condition is far from fulfilled. There is, however, a compensation among the coefficients of the different powers of the concentration. In Fig. 8 is plotted $(\ln \gamma_{MX} - \ln \gamma_{KCl})/M$ for the other three salts and for sodium chloride.[1] The hypothesis of Åkerlöf and Thomas requires that each of these curves be horizontal. This condition is closely approximated for lithium chloride, but not for any of the other salts. The curves do, however, all become flatter with increasing concentration, and our measurements give no evidence against the usefulness of the hypothesis as an empirical approximation for higher concentrations.

Summary

Measurements are made of the freezing point depressions up to one molal of the five possible equimolal mixtures of the reciprocal salt pair: potassium nitrate–lithium chloride, and of two three to one mixtures.

The results of Brönsted's theory of the specific interaction of ions are derived more simply and are extended to the coefficients of the higher powers of the concentration.

The parameters necessary to determine the thermodynamic functions of any mixture of this reciprocal salt pair are determined and found to agree completely with the extended theory of Brönsted. Some of the consequences of this agreement are discussed.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Effect of Electrolytes in Ionic Reactions

BY MARTIN KILPATRICK

In a recent paper La Mer and Greenspan[1] point out that the primary kinetic salt effects in the hydrolysis of acetylated hydroxyl acids are only in qualitative agreement with the Brönsted theory of reaction velocity. For reactions between ions Brönsted's equation is

$$\log k = \log k_0 + z_A z_B \sqrt{\mu} \qquad (1)$$

where k is the observed velocity constant, k_0 the velocity constant at zero ion concentration, z_A and z_B the valencies of the reacting ions and μ the ionic strength. This equation is based on the Debye limiting law

$$-\log f = 0.5\, z^2 \sqrt{\mu} \qquad (2)$$

Although La Mer and Greenspan recognize the fact that their results may have been obtained at too high ionic concentrations to give the theoretical slope, they favor another interpretation of the data.

Without going into this aspect of the problem, it is the purpose of the present paper to show that the failure to find agreement with equation (1) is due to the fact that the experimental results are not in the range of concentration where this equation applies. To do this we will use for the activity coefficients an equation applicable up to ionic strengths of 0.03–0.04. This equation

$$-\log f = 0.5\, z^2 \sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (3)$$

is obtained from the equation of Debye

$$-\log f = 0.50\, z^2 \sqrt{\mu}/(1 + \kappa b)$$

on the assumption that b, the apparent average ionic diameter, is approximately 3.0×10^{-8} cm., κ being equal to $0.33 \times 10^{8} \sqrt{\mu}$ cm.$^{-1}$ at 25°.[2] On this basis equation (1) becomes[3]

$$\log k = \log k_0 + z_A z_B \sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (4)$$

A test of this equation can be made by plotting $\log k$ against $\sqrt{\mu}/(1 + \sqrt{\mu})$ and drawing the theoretical slope, just as La Mer and Greenspan tested equation (1) by plotting $\log k$ against $\sqrt{\mu}$ (see Fig. 1 of their paper). It is, however, more convincing to calculate k_0 from equation (4) and examine its constancy. The results of the computation are given in Table I.

With the exception of acetylbenzilic acid, and 1-acetylmalic acid (for which only two points are given, and at ionic strengths outside the range of applicability of equation (3)), the constancy of k_0 indicates agreement with equation (4). It should be emphasized that a few experimental points, with a relatively small change of ionic strength, are unsuitable for testing equation (1) or equation (4). It seems logical to conclude that, in so far as the accuracy of the experiments and our knowledge of activity coefficients from equilibrium measurements will permit us to judge, the results

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(1) La Mer and Greenspan, THIS JOURNAL, **56**, 1492 (1934).

(2) Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 533 (1934).

(3) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

TABLE I

THE HYDROLYSIS OF ACETYLATED HYDROXY ACIDS

$\sqrt{\mu}$	$k_{\text{obs.}}$	k_0 (calcd. by (4))
Acetylmandelic		
0.107	1.26	1.01
.150	1.32	0.98
.150	1.31	.97
.221	1.48	.97
β-Acetoxy-β-phenylpropionic		
0.108	1.23	0.98
.153	1.32	.97
.156	1.29	.95
.218	1.47	.98
α-Acetoxy-β-phenylpropionic		
0.111	0.566	0.450
.158	.622	.454
.222	.662	.437

$\sqrt{\mu}$	$k_{\text{obs.}}$	k_0 (calcd. by (4))
Acetylsalicylic		
0.110	7.26	5.78
.153	7.36	5.42
.157	7.29	5.34
.218	8.09	5.47
Acetylbenzilic		
0.123	0.01550	0.0120
.175	.01627	.0116
.176	.0166	.0118
.177	.01609	.0114
.247	.01744	.0110
Acetylglycolic		
0.166	3.32	2.39
.206	3.45	2.33
.235	3.58	2.31
1-Acetylmalic		
0.260	0.191	0.0738
.368	.242	.0703

obtained by La Mer and Greenspan are in quantitative agreement with the Brönsted theory. It seems probable that if the experiments could be carried out in sufficiently dilute solution agreement with equation (1) would be obtained.

Equation (3) may prove a convenience in extrapolation, for kinetic measurements of this sort. In the study of the addition of hydrobromic acid to glycid Brönsted, Kilpatrick and Kilpatrick[4] were able to obtain accurate results in sufficiently dilute solution to test and confirm equation (1). The data show a departure from (1) even below $\mu = 0.01$, but a plot corresponding to their Fig. 9, log k against $\sqrt{\mu}/(1 + \sqrt{\mu})$ rather than $\sqrt{\mu}$, shows agreement with equation (4) over the whole range studied. Calculation of log k_0 by equation (4) gives a constant value over the whole range, 0.592 ± 0.001.

Summary

It has been shown that one cannot conclude from the measurements of La Mer and Greenspan on the hydrolysis of the acetylated hydroxy acids that their results are not in quantitative agreement with the Brönsted theory.

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[4] Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SASKATCHEWAN, SASKATOON]

Studies on the Thermochemistry of the Compounds Occurring in the System $CaO-Al_2O_3-SiO_2$. V. The Heats of Formation of Tricalcium Silicate and Dicalcium Silicate[1]

BY O. K. JOHANNSON AND T. THORVALDSON

Introduction

The only data found in the literature from which the heat of formation of tricalcium silicate can be calculated are those obtained by D. Tschernobaeff[2] by firing mixtures of calcium carbonate and silica (quartz) with charcoal in a bomb calorimeter. The average value obtained for the reaction between the calcium carbonate and the silica was 107.9 kg. cal. absorbed per mole of tricalcium silicate. Assuming that on dissociation of calcium carbonate 42.7 kg. cal. per mole are absorbed, the value obtained for the heat of formation of tricalcium silicate from calcium oxide and quartz is 20.2 kg. cal. per mole or 88.5 g. cal. per gram of tricalcium silicate. Tschernobaeff states that the reaction product contained both some combined carbon dioxide and "a great amount of free lime."

Tschernobaeff and Wologdine[3] used the same method to determine the heat of formation of dicalcium silicate. Their calculated value for the heat of formation from calcium oxide and silica (sand) was 28.7 kg. cal. per mole of Ca_2SiO_4.

Nacken[4] determined the heat of solution of γ-dicalcium silicate in a mixture of hydrochloric and hydrofluoric acids. The analysis of the artificially prepared silicate, the concentration of the solution of acids and the temperature of the determinations are not given. The average value recorded for the heat of solution was 537.304 calories per gram or 92.671 kg. cal. per mole of γ-dicalcium silicate. From this value and the heat of solution of an equivalent amount of lime and silica

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[1] The authors wish to acknowledge generous financial assistance rom the National Research Council of Canada.

[2] D. Tschernobaeff, *Revue de Metallurgie*, **2**, 729 (1905).

[3] Tschernobaeff and Wologdine, *Compt. rend.*, **154**, 206 (1912).

[4] Nacken, *Zement*, **19**, 818, 847(1930).