

to an aliquot at the end of the reaction and a subsequent analysis was carried out in order to ascertain whether all the hydroperoxide was destroyed or not.

The experiments on rate studies were carried out in 125-ml. glass-stoppered erlenmeyer flasks immersed in thermostated baths. The same order of addition was followed as outlined in the previous paragraph except where noted. During the addition vigorous mechanical stirring was maintained. At various times an aliquot was transferred by a pipet as rapidly as possible to the colorimeter tube containing the buffered bipyridyl solution and the residual ferrous iron concentration was determined.

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Summary

In dilute aqueous solutions of low pH the stoichiometric ratio of ferrous iron oxidized to CHP consumed in the presence of oxygen is much

greater than two to one and is increased by an increase in the initial ratio of ferrous iron to CHP or by a decrease in the pH of the solution. To account for these facts a possible type of mechanism has been postulated in which it is assumed that the primary reaction results in the formation of $C_6H_5C(CH_3)_2O$ radicals which split off methyl radicals to form acetophenone. More hydroperoxides are formed by reactions involving radicals, oxygen, ferrous iron, hydrogen ions and the product, formaldehyde. These hydroperoxides react with the ferrous iron to produce more radicals. During the initial stages of the reaction the mechanism can be simplified considerably and used to determine the rate constant of the primary reaction which is given by $k_1 = 3.9 \times 10^9 e^{-11,100/RT}$ l. mole⁻¹ sec.⁻¹.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY OF THE UNIVERSITY OF TEXAS]

The Determination of the Activity Coefficients of the Alkaline Earth and Magnesium Perchlorates from Freezing Point Data¹

BY DAN E. NICHOLSON² WITH W. A. FELSING

Introduction

The purpose of this investigation was the experimental determination of the freezing points of the alkaline earth and magnesium perchlorates in order to evaluate the activity coefficients of these solutes over a wide range of solute concentrations at temperatures near 0°. For the most part, the freezing point data in chemical literature were accumulated before the development of precision devices for temperature measurement. Consequently, it is usually not possible to calculate activity coefficients from the data available. An even more serious objection than this lack of accuracy is the lack of sufficient range in concentration to allow a reliable extrapolation to zero ionic strength, involved in the evaluation.

Experimental

The freezing point vessels and stirrers were similar to the apparatus developed and described by Scatchard, Jones and Prentiss.³ The apparatus actually employed in this Laboratory has been reported previously by Jones, Spuhler and Felsing.⁴

(1) For detailed paper and material supplementary to this article order Document 2835 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$0.50 for photocopies (6 × 8 inches) readable without optical aid.

(2) Formerly Research Scientist, Defense Research Laboratory of the University of Texas and 1949-1950 holder of the Humble Oil and Refining Company Fellowship in Chemistry at the University of Texas.

(3) Scatchard, Jones and Prentiss, *THIS JOURNAL*, **54**, 2676 (1932).

(4) Jones, Spuhler and Felsing, *ibid.*, **64**, 965 (1942).

The Thermocouple.—The thermocouple calibration was made by inserting a platinum resistance thermometer in one vessel and measuring the freezing point depressions of solutions of sodium nitrate over a temperature range of 0 to -3°. For the twelve-junction unit used, the relation between the temperature difference θ and the electromotive force E in volts has been found to be

$$\theta = 1.4476E + 0.03606E^2 - 0.01055E^3$$

For depressions greater than about 2.5°, the platinum resistance thermometer, recently calibrated by the National Bureau of Standards, was used directly.

Purification and Analysis of Salts.—Reagent grade of barium, calcium, strontium and magnesium perchlorates from the G. Frederick Smith Chemical Company were used. Analysis by evaporation to dryness in a crucible, with a slight excess of dilute sulfuric, showed a purity of at least 99.9% in all cases. All necessary precautions were taken to prevent spattering. Further recrystallization did not improve the purity of these salts sufficiently to warrant the effort. The solutions in thermal equilibrium with the ice in the freezing point runs were analyzed by the same procedure.

The Data and Their Treatment.—The present investigation involved about fifty freezing point determinations each for barium, calcium, strontium and magnesium perchlorates. The data may be expressed by a listing of j -values, defined by

$$= 1 - (\theta/5.574M)$$

where M is the concentration expressed as weight-molality. The 200 individual determinations are not given here.¹ Figure 1 shows an illustrative graph of j plotted against $M^{1/2}$ from zero to one molal. Scatchard³ has proposed a very useful and

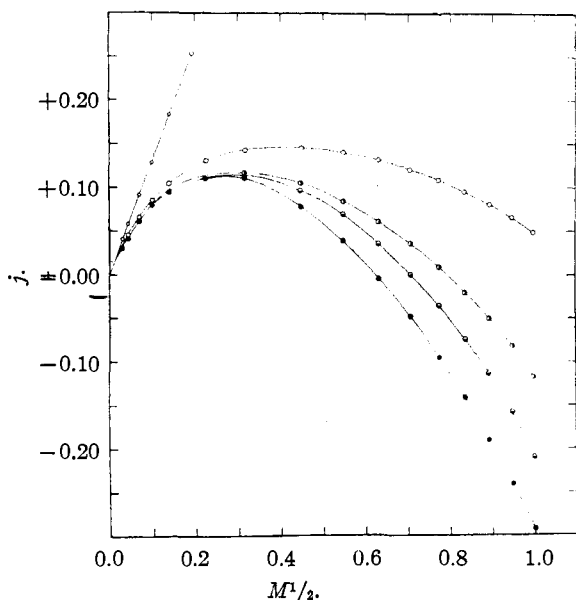


Fig. 1.—The relation of j to $M^{1/2}$: \circ , limiting law; \circ , barium perchlorate; \odot , strontium perchlorate; \ominus , calcium perchlorate; \bullet , magnesium perchlorate.

convenient method for obtaining "smoothed" values by plotting the deviation function

$$\begin{aligned} \Delta j &= j - \frac{A'\sqrt{\mu}}{1 + B'\sqrt{\mu}} - C'\mu \\ &= j - \frac{A\sqrt{M}}{1 + B\sqrt{M}} - CM \end{aligned}$$

where μ is the ionic strength, M , the weight molality, and B and C are empirically determined constants for each salt. When the concentration is expressed as weight-molality, the value of A , from the Debye-Hückel theory, is 1.2948 for the bi-univalent electrolytes. Figure 2 presents the deviation function for barium perchlorate. Tables I and II contain values of j and Δj at rounded concentrations.

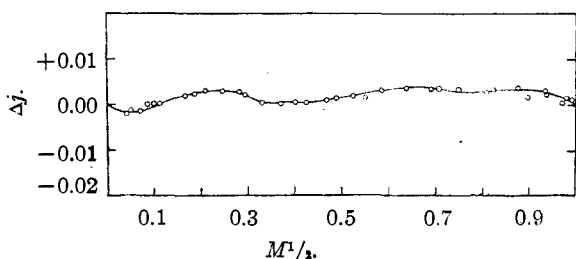


Fig. 2.— Δj values for barium perchlorate.

TABLE I
 j VALUES OF THE ALKALINE EARTH AND MAGNESIUM PERCHLORATES

Molality	Lim. law	Ba-(ClO ₄) ₂	Sr(ClO ₄) ₂	Ca(ClO ₄) ₂	Mg(ClO ₄) ₂
0.001	0.0409	0.0338	0.0312	0.0302	0.0319
.002	.0579	.0451	.0415	.0405	.0426
.005	.0916	.0652	.0609	.0586	.0605
.01	.1295	.0837	.0784	.0769	.0766
.02	.1831	.1047	.0965	.0938	.0942
.05	.2895	.1307	.1135	.1108	.1104
.1	.4095	.1425	.1165	.1135	.1114
.2	.5791	.1451	.1049	.0964	.0774
.3	.7092	.1411	.0841	.0686	+ .0394
.4	.8190	.1329	.0614	.0364	-.0035
.5	.9156	.1212	.0359	+ .0014	-.0484
.6		.1079	.0088	-.0354	-.0947
.7		.0949	-.0199	-.0738	-.1418
.8		.0813	-.0504	-.1141	-.1907
.9		.0661	-.0827	-.1571	-.2413
1.0		.0491	-.1170	-.2095	-.2928

TABLE II
 Δj VALUES OF THE ALKALINE EARTH AND MAGNESIUM PERCHLORATES

Molality	Ba(ClO ₄) ₂	Sr(ClO ₄) ₂	Ca(ClO ₄) ₂	Mg(ClO ₄) ₂
0.001	-0.0013	-0.0030	-0.0038	-0.0024
.002	-.0018	-.0036	-.0044	-.0027
.005	-.0015	-.0020	-.0027	-.0026
.01	-.0006	+ .0002	+ .0000	-.0014
.02	+ .0012	.0032	.0027	+ .0020
.05	.0020	.0045	.0068	.0065
.1	.0014	.0047	.0116	.0119
.2	.0005	.0074	.0180	.0102
.3	.0023	.0094	.0215	.0119
.4	.0036	.0108	.0233	.0210
.5	.0034	.0118	.0240	.0116
.6	.0027	.0120	.0237	.0110
.7	.0031	.0112	.0223	.0100
.8	.0033	.0090	.0196	.0078
.9	.0024	.0054	.0143	.0042
1.0	.0000	.0000	.0000	.0000

Salt	B	C
Ba(ClO ₄) ₂	5.0533	-0.1643
Sr(ClO ₄) ₂	5.9496	-.3033
Ca(ClO ₄) ₂	5.9960	-.3946
Mg(ClO ₄) ₂	5.6168	-.4885

Calculation of Activity Coefficients

Based upon the presentation of Lewis and Randall,⁵ Scatchard, Jones and Prentiss³ derived the relation

$$-\log \gamma' = 0.4343 (j + CM) + 2A/B \log (1 + BM^{1/2}) + \int_0^M \Delta j d \log - 0.000461 \int_0^\theta (1 - j) d\theta$$

for evaluating the activity coefficient. The values of B and C for the various salts have been determined in the usual manner.

The evaluation of the first integral is done ana-

(5) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 286.

lytically from $M = 0$ to $M = 0.001$, assuming that Δj is proportional to M . For the more concentrated solutions, the evaluation is carried out graphically. Table III contains the provisional activity coefficients for the four salts at rounded concentrations.

TABLE III

VALUES OF THE ACTIVITY COEFFICIENT, γ' , FOR THE ALKALINE EARTH AND MAGNESIUM PERCHLORATES

Mol-ality	Lim. law	Ba(ClO ₄) ₂	Sr(ClO ₄) ₂	Ca(ClO ₄) ₂	Mg-(ClO ₄) ₂
0.001	0.910	0.895	0.897	0.897	0.898
.002	.841	.858	.861	.861	.861
.005	.760	.798	.802	.803	.803
.01	.678	.743	.750	.751	.752
.02	.577	.682	.695	.697	.697
.05	.420	.599	.625	.629	.628
.1	.293	.540	.579	.587	.588
.2	.176	.489	.546	.566	.578
.3	.119	.463	.533	.572	.591
.4	.086	.450	.545	.589	.619
.5	.064	.443	.556	.615	.655
.6		.441	.572	.646	.698
.7		.440	.592	.683	.749
.8		.442	.615	.725	.807
.9		.446	.642	.774	.872
1.0		.451	.673	.834	.947

Discussion of Results

It is believed that most of the freezing point data obtained in this investigation are accurate to within 0.05–0.10% of the freezing point depression. In the analysis of the equilibrium solutions,

the mean deviation of three or four determinations was consistently in the range 0.03–0.05%.

Values of the activity coefficients for magnesium perchlorate⁶ in the literature were obtained by the isopiestic method. The differences between these data and those of the present investigation are within the range of the experimental error.

No attempt has been made to correlate the differences of activity coefficients with the size and shape of ions.

Acknowledgment.—This work was made possible, initially, by a grant from the Defense Research Laboratory, The University of Texas, under the sponsorship of the Bureau of Ordnance, Navy Department, Contract NO rd-9195 and, during the year 1949–1950, by the award of a fellowship from the Humble Oil and Refining Company, Houston, Texas.

Summary

1. The freezing point depression method was used to determine the activity coefficients of the alkaline earth and magnesium perchlorates in aqueous solutions over a concentration range 0.003 to 1 molal.

2. The activity coefficients were calculated from j -values listed for rounded concentrations.

3. The activity coefficients are based upon freezing point data accurate to within 0.05 to 0.10% of the observed depression and upon concentration determinations consistent to within 0.03–0.05%.

(6) Stokes and Levien, *THIS JOURNAL*, **68**, 333 (1946).

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Electric Moments of Organosilicon Compounds. I. Fluorides and Chlorides¹

BY COLUMBA CURRAN, ROBERT M. WITUCKI AND PATRICK A. MCCUSKER

The availability of d orbitals for bond formation in elements of the sodium series suggests a potential double bond character in silicon compounds which is not possible in carbon compounds. Contributions of structures containing double bonds are generally more common in elements of the sodium series than in elements of the potassium series. Brockway and Coop² have studied the bond character in the chlorosilanes by means of electron diffraction and electric moment measurements. The low moments for these compounds, SiH₃Cl 1.28, SiH₂Cl₂ 1.17 and SiHCl₃ 0.85, compared to the values for the chloromethanes CH₃Cl 1.87, CH₂Cl₂ 1.56 and CHCl₃ 1.00, were interpreted by these workers as suggesting contributions of structures of the type H₃-Si=Cl⁺ to the chlorosilane molecules. This double bond

character of the silicon-to-chlorine bond is further indicated by the relatively large moments of the corresponding germanium compounds.³

Sauer and Mead⁴ have reported a moment of 0.74 D for hexamethyldisiloxane. In calculating the oxygen valence angle in this compound, these authors neglected potential double-bond character and assumed a Si-C bond moment of 1.0, with the carbon the negative end of the dipole, and a Si-O bond moment of 2.8. More recently Wright and Hunter⁵ have reported the infrared spectra of the methylpolysiloxanes. The intensity of the absorption peak attributed to the Si-O stretching vibration was observed by these workers to be about five times as great as that for the C-O bond in ethers. They interpreted this high intensity as due to a large degree of ionic

(1) Presented at the New York Meeting of the American Chemical Society, September, 1947.

(2) Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(3) Smyth, *THIS JOURNAL*, **63**, 57 (1941).

(4) Sauer and Mead, *ibid.*, **68**, 1794 (1946).

(5) Wright and Hunter, *ibid.*, **69**, 803 (1947).