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THE UTILIZATION OF THE BASE-EXCHANGE REACTION FOR THE DETERMINATION OF ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTES

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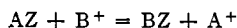
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In the course of an investigation of the cation-exchange reaction of the various types of alumino-silicates the author was impressed with the possibility of utilizing certain of the minerals known as bentonites for the determination of the relative activity coefficients in mixed electrolytes.

Bentonites¹ are a class of clay minerals of the general composition $(MO)_x \cdot Al_2O_3 \cdot (SiO_2)_y \cdot nH_2O$, in which x has a value of 1 or somewhat less, and y has a value of from 3 to 5. The cation M is for the main part magnesium, though it can consist in part of calcium, potassium and sodium. Bentonites occur as very minute micaceous crystals of colloidal dimensions, and they are practically insoluble in water and neutral salt solutions. The bentonites found most suitable for the investigation of activity coefficients are those which approximate the ideal montmorillonite type most closely, montmorillonite having the theoretical composition $MO \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$. About one-third of the cation M can be replaced by other cations simply by shaking or leaching the bentonite with a neutral salt solution, and for any one bentonite the fraction of M that can be thus replaced is a perfectly definite quantity.

A bentonite which has been treated with a solution of a particular cation to the point where it has taken up all of this cation that it is capable of is said to be saturated with this cation; and this cation in turn can be partially or wholly displaced by another. Under certain conditions this cation-exchange reaction of bentonites is entirely reversible. A bentonite saturated with the cation A when treated with a solution of some other cation B would react in the manner



where the symbol Z is used to designate the insoluble complex anion of the bentonite. Given sufficient time for the system to attain equilibrium, the equilibrium conditions are represented by the equation

$$K = \frac{(A^+)}{(B^+)} \times \frac{(BZ)}{(AZ)} \quad (A)$$

All quantities in parentheses are activities. The activities, (BZ) and (AZ) , of the solid phases are easily evaluated. Data being published in a paper soon to appear elsewhere show that the partial substitution of one cation for another results in the formation of mixed crystals and not two in-

¹ C. S. Ross and E. V. Shannon, *J. Am. Ceram. Soc.*, 9, 77 (1926).

dependent solid phases. Furthermore, the complex anion Z behaves as if it were monovalent. If AZ and BZ form mixed crystals, their activities are equal to their mole fractions and Equation A becomes

$$K = \frac{(A^+)}{(B^+)} \times \frac{\frac{BZ}{AZ + BZ}}{\frac{AZ}{AZ + BZ}} = \frac{(A^+)}{(B^+)} \times \frac{BZ}{AZ}$$

The quantity BZ/AZ is simply the ratio of the two cations in the solid phase. Introducing the activity coefficients of the ions in solution our equation can be written in the form

$$K = \frac{\gamma_{A^+}}{\gamma_{B^+}} \times \frac{A^+}{B^+} (\text{in solution}) \times \frac{BZ}{AZ} (\text{in solid phase})$$

The constant K can be evaluated in the following manner. Series of equilibria determinations are made at various concentrations, and the values of K' calculated by means of the equation

$$K' = \frac{A}{B} (\text{in solution}) \times \frac{BZ}{AZ} (\text{in solid phase})$$

are plotted against some function of the ionic strength and extrapolated to infinite dilution. The value of K' at infinite dilution, designated by the symbol K'_∞ , is equal to the equilibrium constant K of Equation A, for at infinite dilution

$$\gamma_{A^+} = 1 \quad \gamma_{B^+} = 1 \quad \text{and} \quad \frac{\gamma_{A^+}}{\gamma_{B^+}} = 1$$

Since

$$K'_\infty = K = \frac{\gamma_{A^+}}{\gamma_{B^+}} \times K'$$

it follows that the ratio of the activity coefficients of the two cations at any concentration c is equal to the ratio of K'_∞ to K' at that concentration, or

$$\left(\frac{\gamma_{A^+}}{\gamma_{B^+}} \right)_c = \frac{K'_\infty}{K'_c}$$

Thus, if we experimentally determine or arbitrarily assign values to the activity coefficients of one of the cations in the solution, we can calculate the activity coefficients of the other cation.

The number of cations in the system need not be restricted to two but can be as large as desired. In a system of cations, A, B, C, D, \dots , in equilibrium with a bentonite, the equilibrium relationships of any pair of cations can be used to calculate their relative activity coefficients. Thus each cation can in turn be compared with the standard cation, and the relative activity coefficients determined in mixed electrolytes of almost any degree of complexity.

The author's experimental application of this method for determining activity coefficients has been extremely limited by necessity. A few experiments have been conducted with the cadmium-barium exchange reaction.

The reaction was first investigated at a constant total concentration of 100 milliequivalents per liter and at a temperature of 25°. A series of eight experiments was performed, in which various amounts of barium-saturated bentonite were used and in which the relative amounts of barium and cadmium in the solutions were also varied, thereby covering the composition range fairly well. After two weeks of stirring in the thermostat they were permitted to settle, the clear supernatant solutions were siphoned off and analyzed for both cadmium and barium. These analytical results, the amounts of barium-saturated bentonite used, and the compositions of the initial solutions are given in Table I, along with the calculated data.

TABLE I
EXPERIMENTAL DATA FOR THE BARIUM-CADMIUM EXCHANGE REACTION AT CONSTANT IONIC STRENGTH

All concentrations expressed as milliequivalents per liter

No.	Initial concns.			Final concns.				K'
	Cd^{++}	Ba^{++}	BaZ_2	By analysis Cd^{++}	By analysis Ba^{++}	Calculated CdZ_2	Calculated BaZ_2	
1	100	0	20	89.0	12.4	11.0	7.6	0.202
2	100	0	40	81.7	19.3	18.3	20.7	.209
3	100	0	60	76.8	24.4	23.2	35.6	.207
4	100	0	80	72.6	28.4	27.4	51.6	.208
5	100	0	100	68.7	31.7	31.3	68.3	.211
6	80	20	80	59.7	39.7	20.3	60.3	.224
7	60	40	60	49.6	50.9	10.4	49.1	.217
8	40	60	40	35.2	64.5	4.8	35.5	.248

The second and third columns give the compositions of the solutions used; the fourth column gives the amounts of barium-saturated bentonite used; the fifth and sixth columns are the amounts of cadmium and barium found by analysis in the equilibrium solutions; the seventh and eighth columns give the composition of the solid phase calculated by difference; and the values in the last column are those of the equilibrium constant obtained by substitution in the equation

$$K' = \frac{Ba^{++}}{Cd^{++}} \times \frac{CdZ_2}{BaZ_2}$$

Since the ionic strength is constant throughout this series of experiments, the activity coefficients probably do not vary greatly, and they have been omitted in the calculations. These experiments were performed merely to show that the assumptions regarding the nature of the reaction are valid; and, judging by the nearly concordant values of K' , I think we are justified in assuming that this exchange reaction is accurately expressed by the equation

$$K = \frac{\gamma_{Ba^{++}}}{\gamma_{Cd^{++}}} \times \frac{Ba^{++}}{Ca^{++}} (\text{in solution}) \times \frac{CdZ_2}{BaZ_2} (\text{solid phase})$$

A series of equilibria determinations were made at various concentra-

tions and at a temperature of 25°. The experimental data are presented in Table II.

TABLE II
EQUILIBRIA DATA FOR THE CADMIUM-BARIUM EXCHANGE REACTION AT VARIOUS CONCENTRATIONS, AND THE COMPARISON OF THE CALCULATED AND THE EXPERIMENTALLY DETERMINED VALUES OF THE RATIO
All concentrations expressed as milliequivalents per liter

No.	Ionic strength	Final concentrations				K'	K'_{∞}/K'	$\frac{\gamma_{\text{BaCl}_2}^3}{\gamma_{\text{CdCl}_2}^2}$
		Ba^{++}	Cd^{++}	BaZ_2	CdZ_2			
1	0.0075	2.13	2.83	2.87	2.17	0.57	2.6	2.0
2	.030	7.64	12.16	12.36	7.84	.40	3.8	3.5
3	.15	32.0	68.5	68.5	31.5	.215	7.0	8.4
4	.30	72.5	128	81.8	18.2	.125	12	14
5	1.50	465	543	94.0	6	.055	27	75

The values of K' in the seventh column were calculated by substitution of the data into the equation

$$K' = \frac{\text{Ba}^{++}}{\text{Cd}^{++}} (\text{in solution}) \times \frac{\text{CdZ}_2}{\text{BaZ}_2} (\text{in solid phase})$$

They were plotted against the square root of the ionic strength and extrapolated to infinite dilution. The data are meager and the extrapolation is not an exact one, but the value $K'_{\infty} = 1.5$ is probably not greatly in error. The next to last column of Table II contains the values of the ratio $\gamma_{\text{Ba}^{++}}/\gamma_{\text{Cd}^{++}}$ calculated from the values of K' and the quantity $K'_{\infty} = 1.5$.

Making use of the published activity coefficient data for barium chloride and cadmium chloride and the hypothesis of Lewis and Randall, that in a dilute solution the activity coefficient of any ion depends solely on the total ionic strength, it is possible to calculate values for the ratio $\gamma_{\text{Ba}^{++}}/\gamma_{\text{Cd}^{++}}$. Using the notation of Lewis and Randall

$$\gamma_{\text{Ba}^{++}} = \frac{\gamma_{\text{BaCl}_2}^3}{\gamma_{\text{Cl}^-}^2} \quad \text{and} \quad \gamma_{\text{Cd}^{++}} = \frac{\gamma_{\text{CdCl}_2}^3}{\gamma_{\text{Cl}^-}^2}$$

Dividing the first equation by the second we get

$$\frac{\gamma_{\text{Ba}^{++}}}{\gamma_{\text{Cd}^{++}}} = \frac{\gamma_{\text{BaCl}_2}^3}{\gamma_{\text{CdCl}_2}^3}$$

The last column of Table II contains the values of $\gamma_{\text{Ba}^{++}}/\gamma_{\text{Cd}^{++}}$ calculated from the activity coefficients of barium chloride and cadmium chloride interpolated from the values published by Scatchard and Tefft.²

It is undoubtedly highly presumptive to extend the hypothesis of Lewis and Randall to such high concentrations as occur in experiments 3, 4, and 5.

The agreement between the calculated and observed values is probably as good as can be expected when consideration is given to the assumptions

² G. Scatchard and R. F. Tefft, *THIS JOURNAL*, **52**, 2272 (1930).

underlying the calculated values and the analytical errors in the experimental determinations. The author is of the opinion that the cation-exchange reactions of bentonites offer an easy experimental way of determining relative activity coefficients with a fair degree of accuracy.

Summary

A method for utilizing the cation-exchange reactions of bentonites for the determination of relative activity coefficients in mixed electrolytes has been presented. The method was applied experimentally to the barium-cadmium exchange reaction; the results are in fair agreement with those calculated from published data of the activity coefficients of barium chloride and cadmium chloride solutions.

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[CONTRIBUTION NO. 224 OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

THE INTEGRAL HEATS OF DILUTION AND THE RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 25°

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I. Introduction

The accurate measurement of heats of dilution of strong electrolytes at concentrations below 0.1 M by Lange and his co-workers¹ and the successful extrapolation of these measurements to infinite dilution permit an evaluation of the relative partial molal heat contents of the components of such solutions in cases where measurements at higher concentrations have already been made. The dilution of very dilute aqueous solutions of strong electrolytes (in general below 0.1 M) evolves heat in every case so far studied, in agreement with the interionic attraction theory,² so that previous extrapolations of dilution measurements to infinite dilution, even when such measurements have been extended to concentrations of a few tenths molal, are often seriously in error. For example, Lewis and Randall³ state that the dilution of a saturated solution of sodium chloride containing one mole of the salt with a very large amount of water absorbs 606 calories at 25° and that this agrees well with the value 598 calories calculated from partial molal heat contents. The measurements on dilute sodium chloride solutions presented here combined with the results of

¹ For a review of this work see Lange and Robinson, *Chem. Rev.*, 9, 89 (1931), which contains complete references.

² Lange and Meixner, *Physik. Z.*, 30, 670 (1929).

³ Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923, p. 95.