutions. Solution analyses were made with a Beckmann DU spectrophotometer at 390 mμ, 510 mμ, and 810 mμ; Lambert–Beer's law was assumed with additive absorbancies of the salts.

The purpose of the cellophane membrane was to allow complete withdrawal of the cavity solutions for analysis. This cell design obviates point analyses and also allows material balances on the system to be made. The membrane has no effect on thermal diffusion equilibrium (2), but it does increase the time necessary to attain it; the membrane is considered to act simply as a porous barrier, thereby reducing the diffusion area. As the equilibrium time of the cell was less than 24 h, all runs were of this length.

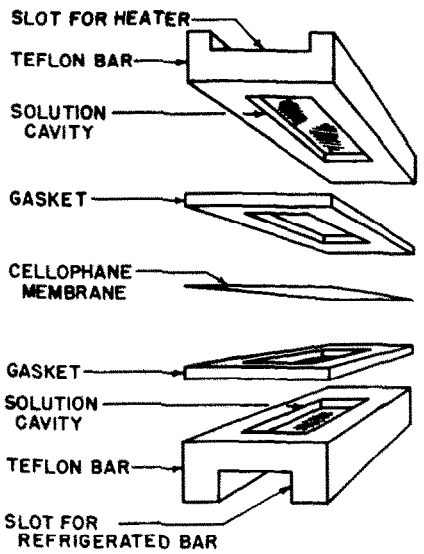

FIG. 1. The Soret cell.

THEORY

By using the equation defining the Soret coefficient

$$J_A = -\rho\left[D' x(1-x)\frac{dT}{dz} + D\frac{dx}{dz}\right] \quad (1)$$

it was shown [2] that the Soret coefficient could be calculated for this cell design by

$$\sigma = \frac{D'}{D} = \frac{2}{T_2 - T_1}\ln\frac{\bar{X}_1}{\bar{X}_2}. \quad (2)$$

It was assumed that there was a negligible temperature drop across the membrane, that the solution was dilute so that $1 - x \cong 1$, and that the temperature distribution in the solutions was linear with distance, as demonstrated experimentally by Bosanquet [1].

Table 1. Soret coefficients of single salt solutions

Salt	Initial molality	Hot side wall temperature (°C)	Temperature differences (degC)	Soret coefficients × 10^3 (degC^{-1})
$CuSO_4$	0·4954	44·5	16·4	7·59
$CoSO_4$	0·5018	43·9	15·6	8·56
$NiSO_4$	0·5056	43·9	16·2	9·49
$Cu(NO_3)_2$	0·5074	43·4	15·3	0
$Co(NO_3)_2$	0·4925	44·5	16·8	0
$Ni(NO_3)_2$	0·5115	44·8	16·9	0

Table 2. Soret coefficients of two salt solutions

Salts	Initial molality	Hot side wall temperature (°C)	Temperature differences (degC)	Soret coefficients × 10^3 (degC^{-1})
$CuSO_4$	0·4887	(1) 44·9	16·3	5·50
$Co(NO_3)_2$	0·4902			4·09
		(2) 43·2	15·8	5·96
				3·60
		(3) 43·2	15·6	6·25
				3·54
		(4) 43·5	16·3	6·54
				3·49
$CuSO_4$	0·4950	(1) 45·2	17·0	7·64
$Ni(NO_3)_2$	0·4810			4·72
		(2) 43·9	16·4	7·58
				4·44
$Cu(NO_3)_2$	0·4811	43·5	15·6	6·49
$CoSO_4$	0·4881			3·04

RESULTS

The experimental results, which are shown in Tables 1 and 2, indicate a most pronounced interaction of the nitrate and sulfate salts. Although the pure nitrates exhibited no thermal diffusion effect, the metal ion in a mixed salt solution exhibited a marked separation. In the mixed salt solutions, although the Soret coefficient of the copper cation was not markedly changed, the coefficients of the nickel and cobalt cations decreased by about half. The data for copper nitrate and cobalt sulfate indicate that the Soret coefficients do not depend on the original anion of the salt put in solution. The possibility of the cellophane membrane being impervious to the nitrates was eliminated by observing ordinary diffusion of the nitrates through the membrane.

These data suggest the possibility of an equilibrium complex in the solution which either does or does not exhibit a thermal diffusion effect.

Further work with mixed anions and mixed cations should also include an analysis scheme for the anions.

REFERENCES

1. L. P. Bosanquet, M.S. Thesis, The University of Tennessee (1960).
2. G. T. Fisher, J. W. Prados and L. P. Bosanquet, *AIChE J.* **9**, 786–793 (1963).

Zusammenfassung—Soretkoeffizienten werden angegeben für Co-, Ni- und Co-Salze mit SO_4- und NO_3-Kationen. Einsalz- und Zweisalzkoeffizienten für Kationen sind für 0,5 molare Lösungen und 16 Celsiusgrad Temperaturdifferenz tabelliert. Benützt wurde eine Diffusionszelle mit einer Cellophanmembrane.

Аннотация—Получены коэффициенты Соре для солей Cu, Ni и Co с катионами SO_4 и NO_3. Коэффициенты (для катионов) даны в одно- и двухкомпонентных растворах при мольной концентрации 0,5 и разности температур 16°C. Использовалась ячейка, в которой диффузия происходила через целлофановую мембрану.