weighed. The amount of polymercuration so determined was added to that found by the carrier technique.

Acknowledgments.—The authors gratefully acknowledge the Fellowship granted to one of us (W. K.) by the Atomic Energy Commission, and the help and coöperation of Dr. Gerhart Groetzinger of the Institute for Nuclear Studies, who bombarded the sodium bromate solution from which some of the needed Br^{82} was obtained.

Summary

1. Both toluene and nitrobenzene were mercurated (a) with mercuric acetate, and (b) with mercuric perchlorate in perchloric acid solution.

2. The amounts of ortho and para and of meta isomers thus formed were determined in each case. The analytical method for the tolyl mercuric salts depended upon converting these compounds to bromotoluenes, and analyzing these by a tracer technique requiring Br^{82}.

3. It was found that mercuration with mercuric perchlorate in perchloric acid solution gave the pronounced orientation effects typical of electrophilic substitution; mercuration with unionized mercuric acetate showed much less strongly marked orientation effects.

CHICAGO, ILLINOIS RECEIVED MARCH 18, 1950

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIV., POLYMER CORPORATION LTD.]

The Decomposition of Cumene Hydroperoxide by Ferrous Iron in the Presence of Oxygen[1]

BY J. W. L. FORDHAM AND H. LEVERNE WILLIAMS

In most low temperature free radical initiated emulsion polymerization recipes the initiating free radicals are formed by the reaction between cumene hydroperoxide (CHP, $C_6H_5C(CH_3)_2OOH$) and complexed ferrous iron. In order to obtain information on the rate of production of these free radicals under various conditions a study of the decomposition of CHP was undertaken. In a previous publication[2] it was shown that in the vicinity of 100° the decomposition of CHP in a styrene solution may be described by two simultaneous reactions, a unimolecular fission presumably at the O—O bond producing two radicals per molecule ($k = 2.7 \times 10^{12}e^{-30,400/RT}$ sec.$^{-1}$). and a radical induced decomposition having no effect on the number of radicals in the system ($k = 1.00 \times 10^{5}e^{-6,500/RT}$ l. mole^{-1} sec.$^{-1}$). The present paper deals with the decomposition of CHP in an acidic dilute aqueous solution at lower temperatures in the presence of ferrous iron and oxygen with particular emphasis on the rate constant of the primary radical producing reaction and as an intermediate step to the study of the decomposition in alkaline medium in the presence of complexed iron. The study was carried out in the presence of oxygen rather than its absence because of the experimental difficulty of removing completely from very dilute solutions the effect of oxygen traces. Very little has been reported on this although Kolthoff and Medalia[3] obtained an approximate value of 27 l. mole^{-1} sec.$^{-1}$ at 27° for the rate constant of the primary radical producing reaction. Baxendale, Evans and Park[4] in a study of the analogous reaction between hydrogen peroxide and ferrous iron found that the rate constant of the reaction is given by $k = 1.78 \times 10^{9}e^{-10,100/RT}$ l. mole^{-1} sec.$^{-1}$.

Stoichiometric Ratios.—Publications[4,5,6] indicate that in dilute aqueous solutions of hydrogen peroxide and ferrous iron the ratio of ferrous iron oxidized to peroxide consumed in an acidic medium is two to one whether the reaction takes place in the absence or presence of oxygen. This fact supports the mechanism proposed for dilute solutions of low *p*H,[4] *i.e.*

$$Fe^{++} + HO_2H \longrightarrow Fe^{+++} + OH^- + HO\cdot$$
$$Fe^{++} + HO\cdot \longrightarrow Fe^{+++} + OH^-$$

However, in the CHP–ferrous iron reaction under similar conditions, the ratio is approximately one to one in the absence of oxygen and varies from slightly less than two to more than four to one depending upon the initial concentration of CHP and ferrous iron in the presence of oxygen.[3] The authors have also found the ratios are considerably greater than two to one in the presence of oxygen. The stoichiometry of the reaction in an alkaline medium could not be investigated in the presence of oxygen because of the rapid oxidation of ferrous iron in the absence of hydroperoxide. The results are in Tables I and II.

From these results it is evident that at a *p*H from 1 to 4 an increase in the initial ratio of ferrous iron to CHP, a decrease in the *p*H of the solution, or a decrease in the initial CHP con-

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[1] Presented at the Detroit Meeting, Division of Physical and Inorganic Chemistry, American Chemical Society, April, 1950.

[2] J. W. L. Fordham and H. L. Williams, *Can. J. Research*, **27B**, 943 (1949).

[3] I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3789 (1949).

[4] J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

[5] I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777 (1949).

[6] I. M. Kolthoff and A. I. Medalia, *ibid.*, **71**, 3784 (1949).

TABLE I

REACTION RATIOS OF CHP WITH Fe^{++} IN 0.1 N H_2SO_4 AT 25.10°

$[CHP]_0$, $M \times 10^5$	$[Fe^{++}]_0/[CHP]_0$	Ratio
2.00	4.00	>4.00[a]
2.00	6.00	5.80
2.00	8.00	6.20
2.00	10.00	6.30
3.00	4.00	>4.00[a]
3.00	6.00	5.75
3.00	8.00	5.85
3.00	10.00	5.95
4.00	4.00	>4.00[a]
4.00	6.00	5.45
4.00	8.00	5.50
4.00	10.00	5.60

[a] Residual CHP present instead of residual Fe^{++}.

TABLE II

REACTION RATIOS OF CHP WITH Fe^{++} IN WATER AT 25.10°

$[CHP]_0$, $M \times 10^5$	$[Fe^{++}]_0/[CHP]_0$	pH_0	pH_f	Ratio
2.00	4.00	5.00	3.88	3.70
2.00	6.00	4.30	3.71	4.35
2.00	8.00	4.30	3.70	4.45
2.00	10.00	4.27	3.68	4.50
3.00	4.00	4.68	3.76	3.85
3.00	6.00	4.20	3.60	4.50
3.00	8.00	4.18	3.54	4.60
3.00	10.00	4.16	3.42	4.75
4.00	4.00	4.62	3.56	3.95
4.00	6.00	4.16	3.48	4.60
4.00	8.00	4.10	3.47	4.75
4.00	10.00	4.09	3.46	3.00

centration at a constant *p*H causes an increase in the stoichiometric ratio. The increase in the ratio with an increase in initial CHP concentration in Table II may be caused by the accompanying decrease of *p*H with the simultaneous increase of ferrous iron concentration; this effect could possibly outweigh the effect of an increase in the initial CHP concentration. As the initial concentration of CHP increases, it is quite probable that some of the hydroperoxide decomposition takes place by radical induced decomposition at the O—O bond. This decomposition does not involve ferrous iron; consequently a lowering of the ratio would occur under these conditions.

Mechanism.—A simple mechanism to fit the observed results does not seem to be available. The results of Tables I and II suggest a mechanism involving some or all of the reactions of the following type in dilute aqueous solutions of low *p*H:

$$Fe^{++} + RO_2H \xrightarrow[k_1]{} Fe^{+++} + OH^- + RO\cdot$$

$$\text{where } RO = C_6H_5C(CH_3)_2O \qquad \text{I}$$

$$RO\cdot \xrightarrow[k_2]{} C_6H_5COCH_3 + CH_3\cdot \qquad \text{II}$$

$$CH_3\cdot + O_2 \xrightarrow[k_3]{} CH_3O_2 \qquad \text{III}$$

$$Fe^{++} + CH_3O_2\cdot \xrightarrow[k_4]{} Fe^{+++} + CH_3O_2^- \qquad \text{IV}$$

$$CH_3O_2^- + H^+ \xrightarrow[k_5]{} CH_3O_2H \qquad \text{V}$$

$$Fe^{++} + CH_3O_2H \xrightarrow[k_6]{} Fe^{+++} + OH^- + CH_3O\cdot \qquad \text{VI}$$

$$CH_3O\cdot + O_2 \xrightarrow[k_7]{} XH + HO_2\cdot$$

$$\text{where } XH = CH_2O \qquad \text{VII}$$

$$Fe^{++} + HO_2\cdot \xrightarrow[k_8]{} Fe^{+++} + HO_2^- \qquad \text{VIII}$$

$$HO_2^- + H^+ \xrightarrow[k_9]{} HO_2H \qquad \text{IX}$$

$$Fe^{++} + HO_2H \xrightarrow[k_{10}]{} Fe^{+++} + OH^- + HO\cdot \qquad \text{X}$$

$$CH_3O\cdot + XH \xrightarrow[k_{11}]{} CH_3OH + X\cdot \qquad \text{XI}$$

$$HO\cdot + XH \xrightarrow[k_{12}]{} HOH + X\cdot \qquad \text{XII}$$

$$X\cdot + O_2 \xrightarrow[k_{13}]{} XO_2\cdot \qquad \text{XIII}$$

$$Fe^{++} + XO_2\cdot \xrightarrow[k_{14}]{} Fe^{+++} + XO_2^- \qquad \text{XIV}$$

$$XO_2^- + H^+ \xrightarrow[k_{15}]{} XO_2H \qquad \text{XV}$$

$$Fe^{++} + XO_2H \xrightarrow[k_{16}]{} Fe^{+++} + OH^- + XO\cdot \qquad \text{XVI}$$

$$XO\cdot + XH \xrightarrow[k_{17}]{} XOH + X\cdot \qquad \text{XVII}$$

$$Fe^{++} + CH_3O\cdot \xrightarrow[k_{18}]{} Fe^{+++} + CH_3O^- \qquad \text{XVIII}$$

$$Fe^{++} + HO\cdot \xrightarrow[k_{19}]{} Fe^{+++} + OH^- \qquad \text{XIX}$$

$$Fe^{++} + XO\cdot \xrightarrow[k_{20}]{} Fe^{+++} + XO^- \qquad \text{XX}$$

The primary radical-producing reaction above is suggested by the high stoichiometric ratio. This is greater than that obtained when hydroxyl radicals are formed under similar conditions during the hydrogen peroxide and ferrous iron reaction. The second equation is supported by the work of Kharasch[7] who reported that the primary radical tended to split off a methyl radical rather than a phenyl radical. The affinity of radicals for molecular oxygen and α-hydrogen atoms is well known.[8] Also the presence of formaldehyde has been detected in the decomposition products of CHP which has been treated with ferrous iron in an acidic medium.[9] Otherwise the equations are purely hypothetical and offer a possible explanation of the stoichiometric ratios observed. By this mechanism the rate of disappearance of the ferrous iron is given by

$$-d[Fe^{++}]/dt = [Fe^{++}](\Sigma k[P] + \Sigma K[A]) \text{ where}$$
$$P = \text{hydroperoxide}$$
$$A = \text{radical} \qquad (1)$$

Applying the steady-state condition for all the radicals and substituting eq. 2 in eq. 1

$$[Fe^{++}]\Sigma k[A] = [Fe^{++}]\Sigma k[P] \qquad (2)$$

$$-d[Fe^{++}]/dt = 2[Fe^{++}]\Sigma k[P] \qquad (3)$$

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(7) M. S. Kharasch, *Chem. Eng. News*, **27**, 1927 (1949).

(8) C. E. Frank, *Chem. Revs.*, **46**, 155 (1950).

(9) Hercules Powder Company, private communication.

At present there does not appear to be any easy method of testing the validity of eq. 3, but if the assumption is made that during the initial stages the only significant reaction between ferrous iron and hydroperoxides is the one involving CHP, eq. 3 may be simplified to

$$-d[Fe^{++}]/dt = 2k_1[Fe^{++}][RO_2H] \quad (4)$$

If it is assumed further that k_2, k_3 and k_4 are very much larger than k_1, then eq. 4 may be written as

$$-d[Fe^{++}]/dt = k_1[Fe^{++}](2a - b + [Fe^{++}]) \text{ where}$$
$$a = [RO_2H]_0 \quad (5)$$
$$b = [Fe^{++}]_0$$

When $2a = b$

$$1/[Fe^{++}] = k_1t + 1/b \quad (6)$$

When $2a \neq b$

$$\ln\left(1 + \frac{2a - b}{[Fe^{++}]}\right) = (2a - b)k_1t + \ln 2a/b \quad (7)$$

Eq. 6 and 7 may be used to evaluate k_1.

Rate Studies.—The greater portion of the experimental work was concerned with a measurement of the rate constant k_1 at various temperatures for later use in polymerization work. The value of this constant is so large that measurements had to be made in a very dilute solution (10^{-5} *M*). From the results in Tables I and II it seemed desirable to use low initial concentrations of CHP, low initial ratios of ferrous iron to CHP and no addition of acid in order to keep the deviation from the simplified expression to a minimum.

The disappearance of ferrous iron was measured by analyzing samples for residual ferrous iron at various times. The results of experiments carried out at three different temperatures are given in Figs. 1, 2, 3 and 4. The quantity f has been introduced merely to separate the curves.

The results in Figs. 1, 2, 3 and 4 obey eq. 6 and 7 during the initial stages of the reaction but in most cases during the later stages the plots are not linear but curved particularly under the conditions in which the reaction ratio is large. This curvature is in agreement with the increased disappearance of ferrous iron as the reaction proceeds because of the formation of other

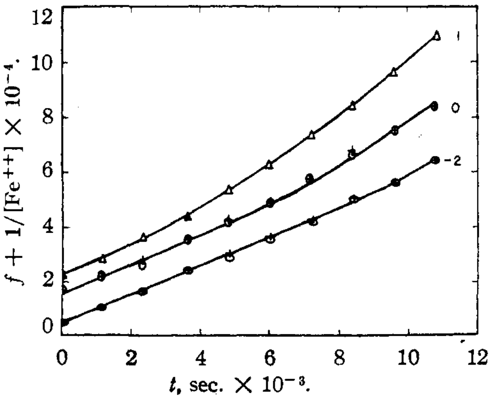

Fig. 1.—Disappearance of Fe^{++} at 0.00° when $2a = b$; values of (f) at right side; lower curve, circles, $a = 2.00 \times 10^{-5}$ *M*, CHP solution added to Fe^{++} solution; crosses, same when Fe^{++} solution added to CHP solution; middle curve same for 3.00×10^{-5} *M* solution; upper curve $a = 4.00 \times 10^{-5}$ *M*.

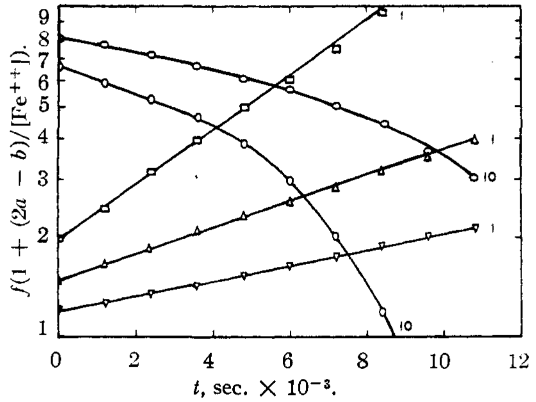

Fig. 2.—Disappearance of Fe^{++} at 0.00° when $2a \neq b$; values of (f) at right side; curves from top to bottom: $a = 2.00$ and $b = 4.99$, $a = 2.00$ and $b = 6.00$, $a = 4.00$ and $b = 4.01$, $a = 3.00$ and $b = 4.01$, and $a = 3.00$ and $b = 4.99$, each $\times 10^{-5}$ *M*.

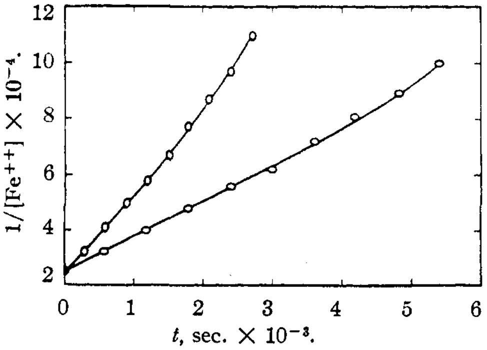

Fig. 3.—Disappearance of Fe^{++} at 12.50 (lower) and 25.10° (upper) when $2a = b$; $a = 2.00 \times 10^{-5}$ *M*.

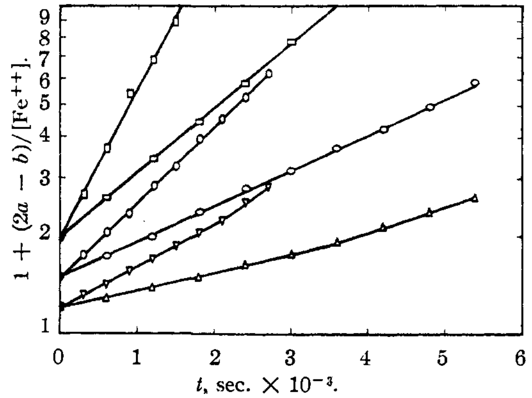

Fig. 4.—Disappearance of Fe^{++} at 12.50 (lower) and 25.0° (upper each pair) when $2a \neq b$; upper pair: $a = 4.00$ and $b = 4.01$, middle pair $a = 3.00$ and $b = 4.01$, and lower pair $a = 3.00$ and $b = 4.99$. each $\times 10^{-5}$ *M*.

hydroperoxides capable of reacting with ferrous iron. In Fig. 1 it is also evident that the order of addition of hydroperoxide and ferrous iron has no effect on a given set of results at this dilution.

Rate constants calculated from the initial slopes of the curves are tabulated in Table III.

TABLE III

PRIMARY RATE CONSTANTS FOR THE CHP-Fe^{++} REACTION AT VARIOUS TEMPERATURES

Temp., °C.	$[CHP]_0$, $M \times 10^5$	$[Fe^{++}]_0$, $M \times 10^5$	k_1 l. mole^{-1} sec.$^{-1}$
0.00	2.00	4.01	5.10
0.00	2.00	4.99	4.85
0.00	2.00	6.00	5.10
0.00	3.00	4.01	4.65
0.00	3.00	4.99	5.05
0.00	3.00	6.00	4.80
0.00	4.00	4.01	4.70
0.00	4.00	8.00	5.30
12.50	2.00	4.01	12.3
12.50	3.00	4.01	12.4
12.50	3.00	4.99	12.1
12.50	4.00	4.01	11.6
25.10	2.00	4.01	27.8
25.10	3.00	4.01	27.0
25.10	3.00	4.99	28.4
25.10	4.00	4.01	26.3

The values of k_1 in Table III indicate that there may be a slight increase in the value as the conditions become more favorable for a larger ratio of ferrous iron oxidized to CHP consumed. This may in turn indicate that the initial slope is composed of more than the k_1 value and consequently these results may be slightly high. This point is being investigated by a study of the reaction in the absence of oxygen and in the presence of acrylonitrile. However, from the values of k_1 at corresponding initial concentrations of ferrous iron and CHP at each of the three temperatures the value of k_1 in the temperature range from 0 to 25° was found to be given by $k_1 = 3.9 \times 10^9 e^{-11,100/RT}$ l. mole^{-1} sec.$^{-1}$.

Discussion.—The presence of ferrous iron along with CHP has provided an alternative reaction for producing free radicals. The frequency factor for the primary radical-producing reaction has been lowered from 2.7×10^{12} in the absence of ferrous iron to 3.9×10^9 in its presence. Simultaneously the activation energy has been lowered from 30.4 to 11.1 kcal. per mole with the net effect that in the temperature range from 0 to 25° there is a much faster rate of production of radicals in the presence of ferrous iron. The substitution of the $C_6H_5C(CH_3)_2$ group for one H-atom of hydrogen peroxide has increased both the frequency factor and the activation energy of the reaction only slightly (1.78×10^9 to 3.9×10^9 and 10.1 to 11.1 kcal. per mole). Nevertheless in this temperature range when CHP reacts with ferrous iron the rate constant is less than one-half the constant when hydrogen peroxide reacts with ferrous iron.

Regarding the complexity of the mechanism, no simple mechanism which would account for the high ratio of ferrous iron oxidized to CHP consumed was apparent. However, it should be noted that traces of impurities would cause an increase in the stoichiometric ratio. This effect could be quite pronounced because of the low concentrations of reactants since these impurities could provide chain carriers similar to the X· radical. An increase in ethanol concentration does result in an increase in this ratio.[3] Under these conditions the mechanism can be simplified by omitting reactions VII to X, XII and XIX and still account for the high stoichiometric ratio but it would still be the same general type of mechanism and lead to the same two simplified algebraic equations (eq. 6 and 7). Other mechanisms could be devised but at the time this one seemed to provide an adequate method of measuring the rate constant of the primary radical producing reaction in which most interest was centered.

Experimental

The source and purity of each of the materials was as follows: 1. Ferrous sulfate heptahydrate. British Drug Houses certified chemical. 2. CHP. Hercules Powder Company commercial grade purified to a purity of 99% as described previously.[2] 3. Water. Distilled water redistilled from an alkaline permanganate solution to remove residual traces of organic material as recommended by Kolthoff and Medalia[9] and then saturated with air. 4. Sulfuric acid. Nichols Chemical Company reagent grade.

The method of analysis for CHP was the iodometric method outlined previously[2]; that for ferrous iron was a slight modification of the one proposed by Jackson[10] using a buffered 2,2'-bipyridyl solution. The residual ferrous iron was measured instead of the ferric iron formed because the addition of the ferrous complexing agent stops the reaction between the ferrous iron and the hydroperoxide for all practical purposes while the analysis is being carried out. Ferrous ammonium sulfate hexahydrate was used as the standard in determining the relationship between the reading of Klett-Summerson colorimeter and the concentration of ferrous iron. Its purity was checked by oxidation of the ferrous iron with nitric acid and titration of the iodine liberated by the ferric iron with the same thiosulfate as used to titrate the iodine liberated in the CHP analysis in order to ensure that any error in the purity of the primary standard for both analyses would be the same. The CHP was assayed as the 99% material and the ferrous iron concentration was determined on an aliquot of the aqueous solution.

The stoichiometry experiments were carried out in 100-ml. beakers immersed in a water-bath thermostated at 25.10°. An aqueous solution of CHP was added with vigorous mechanical agitation to an aqueous solution of ferrous sulfate in order to avoid a relatively large concentration of the hydroperoxide compared to that of the ferrous iron and resulting radical induced decomposition of the hydroperoxide during the addition. When the sulfuric acid was used, it was added as an aqueous solution to the ferrous iron solution before the CHP solution was added. At the end of the reaction two checks of the residual ferrous iron were made at least two hours apart in order to ensure that the reaction was virtually complete. In experiments in which the initial ratio of ferrous iron to CHP was low, a known excess of ferrous iron was added

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(10) S. H. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **10**, 302 (1938).

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.

Acknowledgments.—We thank Polymer Corporation Limited for permission to publish these results. The assistance of G. C. Billett and W. L. McPhee is gratefully acknowledged.

Summary

In dilute aqueous solutions of low *p*H 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 *p*H 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.$^{-1}$.

SARNIA, ONTARIO, CANADA RECEIVED MARCH 3, 1950

[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 Data[1]

BY DAN E. NICHOLSON[2] 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]

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

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

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[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).