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REPORT NO. 43

HYDROGEN PEROXIDE

PART TWO

CHAPTER 5 - PHYSICAL PROPERTIES

CHAPTER 6 - STRUCTURE

A Monograph Prepared with
Support from the
Office of Naval Research
Contract No. N5ori-07819
NR-092-008

BY

W. C. Schumb
C. N. Satterfield
R. L. Wentworth

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Departments of Chemistry and Chemical Engineering Cambridge, Mass

Division of Industrial Cooperation Project 6552
December 1, 1953

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PREFACE

A program of fundamental studies of the properties, formation, and reactions of hydrogen peroxide has been sponsored at M. I. T. since 1945, by the U. S. Navy, Bureau of Ordnance, and later the Office of Naval Research. For some time it has been apparent that the growth of basic knowledge of this chemical, as well as the development of various practical applications, would be furthered by a compilation and evaluation in the form of a monograph of the scientific and technical knowledge available.

The present report constitutes Part II (Chapters 5 and 6) of such a monograph. The remaining parts (I, III, and IV) bear the Report Numbers 42, 44, and 45. Report No. 42 was issued September 15, 1953, and Report 44 was issued November 1, 1953. Report 43 will be issued in the near future. The Table of Contents presented in this report gives a detailed outline of the material presented in Part II and indicates the contents of the other three parts by listing the headings of the chapters which each of them will contain.

Literature appearing up to September 1, 1953, has been consulted in the preparation of Part II of the monograph; in addition a few notes based on later information have been added in proof. It has not been attempted to cite every reference on hydrogen peroxide, but all publications which appeared to the authors to have some present-day usefulness are quoted.

The authors would like to express their appreciation to Professors D. R. Bianco, Paul A. Giguère, and Robert G. Taylor for their helpfulness in supplying data in advance of publication.

Arrangements have been made for this monograph subsequently to be published in book form. The authors will appreciate errors being called to their attention or receiving the comments of readers on the material presented.

Walter C. Schumb
Charles N. Satterfield
Ralph L. Wentworth

December 1, 1953

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PART II, REPORT NO. 43

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CHAPTER FIVE

PHYSICAL PROPERTIES

All of the important physical properties of hydrogen peroxide and its aqueous solutions have been measured or can now be estimated. Many of the physical properties have been subjected to recent re-examination, adding the confidence of improved techniques and the possibility of comparative judgment. In this chapter the recommended values for the properties of hydrogen peroxide and its solutions in water have been given, the material being divided among sections devoted to physical, thermodynamic, electrical, and radiational properties. The discussion of each of the properties includes an indication of the experimental methods used, of the accuracy obtained, and of the choices among the results of different experimenters. Whenever feasible, a tabulation of original data has been included. For the more important properties or for those properties remaining in some doubt, it has been attempted to make the discussion ample enough for independent judgment. The scope of the literature on physical and thermodynamic properties is sufficiently limited that nearly every paper can be mentioned. Thus a number of outmoded values for physical properties have been briefly cited since knowledge of their source may be useful. Figures and curves have been used to illustrate various relationships, but with the exception of a few instances these figures are not of sufficient detail to displace the tabulated data for practical reference; for this purpose figures may be prepared from the tabulated data or reference may be made to such a compilation as that published by the Buffalo Electro-Chemical Co. (1).

It is generally the values of the properties of water solutions of hydrogen peroxide which are needed in everyday practice. No attempt has been made to tabulate separately the

2.

properties of anhydrous hydrogen peroxide, although a tabulation of a limited number of properties has been presented in the discussion of deuterium peroxide for comparative purposes. Unless separate discussion has been warranted, the properties of anhydrous hydrogen peroxide have been presented as terminal values in collections of data for water solutions of hydrogen peroxide. At the other extreme, values for the properties of pure water are included. These data have sometimes been determined as part of the work on hydrogen peroxide solutions; where discrepancies seem to exist reference should be made to such authorities as Dorsey (2) or Keenan and Keyes (3).

A number of measurements of the properties of systems containing components other than hydrogen peroxide and water have been made. These measurements are discussed briefly in a separate section.

Physical properties of hydrogen peroxide of other than natural isotopic composition (at present limited to hydrogen peroxide enriched in deuterium) have been collected in a separate section following the discussion of the properties of normal hydrogen peroxide. A synoptic table, summarizing selected properties of water, heavy water, anhydrous hydrogen peroxide, and anhydrous deuterium peroxide has been presented at the end of this section for easy comparison and quick reference.

The discussion of physical and thermodynamic properties has been limited chiefly to experimentally-measured quantities. The discussion of the molecular structure of hydrogen peroxide and of its physical nature in the various phases and in solution has been left for the following chapter. Secondary information derived from measurements of physical properties and primary experimental data obtained with the principal aim of elucidating structure have been presented in the chapter dealing with structure.

The Designation of Concentration

In the tabulation of properties, concentrations of hydrogen peroxide are expressed on either a weight or a mole basis.

The awkward expression "volume strength" has been much used to designate concentration in the literature of hydrogen peroxide. This is defined as the volume of oxygen gas, measured at 0°C and 1 atm, available from the complete decomposition of one volume of hydrogen peroxide solution, also measured at standard conditions. Thus a 3 wt. % solution is about 10 volume strength and anhydrous hydrogen peroxide is 484.62 volume strength. This is further confused by the system, common in the earlier American literature, of designating the volume strength with reference to the volume of oxygen evolved, not alone from the decomposition of hydrogen peroxide, but the total volume evolved from the reaction of hydrogen peroxide and potassium permanganate in acid solution. The use of the expression "volume strength" is diminishing and is to be discouraged. The same can be said for the expression "volume percent" (volumes of anhydrous hydrogen peroxide per volume of solution or sometimes per volume of pure water). The following equalities* relate the various concentration expressions:

$$\begin{aligned} \frac{x_H}{M_W} &= \frac{m_H}{1000 + m_H M_W} = \frac{c_H}{1000\rho - c_H M_H + c_H M_W} = \frac{W}{M_H(100 - W) + W M_W} \\ &= \frac{\bar{V}_{M_H}}{[(100\rho_0 M_H 22414)/2] - \bar{V}_{M_H}^2 + \bar{V}_{M_H} M_W} \quad (1) \end{aligned}$$

In Table 1 are given equivalent values for the different concentration units, temperature-dependent quantities being given for 25°C. The Normality, defined as the number of equivalents of hydrogen peroxide contained per liter of solution, is obtained from Table 1 as twice the molarity. The molecular weights of the solutions are also given in Table 1.

* A table at the end of this chapter explains the notation used in equations.

TABLE 1
EQUIVALENT VALUES OF CONCENTRATION DESIGNATIONS
FOR HYDROGEN PEROXIDE-WATER SOLUTIONS*

| Weight Percent H_2O_2 | Mole Fraction H_2O_2 | Molarity, g mole/l. at $25^\circ C$ | Molality, g mole/kg H_2O | "Volume Strength" | Molecular Weight |
|----------------------------|---------------------------|---|-------------------------------|----------------------|---------------------|
| 0 | 0.0000 | 0.000 | 0.000 | 0.00 | 18.02 |
| 10 | 0.0556 | 3.034 | 3.256 | 34.03 | 18.90 |
| 20 | 0.1169 | 6.286 | 7.149 | 71.19 | 19.88 |
| 30 | 0.1850 | 9.770 | 12.599 | 110.96 | 20.98 |
| 40 | 0.2610 | 13.505 | 19.599 | 153.68 | 22.19 |
| 50 | 0.3462 | 17.511 | 29.398 | 199.49 | 23.55 |
| 60 | 0.4427 | 21.809 | 44.097 | 248.66 | 25.10 |
| 70 | 0.5527 | 26.421 | 68.595 | 301.46 | 26.86 |
| 80 | 0.6793 | 31.373 | 117.59 | 358.17 | 28.88 |
| 90 | 0.8266 | 36.692 | 264.58 | 419.16 | 31.24 |
| 100 | 1.0000 | 42.404 | ∞ | 484.62 | 34.02 |

Formula and Molecular Weight of Hydrogen Peroxide

The empirical formula of hydrogen peroxide may be regarded as having been established by Thenard as that of a compound containing twice the proportion of oxygen to hydrogen as is found in water, leading to the empirical formula HO for hydrogen peroxide on the basis of the water formula H_2O .

Experiments to determine the molecular weight of hydrogen peroxide by measurement of the freezing point of water solutions of hydrogen peroxide were made by Tamman (4), Carrara (5) and Orndorf and White (6). Solutions of hydrogen peroxide in water approximate ideality over only a limited range of composition, and decomposition affects the precision of freezing point determinations seriously, but a clear choice of a molecular weight of about 34 is allowed by these experiments. The comparison of calculated and observed freezing points of dilute hydrogen peroxide solutions presented by Giguère and Maass (7) and Foley and Giguère (8), substantiates this conclusion of the earlier work.

* A tabulation is given in Chapter 7 of the activities of hydrogen peroxide in aqueous solution.

Measurements of the density of anhydrous hydrogen peroxide vapor at 92°C and a few cm Hg by the Victor Meyer method have been made by Matheson and Maass (9). These results also lead to a molecular weight of 34 and show the vapor to be non-associated. Using the accepted chemical atomic weights (10), $\text{H} = 1.0080$ and $\text{O} = 16.0000$, the molecular weight of hydrogen peroxide is then 34.0160.

In the discussion of the nature of liquid hydrogen peroxide and its solutions in water it will become apparent that there exist attractive forces between hydrogen peroxide molecules and between water and hydrogen peroxide molecules termed hydrogen bonds. The existence of such bonds implies association of the individual molecules H_2O_2 and H_2O ; indeed it may be said that a solution of hydrogen peroxide in water contains polymers and copolymers, $(\text{H}_2\text{O}_2)_x$, $(\text{H}_2\text{O})_y$ and $(\text{H}_2\text{O})_y \cdot (\text{H}_2\text{O}_2)_x$, some of which incorporate large portions of the particular sample taken. The hydrogen bonds which unite the monomers in these polymers are relatively quite strong for intermolecular bonds, but are much weaker than the chemical bonds uniting hydrogen and oxygen in the monomers and are of a transitory nature, continually forming and reforming as they are disrupted by thermal motion. The presence of such polymers or large molecules is not reflected by freezing point determinations; the effective unit of hydrogen peroxide is H_2O_2 and the association through hydrogen bonding is an expression of the intermolecular forces which characterize the liquid.

The Density of Solid Hydrogen Peroxide

The density of solid anhydrous hydrogen peroxide was determined in a dilatometer by Maass and Hatcher (11) as 1.6434 g/cc at -4.45°C and 1.6437 g/cc at -7.45°C . More recently the crystal structure of anhydrous hydrogen peroxide has been determined by Abrahams, Collin and Lipscomb (12) by x-ray diffraction at -20°C . The volume of the tetragonal crystal containing 4 molecules per unit cell was found to be 131.9 \AA^3 . From these data these authors cite a density of 1.70 g/cc. From a

6.

recalculation by the present authors using Bragg's (13) equation (the Avogadro number taken (14) as 6.023×10^{23}) and applying the uncertainties of measurements given by Abrahams et al., the density is found to be $1.71 \pm \begin{matrix} .05 \\ .03 \end{matrix}$ g/cc at -20°C .* This latter figure is the recommended one.

No data are available for the thermal coefficient of cubical expansion of solid anhydrous hydrogen peroxide. The coefficient of cubical expansion for water ice is given as $1.53 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$ by Dorsey (2). If it can be assumed that the coefficient of cubical expansion of solid hydrogen peroxide is of the same order of magnitude as that of water ice, then this coefficient may be used to estimate the temperature range represented by the uncertainty of 0.08 g/cc in the value for density of solid hydrogen peroxide. On this basis it is found that a temperature difference from the freezing point to well below the eutectic temperatures for the water-hydrogen peroxide system would be necessary to bring about a change in the density of the magnitude of the uncertainty in its determination. Until further measurements are available, it will be necessary to use the recommended density at all temperatures.

Giguère and Geoffrion (16) have measured the volume changes occurring as water-hydrogen peroxide solutions were frozen in a dilatometer. The results were somewhat erratic, but showed clearly that solutions containing less than 45 wt. % hydrogen peroxide expand during freezing and that solutions containing more than 65 wt. % hydrogen peroxide contract during freezing, which follows the behavior of the pure component present in greatest proportion. No conclusions could be reached regarding the relative density of the solid compound, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ (48.6 wt. % hydrogen peroxide).

* The density of anhydrous hydrogen peroxide thus increases on freezing, going from 1.47 g/cc for the liquid at its freezing point to 1.71 g/cc for the solid. In this respect hydrogen peroxide is more like the majority of other substances rather than like water, which becomes less dense on freezing, going from a density of 0.9999 g/ml for the liquid to a density of 0.9167 g/ml for the solid at 0°C (15).

In the discussion of the phase relationships of this system given later, work will be cited which shows that true solid solutions do not form. It is nevertheless true that the solid phases obtained on freezing generally contain both components of the system; it is concluded that the solid phase occludes the mother liquor. The volume occupied by a partially frozen hydrogen peroxide solution should then be the sum of the volume of the one-component solid phase plus the volume of the solution containing it. The volumes calculated on this basis by the tie-line method (in which the quantities of solid and liquid present at a given temperature are obtained by making a material balance for water and hydrogen peroxide with reference to a phase diagram) agreed well with the measured volumes in the work of Giguère and Geoffrion. The calculated volumes for hydrogen peroxide-rich solutions are improved by use of the corrected density of solid anhydrous hydrogen peroxide given above. Some uncertainty does remain, since the calculated volume does not vary markedly with composition or density of the solid phase. However, for practical purposes this also implies that volumes calculated by this method will not be far in error.

The Density of Liquid Hydrogen Peroxide

A number of early determinations of the density of liquid hydrogen peroxide and its water solutions are available (17), but these are of uncertain accuracy and do not extend over a sufficiently wide range of composition and temperature. The data provided by Maass and Hatcher (11) in 1920, and later amended for concentrated solutions by Cuthbertson, Matheson and Maass (18) were the first adequate measurements of this property. Since 1948, other measurements of the density of liquid hydrogen peroxide have been reported by Huckaba and Keyes (19) (at 0 and 20°C, and for all compositions), Kubaschewski and Weber (20) (at 18°C, and for compositions up to 82 wt. % hydrogen peroxide), Giguère and Geoffrion (16) (between -50 and 0°C, and for all compositions), and Easton, Mitchell, and Wynne-Jones (21) (at 0, 10, 25, 50, and 96°C, and for all compositions).

In the following paragraphs the experimental methods, portions of original data, correlations, and estimated accuracy for the density determinations of Huckaba and Keyes, Giguère and Geoffrion, and Easton, Mitchell, and Wynne-Jones are briefly discussed. An analytical expression which correlates all of the above data and a chart based on these data are then presented. An accurate measure of the density of hydrogen peroxide-water solutions is thus available over the complete range of composition at temperatures from -50 to 96°C . The data of these three groups of authors are recommended over the other values because of the degree to which decomposition was eliminated in these measurements. The greater densities given by the chosen data indicate that significant decomposition occurred during the measurements of Maass and Hatcher and Kubaschewski and Weber. Huckaba and Keyes spent considerable effort to develop a procedure for eliminating decomposition in their apparatus, as well as benefiting from a recent study (22) of the accuracy of the analytical method used; their data and that consistent with it is thus preferred.

Giguère and Geoffrion measured the density of various solutions at 0°C and also near the freezing point. From these measurements the mean coefficients of cubical expansion over the temperature range from 0°C down to the region of the freezing points of the solutions were derived. Their results, obtained in a dilatometer and agreeing within about 1 part in 1000 with Huckaba and Keyes at 0°C , are given in Table 2. The coefficient of cubical expansion is defined by the equation,

$$v_{t_2} = v_{t_1} [1 + \beta(t_2 - t_1)] \quad (2)$$

Equation (2) is to be used for the calculation of specific volume at temperature t_2 , v_{t_2} , from known values of specific volume at some base temperature, v_{t_1} , using a given set of coefficients of expansion. The reverse procedure, calculation of v_{t_1} from v_{t_2} , cannot be carried out with the same set of coefficients of expansion.

TABLE 2

DENSITY OF HYDROGEN PEROXIDE SOLUTIONS AT 0°C
AND MEAN COEFFICIENTS OF CUBICAL EXPANSION
BELOW 0°C, FROM GIGUÈRE AND GEOFFRION (16)

| Wt. % H ₂ O ₂ | Density, ρ , g/ml at 0°C | Mean Coefficient of Cubical Expansion, β , °C ⁻¹ x 10 ⁴ | Temperature Interval Studied, Δt , °C below 0° |
|-------------------------------------|----------------------------------|---|--|
| 9.32 | 1.0377 | -- | -- |
| 10.21 | 1.0410 | 1.3 ± 0.5 | 8.1 |
| 12.21 | 1.0493 | -- | -- |
| 18.32 | 1.0748 | -- | -- |
| 19.27 | 1.0783 | 3.2 ± 0.3 | 14.9 |
| 29.54 | 1.1209 | 4.6 ± 0.2 | 20.0 |
| 41.23 | 1.1722 | 5.54 ± 0.09 | 50.0 |
| 46.72 | -- | 5.81 ± 0.09 | 50.0 |
| 49.87 | 1.2119 | 6.03 ± 0.11 | 50.0 |
| 68.37 | 1.3006 | 6.7 | 35.0 |
| 69.05 | 1.3037 | -- | -- |
| 78.61 | 1.3535 | 7.1 ± 0.2 | 25.0 |
| 79.63 | 1.3590 | -- | -- |
| 89.64 | 1.4136 | 7.5 ± 0.4 | 10.0 |
| 100.00 | 1.4630* | 7.9* | near fp |

* extrapolated value

The densities of hydrogen peroxide solutions at 0°C determined in special pycnometers by Huckaba and Keyes (19) are given in Table 3. The precision of the density measurements was estimated to be 1 part in 10,000; that of the analyses 1 part in 5000. In terms of specific volume, the data of Table 3 were represented with a maximum deviation of about 1 part in 400 by the equation,

$$\log v = 0.00009 - 0.1676w \quad (3)$$

Huckaba and Keyes also presented tables of the densities and specific volumes at 0°C for each unit interval of weight percent calculated from equation (3) plus the use of a deviation chart in order to preserve the ultimate precision of the data.

The densities of hydrogen peroxide solutions at 20°C were then determined dilatometrically by Huckaba and Keyes, and from these measurements the mean coefficients of cubical expan-

TABLE 3

DENSITIES OF HYDROGEN PEROXIDE SOLUTIONS AT 0°C,
FROM HUCKABA AND KEYES, (19)

| Wt. % H ₂ O ₂ | Measured Density, ρ , g/cc | Wt. % H ₂ O ₂ | Measured Density, ρ , g/cc |
|-------------------------------------|---------------------------------|-------------------------------------|---------------------------------|
| 0.0 | 0.9998 | | |
| 9.657 | 1.0379 | 89.379 | 1.4100 |
| 19.979 | 1.0803 | 95.987 | 1.4483 |
| 40.009 | 1.1660 | 96.228 | 1.4493 |
| 59.171 | 1.2539 | 96.282 | 1.4499 |
| 71.354 | 1.3139 | 99.479 | 1.4681 |
| 80.023 | 1.3590 | 99.605 | 1.4685 |
| | | 100.0 | 1.4709* |

*extrapolated value

TABLE 4

SPECIFIC VOLUMES OF HYDROGEN PEROXIDE SOLUTIONS AT 20°C,
AND MEAN COEFFICIENTS OF CUBICAL EXPANSION
BETWEEN 0 AND 20°C,
FROM HUCKABA AND KEYES, (19)

| Wt. % H ₂ O ₂ | Experimental Specific Volume, v , cc/g | Mean Coefficient of Cubical Expansion $\times 10^4$, β , °C ⁻¹ |
|-------------------------------------|--|--|
| 0.00 | 1.00184* | 0.83 |
| 21.525 | 0.92818 | 4.326 |
| 39.159 | 0.87037 | 5.846 |
| 59.083 | 0.80836 | 6.656 |
| 78.529 | 0.75103 | 7.354 |
| 96.877 | 0.69888 | 7.759 |
| 100.000 | -- | 7.85 |

*from Dorsey (2)

sion between 0 and 20°C were obtained. In Table 4 are presented the specific volumes measured at 20°C, and the mean coefficients of cubical expansion between 0 and 20°C. The coefficients of cubical expansion as defined by equation (2) were calculated from a general equation for the temperature range 0 to 20°C; smoothed values for this coefficient of expansion are presented by Huckaba and Keyes for each unit interval of weight percent hydrogen peroxide.

The measurements of Easton, Mitchell, and Wynne-Jones (21), made at 0, 10, 25, 50, and 96°C, allow extension of the data on liquid density to higher temperatures. The method used in this work was to measure the displacement of liquid by a glass sinker in an apparatus embodying a precise form of the Westphal balance. Particular care was paid to the cleaning of glassware in this work in order to eliminate the chief source of error inherent in this method: the formation of bubbles on the sinker by decomposition. In the measurements at 96°, 81 mg/l of zinc sulphate was added as stabilizer.

The experimental results obtained by Easton, Mitchell, and Wynne-Jones at 0°C are given in Table 5. The agreement of

TABLE 5

DENSITY OF HYDROGEN PEROXIDE SOLUTIONS AT 0°C,
FROM EASTON, MITCHELL, AND WYNNE-JONES (21)

| Wt. % H ₂ O ₂ | Density, ρ , g/cc |
|-------------------------------------|------------------------|
| 0.0 | 0.9999 |
| 7.36 | 1.0291 |
| 17.14 | 1.0690 |
| 24.36 | 1.0987 |
| 33.23 | 1.1370 |
| 44.62 | 1.1860 |
| 55.69 | 1.2373 |
| 65.07 | 1.2822 |
| 74.96 | 1.3321 |
| 83.27 | 1.3759 |
| 91.55 | 1.4221 |
| 96.65 | 1.4517 |

these data with those of Huckaba and Keyes at 0°C and at 20 - 25°C is excellent. Easton, Mitchell, and Wynne-Jones estimated their data at 25°C to have a precision of about 1 part in 5000, at 96° 1 part in 500. Equations of the form:

$$\rho = a + bw + cw^2 + dw^3 \quad (4)$$

have been fitted to their data by Easton, Mitchell, and Wynne-Jones, the agreement of the equations with their data being

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about 1 part in 5000 for all temperatures except 96°C, for which the agreement is 1 part in 1400. The coefficients for equations (4) are given in Table 6.

TABLE 6

COEFFICIENTS FOR EQUATION (4) RELATING DENSITY TO WEIGHT PERCENT HYDROGEN PEROXIDE FROM EASTON, MITCHELL AND WYNNE-JONES (21)

| Temperature, °C | a | b | c | d |
|-----------------|--------|---------|---------|---------|
| 0 | 0.9998 | 0.39939 | 0.01758 | 0.05470 |
| 10 | 0.9997 | 0.36790 | 0.06208 | 0.02954 |
| 25 | 0.9970 | 0.34672 | 0.06995 | 0.02885 |
| 50 | 0.9880 | 0.31382 | 0.09402 | 0.01910 |
| 96 | 0.9612 | 0.27652 | 0.11956 | -- |

In the range of dilute (0 to 5 wt. %) solutions these measurements have been improved in precision by Wynne-Jones (23). Using a dilatometer, the densities of dilute solutions at 0, 10, and 25°C have been determined with a precision of the order of 1 part in 100,000. These results are given in Table 7 along with empirical equations. These equations should not be used to calculate the density of solutions more concentrated than 5 wt. %.

TABLE 7

DENSITY OF DILUTE HYDROGEN PEROXIDE SOLUTIONS AT 0, 10 AND 25°C (23)

| Wt. % | Concentration H ₂ O ₂ Mole fraction | Density, * g/cc | | |
|-------|--|-----------------|----------|----------|
| | | 0° | 10° | 25° |
| 0 | 0 | 0.999849 | 0.999680 | 0.997044 |
| 2.242 | 0.012001 | 1.008725 | 1.008002 | 1.004835 |
| 3.332 | 0.017928 | 1.013097 | 1.012109 | 1.008639 |
| 4.971 | 0.026958 | 1.019626 | 1.018265 | 1.014289 |

*equations fitted to these data are:

$$\begin{aligned} \rho_{0^\circ} &= 0.999841 + 0.3975w \\ \rho_{10^\circ} &= 0.999700 + 0.3725w \\ \rho_{25^\circ} &= 0.997044 + 0.34725w \end{aligned}$$

In order to provide a general equation for the density of hydrogen peroxide solutions at all temperatures between 0°C and 96°C and for all concentrations, the coefficients of equation (4) may in turn be expressed as functions of temperature. In Table 8 are given the coefficients of the equations:

$$b = J_b + K_b t + L_b t^2 + M_b t^3 \quad (5)$$

$$c = J_c + K_c t + L_c t^2 + M_c t^3 \quad (6)$$

$$d = J_d + K_d t + L_d t^2 + M_d t^3 \quad (7)$$

where b, c and d are the coefficients of equation (4).

TABLE 8

COEFFICIENTS FOR EQUATIONS (5), (6), AND (7) RELATING COEFFICIENTS OF EQUATION (4) TO TEMPERATURE

| Coefficient of Equation (4) | J | K x 10 ³ | L x 10 ⁵ | M x 10 ⁷ |
|-----------------------------|---------|---------------------|---------------------|---------------------|
| a* | -- | -- | -- | -- |
| b | 0.39763 | -2.8732 | 3.2488 | -1.6363 |
| c | 0.02206 | 3.5357 | -6.0947 | 3.6165 |
| d | 0.05187 | -1.9414 | 3.9061 | -2.5500 |

* a = density of water at temperature t

The coefficient "a" of equation (4) is simply the density of water at the desired temperature and this may be obtained most conveniently from a table (2) of this property. Equation (4) when used with the coefficients calculated by equations (5), (6), and (7) very nearly preserves the precision estimated by Easton, Mitchell, and Wynne-Jones for equation (4) when using the coefficients derived for their individual temperatures, as may be seen by inspection of the deviations tabulated in Table 9. These deviations also provide a measure of the agreement of the various data. The use of equation (4) with the general coefficients is recommended where precise density values are desired at temperatures and concentrations removed from the experimental conditions, or correlations provided by the original data.

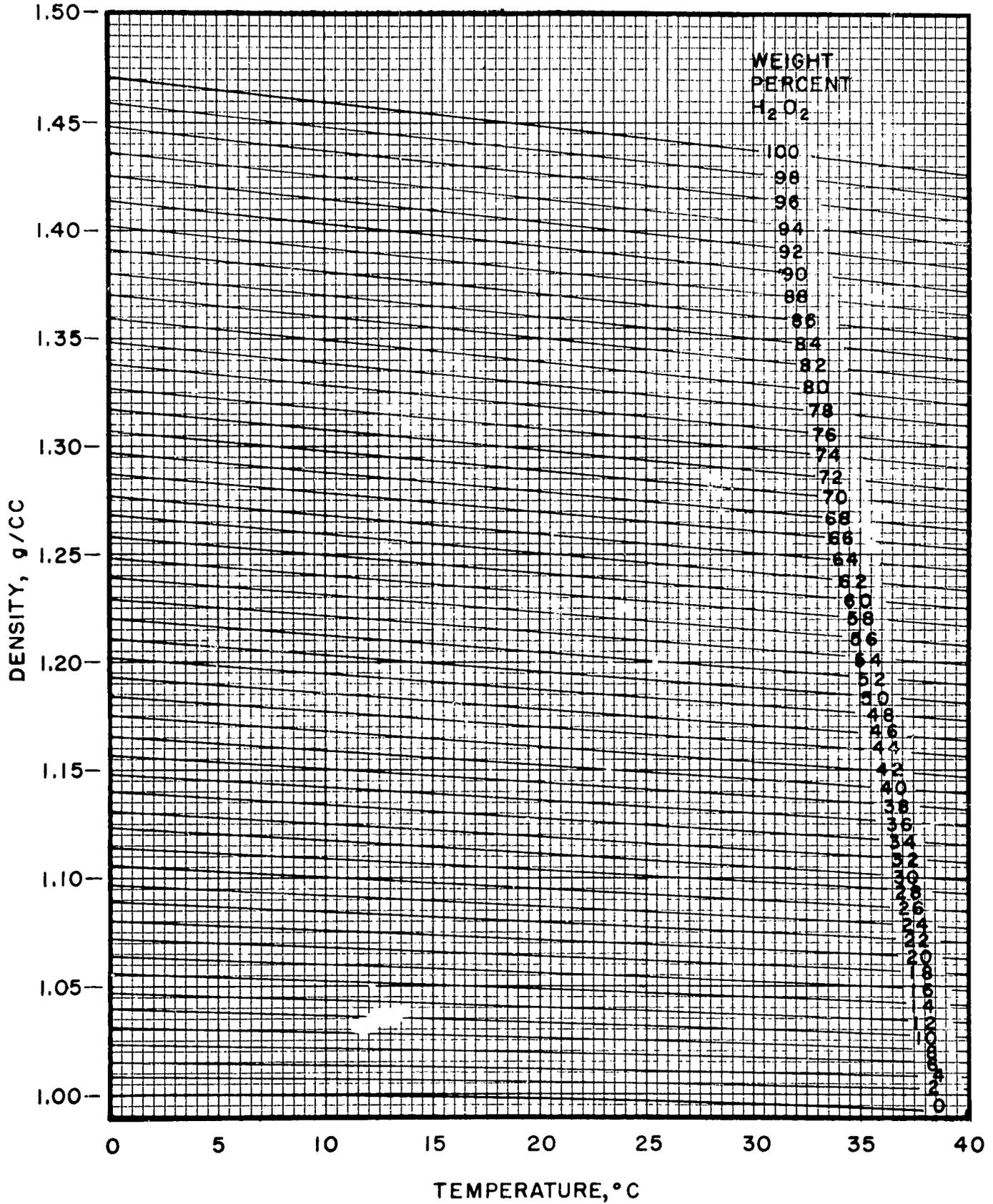


FIG. 1—DENSITY OF HYDROGEN PEROXIDE—WATER SOLUTIONS

TABLE 9

DEVIATION OF EQUATION (4) FROM EXPERIMENTAL DATA
WHEN USING GENERAL COEFFICIENTS OF TABLE 8

| Reference | Temperature, °C | Average Deviation | | Maximum Deviation | |
|---|--------------------|-------------------|-------|-------------------|-------|
| | | Units | % | Units | % |
| Huckaba and Keyes (19) | 0 | 0.00034 | 0.026 | 0.0006 | 0.058 |
| Giguère and Geoffrion (16) | 0 | 0.0015 | 0.117 | 0.0025 | 0.184 |
| Kubaschewski and Weber (20) | 18 | 0.0023 | 0.195 | 0.0056 | 0.478 |
| Easton, Mitch- ell, and Wynne- Jones (21) | 25 | 0.0003 | 0.022 | 0.0007 | 0.056 |
| Easton, Mitch- ell, and Wynne- Jones (21) | 96 | 0.0008 | 0.067 | 0.0016 | 0.144 |

For less precise work Table 10 may be used to obtain the density of hydrogen peroxide solutions at 25°C, and the coefficients of cubical expansion to be used in equation (2) over the temperature range 0 to 96°C. Table 2 provides coefficients of cubical expansion for temperatures below 0°C. Alternately, densities may be obtained graphically from Figure 1. Linear interpolation between values shown in Table 10 and read from Figure 1 is reliable to 1 part in 1000. Routine volumetric or densitometric analysis is generally not carried to superior precision.

Study of these measurements of the density of hydrogen peroxide-water solutions shows that the curves relating density to hydrogen peroxide concentration are everywhere concave upward. This curvature becomes more pronounced as the temperature is increased. The curves relating specific volume to hydrogen peroxide concentration are also everywhere concave upward; but this curvature becomes less pronounced as temperature is increased.

TABLE 10

DENSITY AND MEAN COEFFICIENTS
OF CUBICAL EXPANSION OF HYDROGEN
PEROXIDE SOLUTIONS AT 0 AND 25°C

| Wt. % H ₂ O ₂ | Density, ρ , g/cc | | Mean Coefficient of Cubical Expansion, β , °C ⁻¹ x 10 ⁴ | |
|-------------------------------------|------------------------|---------|---|--------------------|
| | 0°(19) | 25°(21) | from 0 to 25°(19) | from 25 to 96°(21) |
| 0 | 0.9998 | 0.9971 | 0.83 | 5.25 |
| 5 | 1.0193 | 1.0145 | 1.97 | 5.57 |
| 10 | 1.0393 | 1.0324 | 2.92 | 5.91 |
| 15 | 1.0598 | 1.0507 | 3.61 | 6.26 |
| 20 | 1.0804 | 1.0694 | 4.21 | 6.56 |
| 25 | 1.1014 | 1.0885 | 4.70 | 6.82 |
| 30 | 1.1226 | 1.1081 | 5.14 | 7.05 |
| 35 | 1.1441 | 1.1282 | 5.50 | 7.26 |
| 40 | 1.1661 | 1.1487 | 5.83 | 7.46 |
| 45 | 1.1883 | 1.1698 | 6.11 | 7.64 |
| 50 | 1.2110 | 1.1914 | 6.36 | 7.80 |
| 55 | 1.2342 | 1.2137 | 6.57 | 7.93 |
| 60 | 1.2579 | 1.2364 | 6.77 | 8.04 |
| 65 | 1.2822 | 1.2598 | 6.95 | 8.15 |
| 70 | 1.3071 | 1.2839 | 7.11 | 8.24 |
| 75 | 1.3326 | 1.3086 | 7.26 | 8.34 |
| 80 | 1.3589 | 1.3339 | 7.40 | 8.44 |
| 85 | 1.3858 | 1.3600 | 7.53 | 8.50 |
| 90 | 1.4136 | 1.3867 | 7.65 | 8.53 |
| 95 | 1.4421 | 1.4142 | 7.75 | 8.56 |
| 100 | 1.4709 | 1.4425 | 7.85 | 8.58 |

It is seen that the sum of the volumes of the unmixed components is greater than the volume of the mixture. For example, at 0°C the volume shrinks about 1.7% on mixing equal weights of hydrogen peroxide and water; at 96° the shrinkage is only 0.5%. The non-ideality of these solutions is further illustrated by the negative departure of the partial molal volumes of water and hydrogen peroxide in solution from the molal volumes of the pure components. In Figure 2 is shown the quantity $(\bar{v} - \bar{v}_0)$, the difference at 25°C between the partial molal volume of each component in solution and the molal volume of the pure component, calculated through use of equation (4).

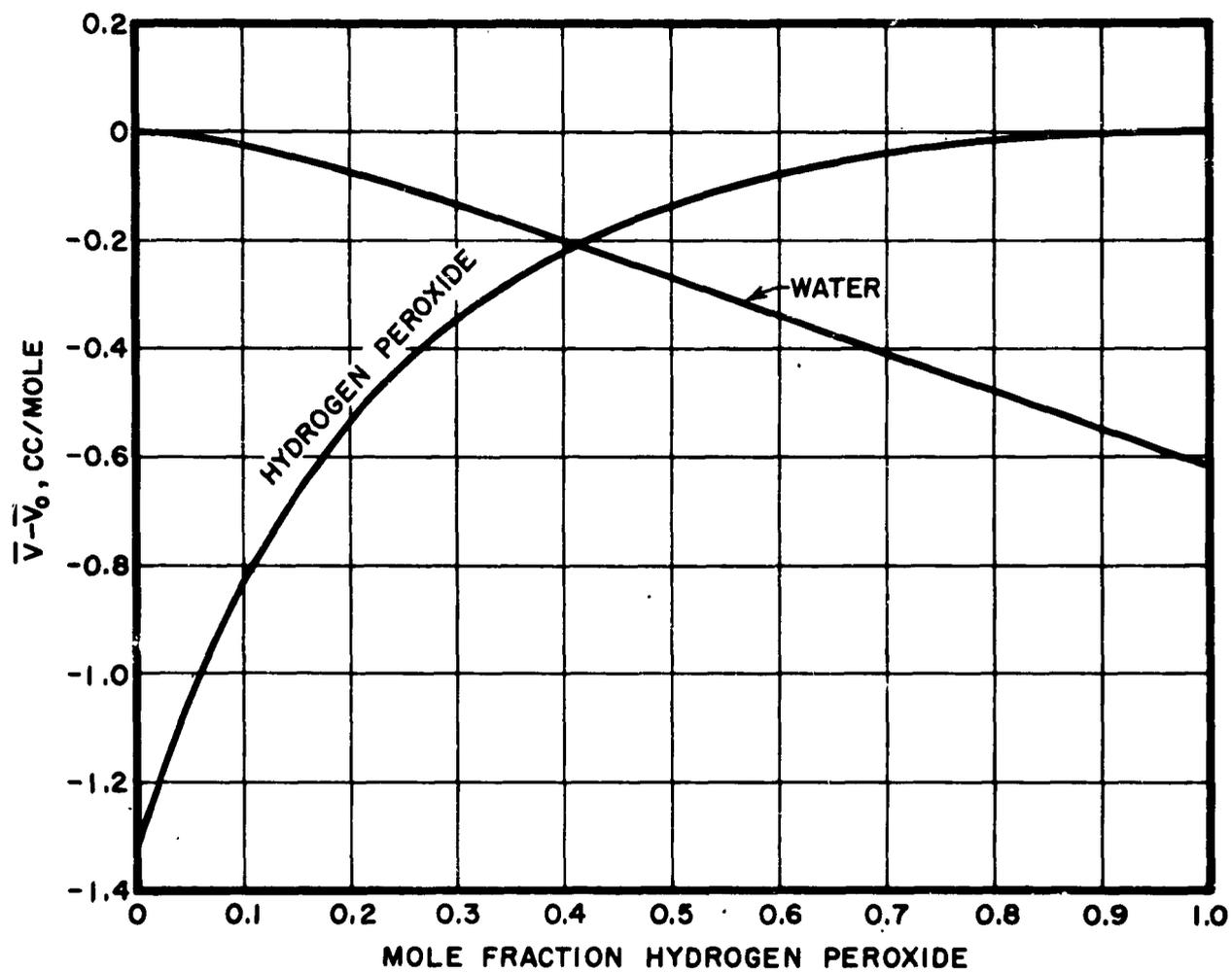


FIG. 2-PARTIAL MOLAL VOLUMES OF WATER AND HYDROGEN PEROXIDE AT 25°C

The coefficients of cubical expansion of solutions and pure hydrogen peroxide are seen to be greater than that of water. Thus the increase in volume with increase in temperature is greater the more concentrated the solution. The effect due to the existence of a maximum in the density of pure water at 4°C upon the density of hydrogen peroxide solutions has been studied by Wynne-Jones (23). It was found that the density maximum of water persists in dilute hydrogen peroxide solutions. As the hydrogen peroxide concentration was increased the temperature at which the maximum density occurred decreased. This decrease was found to be very nearly a linear function of concentration. The maximum was found to occur at 0°C with 2.5 wt. % hydrogen peroxide and by extrapolation would appear to occur at -2°C and 3.5 wt. % hydrogen peroxide on the freezing point curve.

The Density of Hydrogen Peroxide Vapor

The measurements of the vapor density of anhydrous hydrogen peroxide made by Matheson and Maass (9) reveal only that, under the conditions of the experiment, 92°C and 3.5 cm Hg, the perfect gas law is well approximated. This conclusion was checked by Elder and Rideal (24). No other experiments to test directly the deviation from perfect gas behavior have been reported, quite understandable if the difficulties of making precise measurements on vapors having appreciable hydrogen peroxide concentration at conditions where imperfections might be expected to occur are considered. By analogy with water it is recommended that the perfect gas law be used for ordinary temperatures and pressures, using average molecular weights for mixtures of hydrogen peroxide and water. Where an estimate of vapor imperfections is necessary, reference may be made to a chart of compressibility factors, or, preferably, the imperfections occurring for water may be calculated from Keenan and Keyes (3), and by assumption of the theory of corresponding states these may be applied to hydrogen peroxide and mixtures. For this purpose the critical values for anhydrous hydrogen peroxide vapor may be taken as $T_c = 457^{\circ}\text{C}$ (730°K) and $P_c = 214$ atm (see below). Scatchard, Kavanagh and Ticknor (25)

by such a method, using the equations of Keyes, Smith, and Gerry (26), estimated that corrections for gas imperfections amounted to as much as 1 percent of the total vapor pressure at some concentrations in their measurements of the vapor pressure of hydrogen peroxide-water solutions.

The Viscosity of Liquid Hydrogen Peroxide

Measurements of the viscosity of solutions of hydrogen peroxide and water have been made by Maass and Hatcher (11) and Phibbs and Giguère (27), each using the Ostwald viscometer calibrated with water. The agreement of both sets of data is good; those of Phibbs and Giguère, given in Table 11, are recommended because of their use of revised values for the viscosity of water and, possibly, use of hydrogen peroxide of greater purity.

Although it may be seen from Figure 3 that the viscosity of the liquid solutions is approximately linear in wt. % composition over a considerable range, the complicated relationship of viscosity to concentration over the entire composition range indicates that the reciprocal of viscosity, or fluidity, is not an additive property for this system. The prediction of the variation of the viscosity of the solutions with temperature is uncertain. Maass and Hatcher, taking the viscosity of water at 0°C to be 1.778 centipoises, measured the viscosity of anhydrous hydrogen peroxide to be 1.828, 1.456, 1.447, and 1.272 centipoises at the temperatures 0.04, 11.90, 12.20, and 19.60°C, respectively. For anhydrous hydrogen peroxide the temperature variation of viscosity might be estimated using the available measurements on a Dühring-type chart with water as the reference fluid (29). Similarly, each concentration of solution might be considered a unique liquid in such a chart.

It is difficult to reconcile the statement commonly found in the literature to the effect that anhydrous or concentrated hydrogen peroxide is a syrupy liquid with the actual values found for the viscosity. Hydrogen peroxide at room temperature is in fact not noticeably more viscous than water; this error was probably engendered by an observation of a contaminated evaporation residue or

TABLE 11

VISCOSITY OF LIQUID HYDROGEN PEROXIDE SOLUTIONS
AT 0 AND 20°C,
FROM PHIBBS AND GIGUÈRE (27)

| Wt. % H ₂ O ₂ | Viscosity, centipoises | |
|-------------------------------------|------------------------|--------|
| | 0°C | 20°C |
| 0.00 | 1.792 | 1.005* |
| 8.68 | 1.746 | 1.011 |
| 19.06 | 1.746 | 1.045 |
| 25.11 | 1.783 | -- |
| 37.33 | -- | 1.120 |
| 42.72 | 1.844 | 1.140 |
| 49.08 | -- | 1.170 |
| 51.93 | 1.884 | -- |
| 62.37 | 1.917 | 1.219 |
| 69.78 | -- | 1.234 |
| 71.55 | 1.933 | -- |
| 81.21 | 1.919 | 1.266 |
| 91.76 | -- | 1.262 |
| 95.75 | 1.854 | 1.259 |
| 100.00 | 1.819 | 1.249 |

from the choice of words used by Thenard to describe the appearance of hydrogen peroxide and water on mixing. It is, however, true that the viscosities of hydrogen peroxide solutions do increase sufficiently on cooling below 0°C to warrant the description "syrupy." No measurements have been made at low temperatures, but the viscosity of supercooled solutions is high enough to slow markedly the rate of crystallization on seeding. Mironov and Bergman (30) stated that the viscosity of 50 - 80% hydrogen peroxide solutions showed a sudden increase in the vicinity of the freezing point curve.

The Viscosity of Hydrogen Peroxide Vapor

A capillary viscometer was used by Demetriades (31) to determine the viscosity of vapor mixtures of hydrogen peroxide and water containing up to 65 mole % hydrogen peroxide at 1 atmosphere total pressure and at a temperature of 170°C. A few studies

* Value was recently revised to 1.002 by the U. S. Bureau of Standards (28). Since water was used to calibrate the viscometer in the above work, all the listed values above should be reduced by 0.3%.

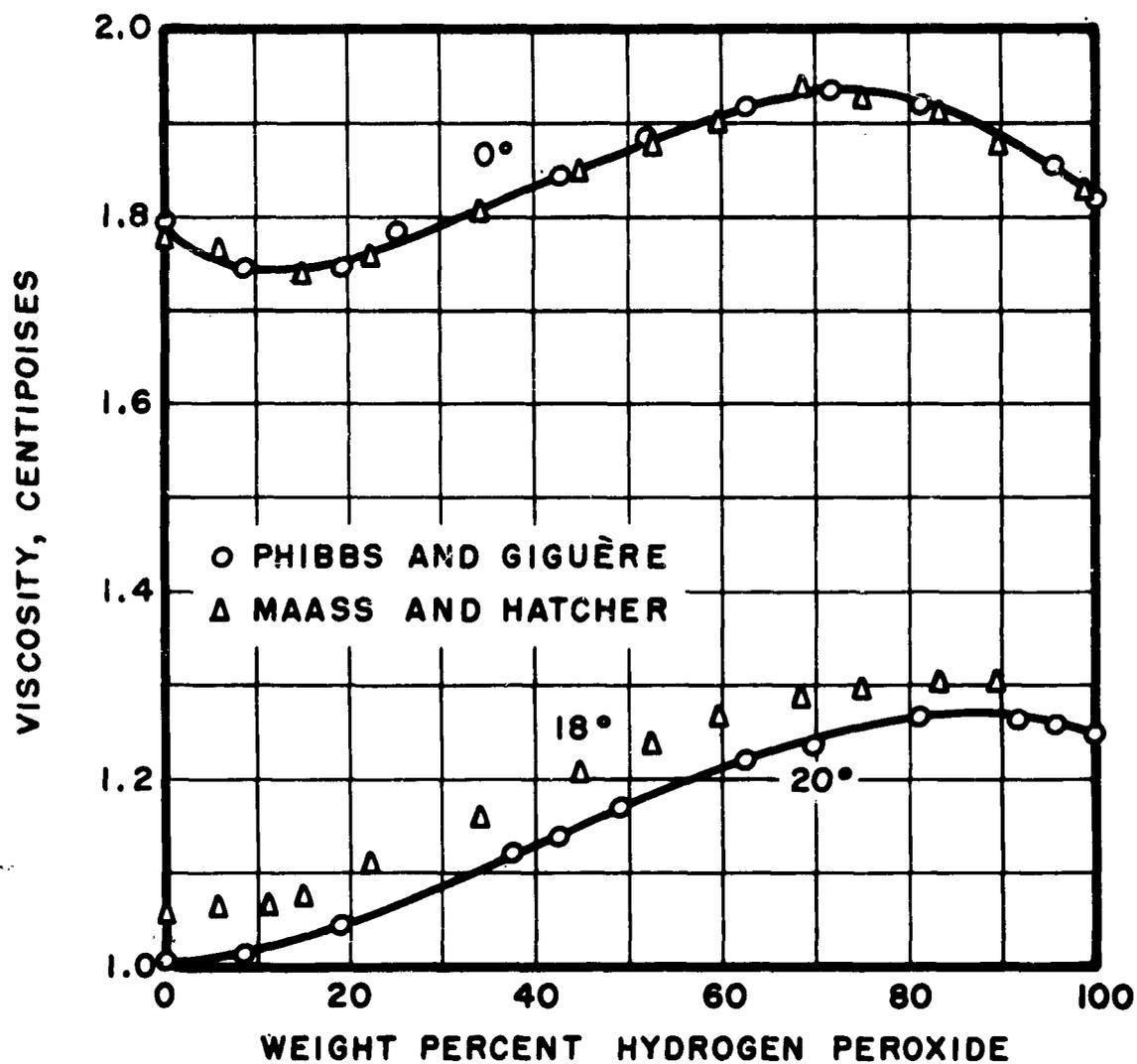


FIG. 3 - VISCOSITY OF LIQUID HYDROGEN PEROXIDE-WATER SOLUTIONS

were also made at 200 and 240°C to provide a basis for estimating the effect of temperature. The viscometer was calibrated with water vapor using the data recommended by Keyes (32). It was shown that the presence of oxygen in the vapor mixture at concentrations below 1 mole % did not affect the precision of measurement.

These experiments showed that the viscosity of hydrogen peroxide-water vapor mixtures is a linear function of the vapor composition. A direct, linear extrapolation was therefore made to obtain the viscosity of anhydrous hydrogen peroxide vapor. There was some indication that the viscosity of hydrogen peroxide vapor varies more slowly with temperature than that of water vapor, but the precision of the results did not permit differentiation of the temperature coefficient of viscosity of hydrogen peroxide vapor from that of water vapor, which changes by 0.35 micropoises per degree centigrade at this temperature level. These data were expressed by the following equation:

$$\mu = 134 + 0.35 (t - 100) - 14y \quad (8)$$

This equation is recommended for the calculation of the viscosity of vapor mixtures of hydrogen peroxide and water over the temperature range of about 100 to 300°C and is believed to have a precision of within $\pm 2\%$.

The absolute accuracy of these viscosity data of course depend in turn on the accuracy of the viscosity of water vapor. Although the water vapor viscosity data used (32) for calibration are probably the most precise available for large ranges of pressure and temperature, other evaluations (33) of the available data indicate that an uncertainty of not less than $\pm 1\%$ exists regarding the exact viscosity of water vapor at 1 atm near 200°C.

The fact that the viscosity of this mixture follows a linear composition relationship underscores the similarity of the two kinds of molecules with respect to their mass, structure and molecular interaction potential.

The Surface Tension of Liquid Hydrogen Peroxide

The surface tension of water solutions of hydrogen peroxide has been measured by Spring (17), Maass and Hatcher (11), and Phibbs and Giguère (27), using the capillary rise method. Judging by comparison with his data for water, the values obtained by Spring appear to contain a large error. Maass and Hatcher reported a linear relationship between surface tension and wt. % composition, obtaining the values 78.76 dynes/cm at 0°C and 75.99 dynes/cm at 18° for anhydrous hydrogen peroxide. The measurements of Phibbs and Giguère are not in agreement with those of Maass and Hatcher, showing higher values and a definite departure from a linear relationship. A part of this discrepancy may be due to the difference in density values used, but it appears to have been caused chiefly by the presence of surface-active impurities in the solutions used by Maass and Hatcher. The basis for this belief is the fact that it was necessary for Maass and Hatcher to purify and concentrate an impure 3% solution for their work. Phibbs and Giguère reported that it was difficult to obtain consistent results even though working with 90% hydrogen peroxide of high purity made by a commercial electrolytic process; most troublesome was the presence in the solution of a surface-active agent found to have been a plasticizer derived from the plastic stopper for the hydrogen peroxide container. The results were also quite sensitive to the slightest bubble formation.

The data of Phibbs and Giguère (27) are presented in Table 12 and Figure 4. These authors also presented a measurement on 97.8% hydrogen peroxide which indicated a slight maximum in the value of the surface tension at about this composition. Although the surface tension of mixtures in other systems (e.g., water-sulfuric acid (34), water-hydrazine (35)) may show a maximum at an intermediate composition, Giguère (36) has stated that the "maximum" indicated by the 97.8% point was not real and this measurement has been rejected. The values for anhydrous hydrogen peroxide were obtained by direct, graphical extrapolation. There is no indication, within the precision of the data,

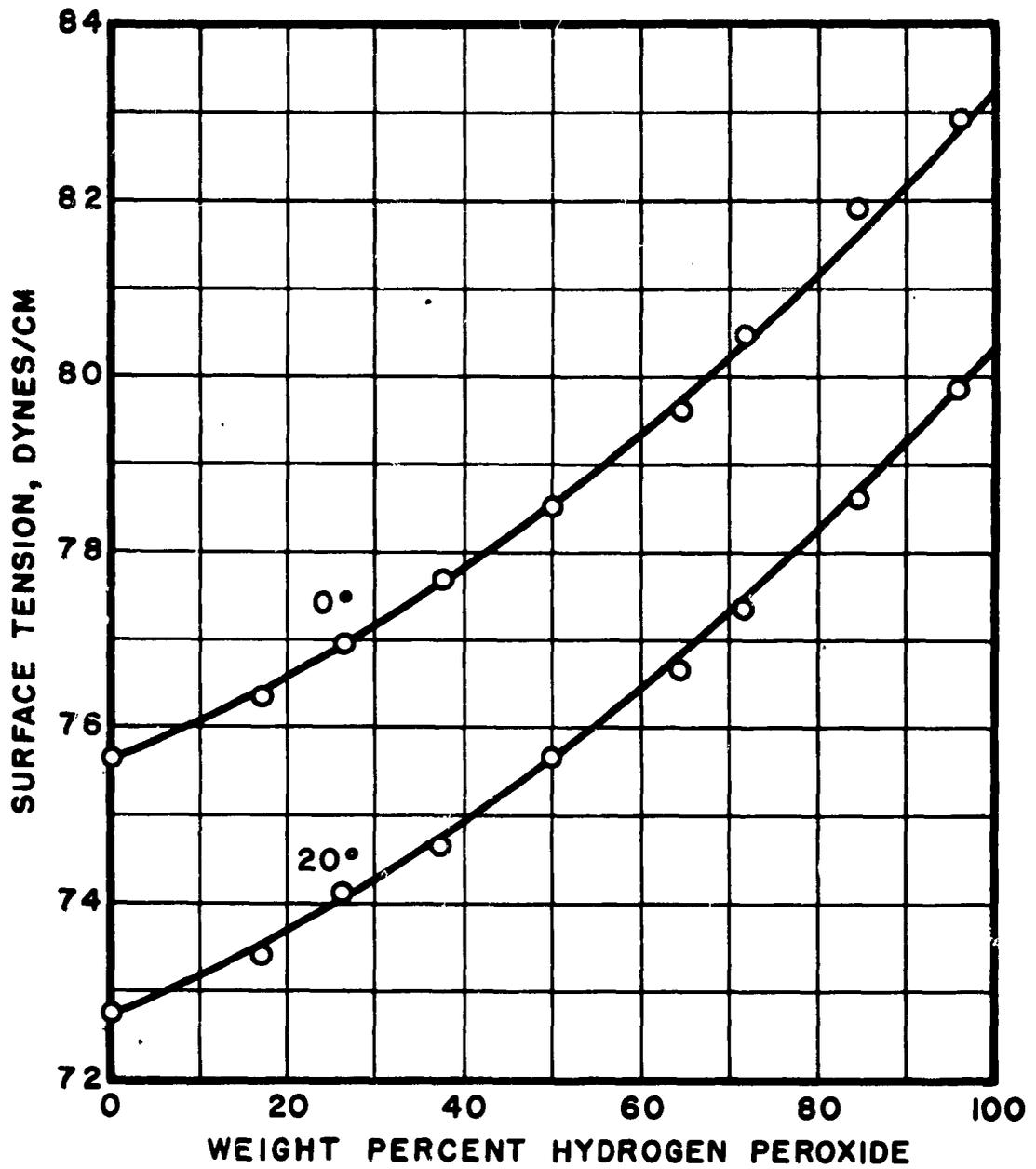


FIG. 4 - SURFACE TENSION OF HYDROGEN PEROXIDE-WATER SOLUTIONS

TABLE 12

THE SURFACE TENSION OF HYDROGEN PEROXIDE
SOLUTIONS AT 0 AND 20°C,
FROM PHIBBS AND GIGUÈRE (27)

| Wt. % H ₂ O ₂ | Surface Tension, dynes/cm | |
|-------------------------------------|---------------------------|-------|
| | 0°C | 20°C |
| 0.00 | 75.65 | 72.75 |
| 17.05 | 76.36 | 73.41 |
| 26.31 | 76.95 | 74.12 |
| 37.33 | 77.69 | 74.67 |
| 49.76 | 78.41 | 75.68 |
| 64.33 | 79.62 | 76.65 |
| 71.55 | 80.48 | 77.36 |
| 84.12 | 81.92 | 78.61 |
| 95.75 | 82.93 | 79.87 |
| 100.00 | 83.3* | 80.4* |

* extrapolated value, precision: ± 0.05 dyne/cm

that the temperature coefficient of surface tension for hydrogen peroxide and solutions differs from that of water. The curves in Figure 4 have accordingly been drawn parallel.

The Coefficient of Diffusion for Liquid Hydrogen Peroxide

Interest in the determination of the coefficient of diffusion in liquid hydrogen peroxide was first raised by the desire to apply the hypothesis of Noyes and Whitney, as developed by Nernst, regarding the kinetics of heterogeneous reactions to the case of the catalytic decomposition of hydrogen peroxide. This hypothesis brought into consideration the effect on the observed reaction rate of the rate of transport or diffusion of a reactant in solution to the surface of a solid where reaction occurred. It was realized that if the rate of diffusion were slow relative to the possible rate of reaction at the surface, then the rate of diffusion would limit and become a measure of the rate of reaction.

Henri (37) treated the case of catalytic decomposition of hydrogen peroxide by colloidal platinum in this way, using an estimate of the diffusion coefficient of $0.86 \text{ cm}^2/\text{day}$. Bredig (38)

applied this estimate more successfully to the results of decomposition on sheet platinum. Weigert (39) based his comparison of calculated and measured rates of decomposition of hydrogen peroxide on a measurement of the diffusion coefficient. Again using the theory developed by Nernst, Weigert determined the apparent thickness of the film of liquid through which it was necessary for potassium permanganate, while acting as a depolarizer, to diffuse to the surface of a rotating platinum electrode. From the known diffusion coefficient for potassium permanganate and the measured current the diffusion distance was determined as a function of rotation velocity. These diffusion distances were then used to obtain the diffusion coefficients from experiments in which hydrogen peroxide acted as depolarizer on the same electrode. For 0.014 N hydrogen peroxide Weigert obtained values of D , the diffusion coefficient, ranging from 1.2 to 1.37 cm^2/day at 18°C . For 0.049 N hydrogen peroxide he obtained $D = 1.2 \text{ cm}^2/\text{day}$. These values were found to check the rates of decomposition of hydrogen peroxide on the rotating platinum electrode when no current was flowing.

Heymann (40) made experiments like those of Weigert, calibrating his electrode with an iodine solution. The diffusion distances so obtained were used to calculate diffusion coefficients for hydrogen peroxide from decomposition rate measurements. Values for the diffusion coefficient of 1.17 to 1.20 cm^2/day at 18°C were obtained for hydrogen peroxide concentrations varying from 0.1 to 0.3 N. As a check on these results Heymann made direct measurements of the diffusion coefficient of hydrogen peroxide by allowing diffusion into a column of water from a layer of hydrogen peroxide solution. For 0.1 N hydrogen peroxide Heymann obtained a diffusion coefficient of 0.97 cm^2/day at 11°C by this method and believed that this might be extrapolated to 1.10 cm^2/day at 18°C .

There is no doubt of the validity of Nernst's diffusion hypothesis nor of its applicability to the decomposition of hydrogen peroxide by platinum. However, it is doubtful

whether reliable diffusion coefficients may be obtained so simply and directly from such measurements. For example, the effect of the release of oxygen in the reaction may provide additional stirring, may blanket a part of the surface, or may allow vapor phase diffusion. Similarly, the technique of the direct measurements of Heymann was not of the best. More acceptable are the results of Stern (41) obtained by the diaphragm cell method (42) in which diffusion proceeds under steady-state conditions from a solution reservoir through a porous diaphragm (here G-4 Jena glass) into a solvent reservoir. Stern calibrated his cell at 20°C with potassium iodide, 0.1 N, (D taken as 1.448 cm²/day) and suppressed hydrogen peroxide decomposition on the diaphragm with the addition of urea or acetanilide, both found to be without effect on the results. A selection of the differential diffusion coefficients of hydrogen peroxide in water solutions containing 0.1% or less of acetanilide calculated from the experiments of Stern are presented in Table 13. Values obtained by Stern for diffusion of 0.1 N hydrogen peroxide in water solutions containing other additives lie within 10% of the values given in Table 13. The effect of variation of concentration cannot be deduced from these experiments; the dependence of diffusion coefficient on temperature for 0.1 N hydrogen peroxide appears to be linear within the precision of the data, the change being about 0.03 cm²/day per °C. Stern attached some significance to the apparent upturn of the diffusion coefficient below 5°C, but this does not seem to be justified.

The data of Graupner and Winter (43) for the self-diffusion of water may be cited for comparison with hydrogen peroxide. Using solutions of deuterium oxide and water enriched in O¹⁸ containing less than 1 atom percent of the heavy isotope, Graupner and Winter measured the self-diffusion of water over the temperature range 15 to 45°C. At 25°C, for example, the diffusion coefficient of water in water was found to be 1.80 cm²/day. The ratio of the diffusion coefficient for water to that of hydrogen peroxide at the concentrations studied by Stern is approximately that of the ratios of molecular weights over the

TABLE 13

THE COEFFICIENT OF DIFFUSION
OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION,
FROM STERN (41)

| H_2O_2 Concentration, Normality | Temperature, °C | Coefficient of Diffusion, D, cm^2/day |
|--------------------------------------|-----------------|--|
| 0.102 | 40 | 1.48 |
| 0.104 | 30 | 1.18 |
| 0.103 | 25 | 1.03 |
| 4.78 | 20 | 1.12 |
| 0.85 | 20 | 1.18 |
| 0.107 | 20 | 0.84 |
| 0.011 | 20 | 0.76 |
| 0.098 | 15 | 0.78 |
| 0.102 | 10 | 0.46 |
| 0.101 | 5 | 0.39 |
| 0.102 | 0 | 0.53 |

experimental temperature range. The fact that Graupner and Winter found no difference in the diffusion coefficient when either the deuterium oxide or O^{18} -enriched water was used indicates that, for water, the molecule diffuses as a whole.

Measurements of the coefficient of diffusion of hydrogen peroxide into methyl alcohol, ethyl alcohol, acetone, and ether were also made by Stern (41). These coefficients were found to differ significantly from those found for diffusion into water. No constancy for the diffusion coefficient-solvent viscosity product was observed among the various solvents, and calculation of the coefficient of diffusion of hydrogen peroxide by a generalized method such as that of Wilke (44) gives poor agreement with experiment.

The permeability of a collodion membrane to hydrogen peroxide was measured by Collander (45). Using the molecular refractivity as a measure of molecular volume, Collander expressed the rate of transport through the membrane as a function of the molecular refractivity for a large number of substances and obtained a reasonable correlation. The permeability as he formulated it was reported to be much less than the diffusion

coefficients of the substances studied, and the permeability of hydrogen peroxide was low in relation to its molecular refractivity; these data are probably only of value as a relative measure of diffusional properties.

The Coefficient of Diffusion of Hydrogen Peroxide Vapor

McMurtrie and Keyes (46) have measured the rate of diffusion of anhydrous hydrogen peroxide vapor through a column of air, using the method of Stefan. A liquid 99 wt. % hydrogen peroxide solution at 60°C was allowed to evaporate into and diffuse upwards in a tube of 6.32 cm² cross-sectional area and 17.62 cm length; zero concentration of hydrogen peroxide vapor was maintained at the upper end of the tube by conducting a steady stream of air across the end of the tube. The rate of diminution of liquid volume, after correction for that due to decomposition, was used directly to calculate the coefficient of diffusion, from the equation for steady-state unidirectional diffusion of one gas through a second stagnant gas under a fixed concentration gradient. Corrections for the co-current diffusion of the small amount of oxygen derived from decomposition and for the small change in vapor pressure as dilution caused by decomposition occurred were found to be negligible. The adequacy of the apparatus and procedure was checked further by measurements of the rate of diffusion of water vapor through hydrogen at several temperatures. McMurtrie and Keyes obtained the value 0.188 ± 0.004 cm²/sec as the average of three determinations of the coefficient of diffusion of hydrogen peroxide vapor through air at 60°C and 1 atmosphere.

This experimentally determined coefficient of diffusion is reproduced well by the correlation of Gilliland (47) which uses empirical atomic volumes; a value of 0.189 cm²/sec is obtained. The coefficient obtained by the generalized equation of Andrussov (48) does not check the experimental value as well. A comparable value for the diffusion coefficient of water vapor in air is 0.320 cm²/sec at 60°C and 1 atmosphere (49).

Solid-Vapor Phase Relations for Hydrogen Peroxide

No direct measurements of the vapor pressure of solid hydrogen peroxide or its solutions have been recorded. The vapor pressure at the triple point (-0.461°C) may be calculated from the data of Scatchard, Kavanagh, and Ticknor (25) as 0.26 mm Hg. The heat of sublimation at the freezing point obtained by addition of the heats of vaporization and fusion is 456.2 cal/g or 15,510 cal/mole. Using these figures Foley and Giguère (8) calculated by the Clapeyron equation the slope, dp/dT , of the solid-vapor equilibrium curve at the triple point to be 3.6×10^{-5} atm/ $^{\circ}\text{K}$.

Solid-Liquid Phase Relations for Hydrogen Peroxide

The solid-liquid phase diagram for the system hydrogen peroxide-water is of a relatively simple type showing depression of the freezing point of each component by the addition of the other and two eutectic points for the mixtures ice-- $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ --solid hydrogen peroxide with a congruent melting point for the compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ between them. True solid solutions are not formed, but the solid phases tenaciously occlude the mother liquor. All the available data with the exception of those for dilute water-rich solutions and those for solid compositions between the eutectics are presented in Figure 5 along with the recommended curve. The numerous determinations of the freezing points of very dilute solutions are not included since they serve only to check the ideal freezing points (shown in Figure 5) in this range. In the region between the eutectics the points found for liquid compositions are mingled with those for solid compositions; to avoid confusion only the liquid composition points are shown. A discussion of the freezing point curve is given first. Determination of solid phase compositions and observations of the appearance on freezing and of the decomposition attending melting are next presented. Observations and measurements relating to possible solid-solid phase transformations at temperatures below the eutectic temperatures are cited at the end of this section. A discussion of supercooling and data for the heat of fusion are presented in following sections.

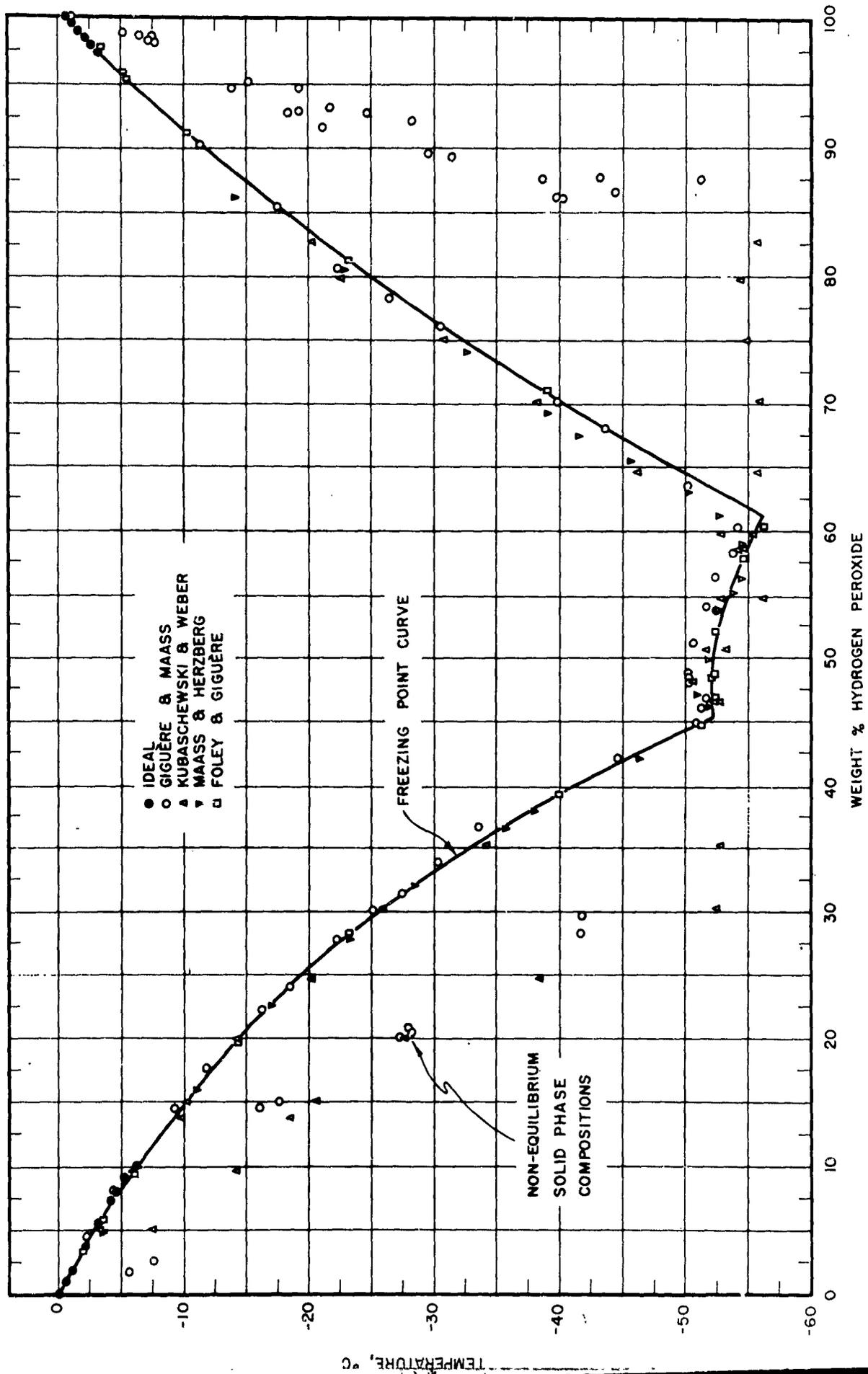


FIGURE 5 — SOLID-LIQUID PHASE DIAGRAM FOR THE SYSTEM HYDROGEN PEROXIDE-WATER

A number of measurements, by Tammann (4), Carrara (5), Orndorf and White (6) and Menzel (50), have been made of the freezing point depression of dilute (less than about 5 wt. %) hydrogen peroxide solutions. These results are, in general, in good accord with the freezing points calculated for an ideal solution. Such ideal freezing points are presented in Figure 5 for both dilute and concentrated solutions. The true freezing points lie less than 0.5°C below the ideal freezing points at concentrations of less than about 10 wt. % hydrogen peroxide, and less than 0.1°C below ideal at less than 5 wt. % concentration. In hydrogen peroxide-rich solutions the true freezing points lie less than 0.5°C below the ideal freezing points at concentrations of more than 94 wt. %, and less than 0.1°C below ideal at concentrations above 97.5 wt. %. These estimates were arrived at through use of the activities obtained by Scatchard, Kavanagh, and Ticknor (25) and use of pure component heats of fusion.

A complete investigation of the freezing points over the entire range of composition was first made by Maass and Herzberg (51). These measurements have been repeated by Giguère and Maass (7), Kubaschewski and Weber (20), Foley and Giguère (52), and Mironov and Bergman (30). Measurements with particular concern for the value of the freezing point of anhydrous hydrogen peroxide have been made by Maass and Hatcher (11) (-1.70°C), Guthbertson, Matheson, and Maass (18) (-0.89°C), Egerton, Emte, and Minkoff (53) (-1.8°C), and Foley and Giguère (52) (-0.461°C). This latter value is the recommended one for the freezing point of anhydrous hydrogen peroxide; extreme care was taken in purification of the sample and the reproducibility of this highest of observed freezing points was excellent. The data reported by Maass and his co-workers were obtained by observations of the temperature at which the last crystals melted in a partially frozen solution. The data of Kubaschewski and Weber, Foley and Giguère, and Mironov and Bergman, were obtained by the method of thermal analysis with free cooling.

As may be seen in Figure 5 these sets of data* show good consistency. The chief uncertainties are in the region between the eutectic compositions and in the slightly higher values shown by Giguère and Maass at concentrations below 60 wt. %. The coordinates chosen by the various investigators for the compound and eutectics are given in Table 14.

TABLE 14

SOLID-LIQUID PHASE DIAGRAM
FOR THE SYSTEM HYDROGEN PEROXIDE-WATER;
COMPOSITION-TEMPERATURE COORDINATES OF
COMPOUND AND EUTECTICS,
FROM FOLEY AND GIGUÈRE (52)

| First Eutectic | | Compound | | Second Eutectic | | Reference |
|-------------------------------------|-----------|-------------------------------------|-----------|-------------------------------------|-----------|-------------|
| wt. % H ₂ O ₂ | Temp., °C | wt. % H ₂ O ₂ | Temp., °C | wt. % H ₂ O ₂ | Temp., °C | |
| 45 | -53 | 48.6 | -51 | 59 | -56 | 51 |
| 46 | -51.5 | 48.6 | -50.3 | 60 | -56.5 | 7 |
| 45.8 | -52.5 | 48.6 | -50.3 | 59.0 | -55.5 | 20 |
| 45.2 | -52.4 | 48.6 | -52.1 | 61.2 | -56.5 | 52 |
| 46.1 | -52.5 | 48.6 | -50.2 | 60.2 | -55.7 | 30 |
| 45.2 | -52.25 | 48.6 | -52.0 | 61.2 | -56.1 | 36 |
| 45.2 | -52.2 | 48.6 | -52.0 | 61.2 | -56.1 | recommended |

The coordinates of the recommended freezing point curve are given in Table 15. Probably the greatest uncertainty is centered in the region of the eutectics. The rather flat maximum in the freezing point curve, indicating virtually complete dissociation of the molecular compound H₂O₂·2H₂O on passing into the liquid phase, makes it difficult to obtain well-defined points in this region.

Not shown on the freezing point curve in Figure 5 is the break at -29° and 76.5 wt. % hydrogen peroxide believed to exist by Mironov and Bergman (30). These authors found that their freezing points above the eutectic on the hydrogen peroxide

* Mironov and Bergman presented their data only in a small figure. These data could not be read with sufficient precision for inclusion in Figure 5; in general they support the recommended curve.

TABLE 15

RECOMMENDED COORDINATES OF SOLID-LIQUID PHASE
DIAGRAM FOR HYDROGEN PEROXIDE-WATER SYSTEM

| Concentration H_2O_2 , wt. % | Freezing Point, $^{\circ}\text{C}$ |
|---|---------------------------------------|
| 0 | 0 |
| 5 | -2.9 |
| 10 | -6.4 |
| 15 | -10.3 |
| 20 | -14.6 |
| 25 | -19.5 |
| 30 | -25.7 |
| 35 | -33.0 |
| 40 | -41.4 |
| 45 | -51.7 |
| 45.2 | -52.2 Eutectic |
| 48.6 | -52.0 Compound |
| 50 | -52.2 |
| 55 | -53.3 |
| 60 | -55.5 |
| 61.2 | -56.1 Eutectic |
| 65 | -49.0 |
| 70 | -40.3 |
| 75 | -32.3 |
| 80 | -24.8 |
| 85 | -17.9 |
| 90 | -11.5 |
| 95 | -5.6 |
| 100 | -0.461 |

side could be joined by a curve of two branches with intersection at these latter coordinates. The break was not pronounced. Such a break or invariant point indicates, for this system, the presence of two solid phases just as at the eutectic points. The break may then be either a peritectic point showing equilibrium of the liquid with a solid compound $x\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ (where $x > 1$) which is unstable above -29° or a transition point at which solid hydrogen peroxide undergoes an allotropic modification. Since there has been no other indication of such a point, and since subsequent thermal analysis conducted by Giguère (36) has shown no evidence of a halt at -29° , the existence of this break appears highly doubtful.

There has been considerable uncertainty regarding the composition of the solid phases obtained on freezing hydrogen peroxide solutions, but recent work now affords a much improved understanding of this subject. In Figure 5 are included observed values for the composition of the solid phases presumed to be in equilibrium with the liquid. Not included in the figure are the points representing solid phase compositions in the region between the eutectics. Such points fall within limits of variation of liquid phase composition of the several determinations and are left out to avoid confusion. These solid phase composition data are based on measurements of phase composition after separation by Giguère and Maass (7) and on the thermal analysis made by Kubaschewski and Weber (20). Without further information, this melting point curve or solidus line would indicate the formation of solid solutions. It is a fact that, except for the most dilute and most concentrated solutions, the solid obtained by the partial freezing of hydrogen peroxide solutions contains both water and hydrogen peroxide, even under conditions encouraging attainment of equilibrium. It has been conclusively shown, however, that these solids of mixed composition are not true solid solutions; however, since much controversy exists in the literature, the principal evidence for and against this conclusion is cited as follows.

Evidence for the formation of solid solutions: (1) It has been known since Thenard's time that fractional crystallization constitutes an inefficient method for the preparation of concentrated or pure hydrogen peroxide. Giguère and Maass (7) stated that the effective increase in concentration obtained in one operation was usually about 2% and never greater than 4%, making it uneconomical to attempt the preparation of anhydrous hydrogen peroxide by freezing from solutions of any concentrations below 90 wt. %. (2) The crystal habits of solid water and hydrogen peroxide, hexagonal and tetragonal, are not isomorphous, but have similar dimensions. Other non-isomorphous systems of lesser dimensional similarity are known to form solid solutions. (3) By two methods of determining solid phase composition at

the melting point (by phase separation with direct analysis (7, 11) and by thermal analysis (20)) the results indicate the formation of solid solutions. (4) The solid phase obtained by partial freezing of a hydrogen peroxide solution may be separated from the mother liquor so completely as to appear quite dry. By the analysis of such a solid it is determined that to consist of one-component solid with adherent or occluded mother liquor it would be necessary for the solid to carry as much as or more than its own weight of liquid.

Evidence against the formation of solid solutions:

(1) X-ray analysis of 82 and 90 wt. % hydrogen peroxide solutions made by Natta and Rigamonti (54) indicated that hydrogen peroxide does not take water or $H_2O_2 \cdot 2H_2O$ into solid solution; the lattice constant of solid hydrogen peroxide is seen to be unaltered in the frozen solutions. (2) The total volume of partially-frozen solutions can be calculated quite closely on the basis of the assumption of the formation of one-component solid phases. (3) Systems forming solid solution phases in which one component is water ice are rare if, indeed, they occur at all. (4) Giguère and Geoffrion (16) found that crystallization could be induced in a 41.8% solution and the system then supercooled (to -60°) with respect to the first eutectic. The liquid on separation from the solid was found to be 48.4% hydrogen peroxide; crystallization could not be induced in this liquid by seeding with water ice, but a trace of a crystal from a 45% hydrogen peroxide solution frozen completely caused immediate solidification. It is reasoned from this experiment that the solid first deposited was water ice and that this did not initiate separation of the eutectic containing the compound $H_2O_2 \cdot 2H_2O$. (5) Deviations of freezing points as calculated for ideal solutions from freezing points obtained experimentally for concentrated solutions, earlier believed to be due to the necessity of correcting for the formation of solid solutions, have now been shown to be due to the use of a low value for the heat of fusion of anhydrous hydrogen peroxide. (6) Foley and Giguère (52) examined the composition of the phases obtained on partial freezing

of hydrogen peroxide solutions by applying the wet residue method of Schreinemakers, using potassium chloride as the third component. The results showed conclusively that solid solutions were not formed. (7) To eliminate the possibility that the potassium chloride altered the phase equilibrium in the latter experiments, similar experiments were made to measure the proportional solubility of a trace of radioactive potassium dihydrogen phosphate in the phases. Formation of solid solutions was again denied. (8) By the method of thermal analysis, Mironov and Bergman found no evidence for solid solutions.

The evidence is completely against the formation of true solid solutions; this conclusion being made certain by the experiments with an added inert component. The confusion regarding solid phase composition has undoubtedly been introduced by difficulty in obtaining complete phase separation on freezing hydrogen peroxide solutions, and it is difficult to decide from the experimental evidence what apparent solid compositions are to be expected in practice. Without further data, the apparent solid phase compositions reported by Maass and Hatcher, Giguere and Maass, and, to a lesser extent, Kubaschewski and Weber*, shown in Figure 5, must be relied upon to represent

* An interesting question regarding the nature of the process of phase separation is raised by the thermal analysis data of Kubaschewski and Weber, which agree with the direct analysis data of Giguere and Maass. It is demonstrated by the coincidence of the freezing point curves determined by last crystal melting and by analysis of partially frozen solutions that the liquid occluded in the solid is of the same composition as the free liquid surrounding the solid. In the absence of any further information regarding the state of the solid plus occluded liquid it would appear that a eutectic arrest should be shown by thermal analysis of a solution of any composition. This was the experience of Mironov and Bergman. Kubaschewski and Weber, on the other hand, reported breaks but no eutectic arrests in the cooling or heating curves of certain solutions (indicated in Figure 5) even though rather large proportions of the systems existed as liquid occluded in the crystals. Although such a system has not changed from a variance of one, the behavior indicates that cooling can occur without further formation of the solid phase after the point of apparent solidification has been reached. This behavior as an apparently bivariant system and the dry appearance of the solid indicate an incorpora-

the compositions likely to be obtained after any but the most prolonged freezing. Some practical observations on the compositions and proportions of the solids frozen out of hydrogen peroxide solutions were made by Steindl (55). Giguère (36) reported that a variation from the solid phase compositions indicated in Figure 5 could be obtained, e.g., in a 10% partly frozen solution placed outdoors during a long period of cold weather the mass of microcrystals was gradually transformed into a large transparent mass of nearly pure water ice.

The appearance of the crystals obtained on freezing hydrogen peroxide solutions was described by Giguère and Geoffrion (16). The solid obtained in dilute solutions (less than 45 wt. %) appears as tiny white flakes on the walls of the container. The formation of these prisms is easily initiated or spontaneous, and they grow quickly by branching, somewhat like hoarfrost. The solid obtained in concentrated solutions (more than 65 wt. %) appears as long, clear needles growing up in a bundle from the bottom of the liquid. Concentrated solutions show a marked tendency to supercool, and when crystallization begins it proceeds slowly, even in markedly supercooled solutions, because of the high viscosity of the solution at these low temperatures. Indeed, so slow is the rate of crystallization relative to the rate of heat transmission from a container that the temperature of such a supercooled solution may rise little or not at all during solidification.

A phenomenon of practical as well as theoretical interest

tion of the liquid into the mass of solid crystals that is remarkably firm. The solid and liquid combined in this state may well remain stable with respect to phase separation until temperatures below the eutectic temperatures are reached, whereupon the occluded liquid becomes unstable with respect to the solid compound $H_2O_2 \cdot 2H_2O$. The magnitude of the heat effect under measurement in the thermal analysis and the reliability of the experimental work must be considered, but the above speculation receives some support from the observations on transition to eutectic composition made by Giguère and Geoffrion (16) and reported below in the description of decomposition on thawing.

is that of decomposition in hydrogen peroxide solutions on melting. This commonly-observed action hinders the procedure of purification and rejection of dissolved gas by alternate freezing and thawing. Giguere and Geoffrion (16) found that this decomposition occurred only in the eutectic mixtures. The observations are as follows: frozen hydrogen peroxide solutions (carbon dioxide at -78°C generally used for this) begin to evolve gas on thawing; on stopping the melting, gassing ceases; presence or absence of dissolved gas has no effect (as when the solution is frozen in vacuum, or when crystals of completely frozen 52% solution evolve a stream of bubbles as they melt on being dropped into freshly distilled water). Such decomposition does not occur on melting the first crystals obtained by slow freezing. But, as Giguère and Geoffrion say, "If these original crystals are cooled to low enough temperatures, around -70°C , and kept there for some time, a gradual transformation takes place as evidenced by sharp clicks and a progressive contraction of the mass, which assumes then the appearance of finely fritted glass or compressed snow and becomes detached from the walls of the container. On partial melting, this snowy mass is found to consist of minute needles, less than 1 mm long, and oriented at random. Under magnification the gas bubbles may be seen to appear in the liquid at the tip of these micro-crystals."

Thus Giguère and Geoffrion lay this behavior to the decomposition of the hydrogen peroxide in the addition compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, believing that the hydrogen peroxide molecule must be seriously distorted in order to fit into the crystal structure of this compound and that the disruption of the crystal on melting leads to dissociation of the hydrogen peroxide rather than relief of the strain. They do not, however, rule out the possibility that this behavior is simply a manifestation of catalytic decomposition on the crystal surfaces. It is possible, too, that decomposition in the crystalline state and retention within the solid of the oxygen from this decomposition is responsible for this behavior.

From the above discussion it should be clear that the solid phases in equilibrium with the liquid are water ice, the compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, or solid hydrogen peroxide, depending on the composition of the original solution. Below the eutectic temperatures the completely solidified solutions will consist of mixtures of water ice and the compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ or of solid hydrogen peroxide and the compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, depending upon whether the initial solution was below or above 48.6 wt. % hydrogen peroxide. Further solid-solid phase transitions at temperatures below the eutectics, as suggested by Kubaschewski and Weber and required if solid solutions are formed, are seen to be uncalled for. At very low temperatures (ca. -110°C) it is possible that further phase transition occurs. Geib and Harteck (56) and Jones and Winkler (57) found that hydrogen peroxide formed at temperatures below -110°C by the union of atomic hydrogen and molecular oxygen or by the products of the dissociation of water vapor would partially decompose and change appearance on being warmed to temperatures above -120°C . It was suggested that two tautomeric forms of hydrogen peroxide are stable at the lower temperatures, one decomposing above -120°C , the other being "normal" hydrogen peroxide. Further work will be necessary before this behavior is understood but it would appear that equilibrium is not established between the proposed tautomers. NeYding and Kazarnovskii (58) found no evidence of transition at this temperature level when magnetic susceptibility measurements were made with hydrogen peroxide cooled down from room temperature. Similarly, Mironov and Bergman (30) obtained no evidence of transformation on carrying a thermal analysis to -180°C . Bawn and Hogg (59) made calorimetric measurements of the transition at -115°C , finding that a heat change of a few hundred calories occurred. Because of the magnitude of the heat effect they suggested that this was evidence that a phase change occurs. Desorption of gas or chemical reaction as causes of this heat effect are by no means ruled out, however. Further consideration is given the subject of possible equilibrium between isomeric forms of hydrogen peroxide in the chapter on structure.

Supercooling of Hydrogen Peroxide Solutions

No extensive study of supercooling in solutions of hydrogen peroxide has been reported, but there is common agreement that supercooling is easily achieved in these solutions and that it is most marked at high concentrations. Perhaps the most striking evidence of this is the fact that stocks of commercial 90% hydrogen peroxide are commonly stored outdoors by manufacturers in the northern United States. Winter temperatures in this region may often reach well below -11°C (12°F), the freezing point for 90%, yet freezing has never been noted in these unprotected storage tanks. This tendency to supercool along with the considerable freezing point depression should make for safe outdoor storage of all but the most dilute solutions. Without a thoroughgoing investigation of supercooling in hydrogen peroxide solutions the best statement that can be made is that it may be expected at all concentrations, most markedly at concentrations above 50% hydrogen peroxide where supercooling of 10° to 50°C below the freezing point is not uncommon (1).

A considerable clarification of the facts about supercooling and an insight into its cause both in water and in hydrogen peroxide and its solutions is provided by the study made by Dorsey (60). In systematic experiments Dorsey found that nearly any sample of water could be supercooled several degrees without special treatment. Purified samples of water could be brought to temperatures of about -15°C easily, although one particular sample of untreated tap water reached -22°C . The lowest recorded supercooling discovered in the literature by Dorsey was -40°C . Contrary to the usual supposition, Dorsey found that the temperature to which a sample could be supercooled, called the temperature of spontaneous freezing by him, was reproducible and unaffected by prolonged chilling. The temperature of spontaneous freezing possessed by any given sample changed slowly with age, generally downward, and usually in discrete steps, giving the impression of the existence of preferred temperature levels. Treatment by

boiling of sealed samples both with and without contained air was an effective method of depressing the temperature of spontaneous freezing. Distillation and filtration were also effective in this manner. External shock, pouring, and any but the most violent shaking did not induce crystallization. Only the action of rubbing of the container walls or of two other surfaces within the liquid was effective in causing freezing, and the temperature at which rubbing was effective was also fairly reproducible, at a temperature a few degrees above the temperature of spontaneous freezing.

Dorsey concluded that these facts could only be explained on the basis of initiation of crystallization by foreign matter; i.e., that nucleation could only be brought about by motes of particular size and surface nature and that size and surface determine the temperature of spontaneous freezing. This "heterogeneous theory" seems quite applicable to the case of hydrogen peroxide and its solutions. In particular it appears that the reactive, solubilizing property of hydrogen peroxide may be effective, as is the boiling of water, in taking into solution or reducing the size of motes capable of inducing freezing. This "built-in" scavenging action of hydrogen peroxide may well account for its ready and marked supercooling. Such action is aided in effectiveness by the extreme care taken, at least for the higher concentrations, in the manufacture of hydrogen peroxide; commercial solutions are regularly prepared with purity comparable to that of carefully distilled water. The belief that the presence of bubbles in the liquid inhibits supercooling would appear to be unfounded, both by extension of Dorsey's experience and by consideration of the necessarily polarized nature of a gas-water interface, which, as Weyl (61) points out, cannot, when so distorted by polarization, assume the structure of the solid. It is likely, too, that nuclei in hydrogen peroxide solutions may become surrounded by a film of oxygen derived from decomposition. Such a film might be expected to alter radically the effectiveness of nuclei.

Supercooling thus appears to be a somewhat random phenomenon, a reflection of the purity of the sample with respect to a particular type of contaminant. In such a case, little can be said to predict the behavior of a given sample and such statements as that of Kubaschewski and Weber to the effect that stirring was effective in preventing supercooling cannot be accepted as a general guide. Only seeding or exposure to intense cold can be counted upon to prevent supercooling.

The Heat of Fusion of Hydrogen Peroxide

The heat of fusion of anhydrous hydrogen peroxide was estimated by de Forcrand (62) to be 2700 cal/mole by multiplication of the value for water by the ratio of molecular weight of hydrogen peroxide to water. The value was first determined from experimental measurements by Maass and Hatcher (11) to be 74 cal/g or 2516 cal/mole. Foley and Giguère (8) believe this result to have been affected by the presence of some water in the sample taken for measurement. From their experiments, using an ice calorimeter and hydrogen peroxide derived from a 99.6% solution many times recrystallized and determined to be anhydrous, Foley and Giguère determined the heat of fusion to be 85.83 ± 0.18 cal/g or 2920 cal/mole. Specific heats for solid and liquid used in this work are detailed later. The accepted value for the heat of fusion of water is 79.72 cal/g or 1436.3 cal/mole.

Using this datum and the densities of solid and liquid, and the freezing point, the slope, dp/dT , of the solid-liquid equilibrium line at the triple point for hydrogen peroxide may be calculated by the Clapeyron equation to be 136 atm/ $^{\circ}$ K. The chief uncertainty in this value is due to the choice of the solid density, e.g., on the basis of a different density the value 143 atm/ $^{\circ}$ K is given by Foley and Giguère (8). For water the value is -134 atm/ $^{\circ}$ K. The value of the cryoscopic constant for hydrogen peroxide is similarly calculated to be 1.72 $^{\circ}$ C/mole, compared to 1.86 $^{\circ}$ C/mole for water.

Liquid-Vapor Phase Relationships for Hydrogen Peroxide

In the system water-hydrogen peroxide the liquid components are completely miscible and water is the more volatile to a considerable degree. The system shows negative deviations from Raoult's law; partial pressures of the components in the vapor over the liquid are less than those calculated for ideal solutions. Since there is a large difference in the vapor pressure of the pure components this deviation is not extreme enough to lead to the formation of azeotropes; no vapor pressure minimum or boiling point maximum exists.

The measurement of vapor pressures of hydrogen peroxide and its solutions is complicated by the decomposition that inevitably occurs on heating and concentrating a hydrogen peroxide solution which is not of the highest purity. At the same time the large differences in volatility make for relatively easy concentration in simple equipment of dilute products to the strengths of up to 30 wt. % or higher common in commerce. These facts undoubtedly retarded the undertaking of a precise determination of the vapor-liquid equilibrium relationships of hydrogen peroxide; in the early literature only scattered boiling point data, reported incidentally in studies of concentration techniques, are available (63). More recent and extended vapor-liquid equilibrium data are given by Sidersky (64), and Uchida, Ogawa, and Yamaguchi (65) for a limited range of conditions, by Maass and Hiebert (66) and Egerton, Emté, and Minkoff (53) for essentially anhydrous hydrogen peroxide, and by Giguère and Maass (67) and Scatchard, Kavanagh, and Ticknor (25) for a wide range of temperature and composition. The agreement among all these sources of data is good, particularly at lower temperatures, but it is believed that the highest degree of accuracy and best experimental procedure was attained by Scatchard, Kavanagh and Ticknor. Their data will be accepted here, and, because of the importance of vapor-liquid equilibrium measurements in establishing many of the properties of hydrogen peroxide-water mixtures, these data and their treatment will be discussed in some

detail. Some aspects and calculations are presented that were not given in their paper.

The chief problem to be met in the measurement of the vapor pressure and composition over hydrogen peroxide solutions is the avoidance or allowance for the change in composition or pressure which may be caused by decomposition. In most of the work cited the measurements have been carried out in a static system and some criterion was used for rejection of results or else a means of extrapolation of a pressure-time curve was applied to take into account the effect of the small but important decomposition which occurred in the highly purified hydrogen peroxide samples undergoing test. An alternative technique, which reduces the uncertainty due to decomposition, is to conduct the measurements in a dynamic system allowing continuous boiling under controlled pressure. The experiments of Scatchard, Kavanagh, and Ticknor (and those of the Japanese workers (65)) were performed in such an apparatus. In this procedure there was a continuous production of vapor and subsequent condensation and return of the condensate to the boiler. Within the condenser there was established an interface between the hydrogen peroxide vapor and helium, which was in turn in contact with the mercury in the manometer. The desired temperature was attained by regulating the pressure of helium admitted to the system, and the rate of vaporization was regulated by control of the heat input to the boiler. Assuming that the rate of production of oxygen by decomposition is a function only of temperature and quantity of liquid in the boiler, the partial pressure of oxygen in the vapor space in this apparatus was then determined by the ratio of vaporization rate to decomposition rate, the vapor acting to sweep the oxygen into the helium reservoir. The large volume of this reservoir and the provision of means for periodic adjustment of pressure made it possible to reduce the effect of decomposition on system pressure to negligible proportions. Samples for the determination of liquid composition and temperatures were taken from a secondary or "inner" boiler surrounded by the vapors arising from the primary boiler to which the condensate returned. All vapor

passed over a cooling surface for regulating the amount of condensation into the inner boiler and through the liquid in the inner boiler. By proper regulation of the cooling surface a steady state, i.e., constant level of liquid in the inner boiler, could be attained.

The original data obtained by Scatchard, Kavanagh and Ticknor are presented in Table 16. These authors believed

TABLE 16

VAPOR PRESSURE OF HYDROGEN PEROXIDE-WATER SOLUTIONS,
FROM SCATCHARD, KAVANAGH, AND TICKNOR (25)

| Temp., °C | Liquid Composition, mole fraction H ₂ O ₂ | Total Vapor Pressure, mm Hg at 0°C | Vapor Composition, mole fraction H ₂ O ₂ |
|--------------|--|---------------------------------------|---|
| 44.50 | 0.5140 | 27.47 | 0.1273 |
| 60.00 | 0.0905 | 135.35 | 0.0054 |
| 60.00 | 0.2036 | 114.82 | 0.0104 |
| 60.00 | 0.2810 | 99.25 | 0.0397 |
| 60.00 | 0.4075 | 76.21 | 0.0849 |
| 60.00 | 0.5823 | 52.01 | 0.1757 |
| 60.00 | 0.6831 | 39.79 | 0.2951 |
| 60.00 | 0.8423 | 26.31 | 0.5699 |
| 60.00 | 0.9619 | 19.43 | 0.8972 |
| 75.00 | 0.0745 | 267.24 | 0.0036 |
| 75.00 | 0.1972 | 225.29 | 0.0167 |
| 75.00 | 0.2777 | 196.43 | 0.0267 |
| 75.00 | 0.3241 | 180.44 | 0.0468 |
| 75.00 | 0.4899 | 128.88 | 0.1076 |
| 75.00 | 0.4963 | 127.09 | 0.1114 |
| 75.00 | 0.5751 | 105.30 | 0.1834 |
| 75.00 | 0.7450 | 69.86 | 0.3907 |
| 75.00 | 0.8572 | 53.35 | 0.6381 |
| 75.00 | 0.9596 | 42.28 | -- |
| 90.00 | 0.0994 | 471.07 | 0.0089 |
| 90.00 | 0.1954 | 411.73 | 0.0235 |
| 90.00 | 0.3257 | 331.99 | 0.0459 |
| 90.00 | 0.4980 | 234.54 | 0.1342 |
| 90.00 | 0.5118 | 227.24 | 0.1516 |
| 90.00 | 0.6546 | 165.37 | 0.2716 |
| 90.00 | 0.8418 | 109.63 | 0.5982 |
| 90.00 | 0.9597 | 84.92 | 0.8858 |
| 105.00 | 0.4985 | 413.33 | 0.1494 |

the pressure measurements to be of greater accuracy than the vapor composition measurements, because of fractionation in the boiler and experimental difficulties in maintaining steady state conditions. They have, accordingly, depended solely on the vapor pressure data for the calculation of vapor compositions, extrapolation of the data, and derivation of thermodynamic properties of the solutions.

The method used by Scatchard, Kavanagh and Ticknor for smoothing and extrapolating the vapor pressure data is as follows. It was assumed that the excess free energy of mixing per mole of solution could be represented by an equation of the form:

$$F_X^E = x_W(1 - x_W) \left[B_0 + B_1(1 - 2x_W) + B_2(1 - 2x_W)^2 \right] \quad (9)$$

The excess free energy of mixing is defined as the excess or difference between the measured free energy and that defined for an ideal solution. The free energy is in turn related to the chemical potential or partial molal free energy and the activity coefficient by the equations,

$$\mu_a = \frac{\partial F}{\partial n_a} \quad (10)$$

$$F = \mu_1 n_1 + \mu_2 n_2 \quad (11)$$

$$\mu_a^E = RT \ln \delta_a \quad (12)$$

The total vapor pressure of the solution is then given by the relation

$$P = P_{W0} \cdot x_W \exp \left(\frac{1}{RT} \left[\mu_W^E - (\beta_W - v_W)(P - P_{W0}) \right] \right) + \\ P_{H0} (1 - x_W) \exp \left(\frac{1}{RT} \left[\mu_H^E - (\beta_H - v_H)(P - P_{H0}) \right] \right) \quad (13)$$

The first additive term is thus the partial pressure of water and the second that of hydrogen peroxide.

After multiplication of equation (9) by the term $(n_W + n_H)$ to express F_x^E in terms of the total moles of solution and differentiation according to equation (10) there are obtained the following expressions for the excess chemical potentials of the components.

$$\mu_W^E = (1 - x_W)^2 \left[B_0 + B_1(1 - 4x_W) + B_2(1 - 2x_W)(1 - 6x_W) \right] \quad (14)$$

$$\mu_H^E = x_W^2 \left[B_0 + B_1(3 - 4x_W) + B_2(1 - 2x_W)(5 - 6x_W) \right] \quad (15)$$

Equations (14) and (15) may now be substituted into equation (13) and equation (13) fitted to the measured vapor pressures. In fitting this equation to their data Scatchard, Kavanagh, and Ticknor used the following procedure:

(1) The vapor pressure of water was calculated from the equation given by Keyes (68).

(2) The gas corrections for water were estimated by the method of Keyes, Smith, and Gerry (26). The corrections for hydrogen peroxide, after estimation of the critical constants, were obtained from the equation recommended for water.

(3) The vapor pressure of anhydrous hydrogen peroxide was obtained, first by graphical extrapolation of the data for solutions, then from analytical extrapolation of the successive approximations to the equation fitting the experimental vapor pressures.

(4) On the basis of the three foregoing procedures the constants were fitted to the data at each temperature by a successive approximation form of the method of least squares. The constants obtained were then smoothed with temperature, the following values being obtained:

$$B_0 = -752 + 0.97t = -1017 + 0.97T \quad (16)$$

$$B_1 = 85 \quad (17)$$

$$B_2 = 13 \quad (18)$$

The expression for the vapor pressure of anhydrous hydrogen peroxide was obtained in the following manner. Although a linear $\log p_{\text{H}_2\text{O}}$ vs. $1/T$ relationship was used within the range of experimental temperatures in the process of evaluating the constants, the $\log p$ to $1/T$ relationship for the obvious reference substance, water, deviates appreciably from the simple linear form over large temperature ranges. The Ramsay-Young method of extrapolating vapor pressures was therefore used, with water as a reference substance. The vapor pressure, 17.7 mm Hg, at 60°C was used as the reference pressure and the vapor pressure, 78.4 mm Hg, at 90°C was used to obtain the difference of the slopes of the $\log p$ vs. $1/T$ curves. This difference was found to be -1.5×10^{-5} . A four constant equation fitted to the derived vapor pressure curve at the temperatures 75° , 150° , 300° , and 450°C . The equation expressing the vapor pressure of anhydrous hydrogen peroxide so obtained was:

$$\log p_{\text{H}_2\text{O}}(\text{mm}) = 44.5760 - \frac{4025.3}{T} - 12.996 \log T + .0046055 T \quad (19)$$

With equation (19) for the vapor pressure of hydrogen peroxide, Keyes' (68) equation for the vapor pressure of water, and the values for the constants B_0 , B_1 , and B_2 , a table of partial pressures and of vapor pressures at various temperatures for all compositions of hydrogen peroxide solutions may be prepared. It was believed that the corrections for gas imperfection were of a magnitude comparable to experimental error and that the inclusion of deviations from perfect gas behavior was not warranted in the preparation of an extrapolated table of vapor pressures and vapor

TABLE 17

TOTAL VAPOR PRESSURE (mm Hg) OF HYDROGEN PEROXIDE-WATER SOLUTIONS,
FROM SCATCHARD, KAVANAGH, AND TICKNOR (25)

| Temp. °C | Mole Fraction Hydrogen Peroxide in Liquid | | | | | | | | | | |
|-------------|---|------|------|------|------|------|------|-------|-------|-------|-------|
| | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
| 0 | 4.58 | 4.06 | 3.45 | 2.81 | 2.20 | 1.66 | 1.21 | 0.856 | 0.593 | 0.404 | 0.272 |
| 10 | 9.20 | 8.17 | 6.96 | 5.70 | 4.49 | 3.42 | 2.53 | 1.83 | 1.30 | 0.915 | 0.642 |
| 20 | 17.5 | 15.6 | 13.3 | 10.9 | 8.69 | 6.68 | 5.00 | 3.66 | 2.64 | 1.89 | 1.36 |
| 25 | 23.7 | 21.1 | 18.1 | 14.9 | 11.9 | 9.17 | 6.90 | 5.09 | 3.71 | 2.69 | 1.95 |
| 30 | 31.8 | 28.3 | 24.3 | 20.1 | 16.0 | 12.4 | 9.41 | 6.99 | 5.14 | 3.77 | 2.77 |
| 40 | 55.3 | 49.3 | 42.4 | 35.2 | 28.3 | 22.2 | 17.0 | 12.8 | 9.55 | 7.14 | 5.36 |
| 50 | 92.6 | 82.5 | 71.1 | 59.3 | 48.1 | 37.9 | 29.3 | 22.4 | 17.0 | 12.9 | 9.90 |
| 60 | 149 | 133 | 115 | 96.6 | 78.7 | 62.6 | 49.0 | 37.8 | 29.1 | 22.5 | 17.5 |
| 70 | 234 | 209 | 181 | 152 | 125 | 100 | 79.0 | 61.8 | 48.2 | 37.8 | 29.8 |
| 80 | 355 | 318 | 216 | 233 | 192 | 155 | 124 | 97.8 | 77.2 | 61.3 | 49.1 |
| 90 | 526 | 471 | 410 | 348 | 289 | 235 | 189 | 150 | 120 | 96.5 | 78.2 |
| 100 | 760 | 682 | 595 | 507 | 422 | 346 | 280 | 226 | 182 | 148 | 121 |
| 110 | 1074 | 965 | 845 | 722 | 605 | 499 | 407 | 331 | 269 | 221 | 182 |
| 120 | 1489 | 1339 | 1175 | 1008 | 848 | 704 | 578 | 474 | 389 | 322 | 269 |
| 130 | 2025 | 1824 | 1604 | 1381 | 1168 | 974 | 807 | 666 | 552 | 460 | 387 |
| 140 | 2709 | 2443 | 2153 | 1860 | 1580 | 1326 | 1105 | 919 | 767 | 645 | 546 |
| 150 | 3568 | 3222 | 2847 | 2467 | 2105 | 1776 | 1489 | 1247 | 1048 | 887 | 755 |

TABLE 18
 VAPOR COMPOSITION (mole fraction H_2O_2) OVER HYDROGEN PEROXIDE-WATER SOLUTIONS,
 FROM SCATCHARD, KAVANAGH, AND TICKNOR (25)

| Temp. C | Mole Fraction Hydrogen Peroxide in Liquid | | | | | | | | | |
|------------|---|-------|-------|-------|-------|-------|-------|-------|-------|--|
| | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | |
| 0 | 0.002 | 0.006 | 0.015 | 0.031 | 0.060 | 0.112 | 0.202 | 0.352 | 0.600 | |
| 10 | 0.003 | 0.008 | 0.018 | 0.037 | 0.070 | 0.128 | 0.224 | 0.381 | 0.626 | |
| 20 | 0.003 | 0.009 | 0.020 | 0.041 | 0.077 | 0.138 | 0.238 | 0.397 | 0.640 | |
| 25 | 0.003 | 0.010 | 0.022 | 0.044 | 0.081 | 0.144 | 0.247 | 0.407 | 0.648 | |
| 30 | 0.003 | 0.010 | 0.023 | 0.046 | 0.085 | 0.151 | 0.255 | 0.417 | 0.656 | |
| 40 | 0.004 | 0.012 | 0.026 | 0.052 | 0.094 | 0.163 | 0.272 | 0.435 | 0.671 | |
| 50 | 0.005 | 0.014 | 0.030 | 0.057 | 0.103 | 0.175 | 0.287 | 0.452 | 0.684 | |
| 60 | 0.005 | 0.015 | 0.033 | 0.063 | 0.111 | 0.187 | 0.302 | 0.468 | 0.696 | |
| 70 | 0.006 | 0.017 | 0.036 | 0.068 | 0.120 | 0.199 | 0.316 | 0.482 | 0.707 | |
| 80 | 0.007 | 0.019 | 0.040 | 0.074 | 0.128 | 0.210 | 0.329 | 0.495 | 0.716 | |
| 90 | 0.007 | 0.021 | 0.043 | 0.080 | 0.136 | 0.221 | 0.342 | 0.508 | 0.725 | |
| 100 | 0.008 | 0.023 | 0.047 | 0.085 | 0.144 | 0.231 | 0.354 | 0.519 | 0.733 | |
| 110 | 0.009 | 0.025 | 0.051 | 0.091 | 0.152 | 0.241 | 0.365 | 0.530 | 0.740 | |
| 120 | 0.010 | 0.027 | 0.054 | 0.097 | 0.160 | 0.251 | 0.376 | 0.540 | 0.747 | |
| 130 | 0.011 | 0.029 | 0.058 | 0.102 | 0.168 | 0.260 | 0.386 | 0.549 | 0.753 | |
| 140 | 0.012 | 0.031 | 0.061 | 0.108 | 0.175 | 0.269 | 0.396 | 0.558 | 0.758 | |
| 150 | 0.013 | 0.033 | 0.065 | 0.113 | 0.182 | 0.278 | 0.405 | 0.566 | 0.763 | |

compositions. Thus, for this purpose, the terms of equation (13) containing the gas correction factor, β , were dropped. In terms of the activity coefficient, γ , equation (13) without the gas corrections becomes, by substitution of equation (12):

$$P = P_{W_0} x_W \gamma_W + P_{H_0} (1 - x_W) \gamma_H \quad (20)$$

It may be seen that the activity coefficients are expressed as follows:

$$\gamma_W = \exp\left(\frac{(1-x_W)^2}{RT} \left[B_0 + B_1(1-4x_W) + B_2(1-2x_W)(1-6x_W) \right]\right) \quad (21)$$

$$\gamma_H = \exp\left(\frac{x_W^2}{RT} \left[B_0 + B_1(1-4x_W) + B_2(1-2x_W)(1-6x_W) \right]\right) \quad (22)$$

The vapor compositions may be calculated from the relation:

$$y_H = \frac{P_{H_0} x_H \gamma_H}{P} = \frac{P_{H_0} x_H \gamma_H}{(P_{W_0} x_W \gamma_W) + (P_{H_0} x_H \gamma_H)} \quad (23)$$

Total vapor pressures and vapor compositions calculated by the use of equations (20) and (23) for hydrogen peroxide solutions of all composition over the temperature range 0 - 150°C are presented in Tables 17 and 18.* The data of Tables 17 and 18 have been presented in part in Figures 6, 7, and 8, which show for comparative purposes the vapor-liquid equilibrium relationships of the solutions at selected temperatures and pressures.

The total vapor pressures calculated by Scatchard, Kavanagh, and Ticknor by means of equation (10) have an average deviation of 0.44% and a maximum deviation of 1.38% from the experimental values given in Table 16. At temperatures up to 75°C, equation (19) for the vapor pressure of anhydrous hydrogen peroxide reproduces within a few tenths of a milli-

* Extension of the tabulated data may be accomplished with these equations or an alternative method (69), employing a Dühring plot, may be used.

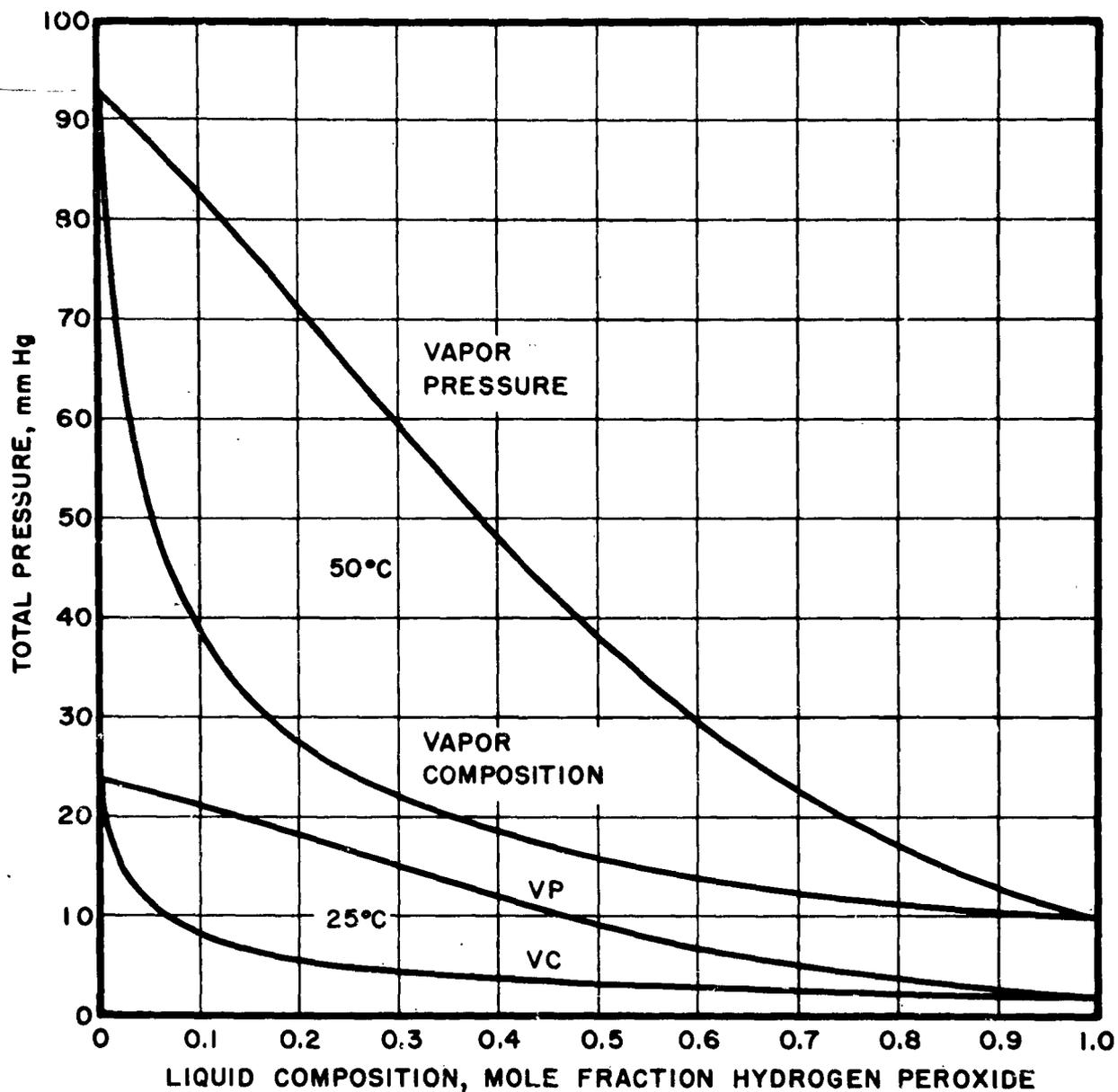


FIG. 6 - COMPOSITION AND PRESSURE OF VAPOR OVER HYDROGEN PEROXIDE-WATER MIXTURES AT 25 AND 50°C

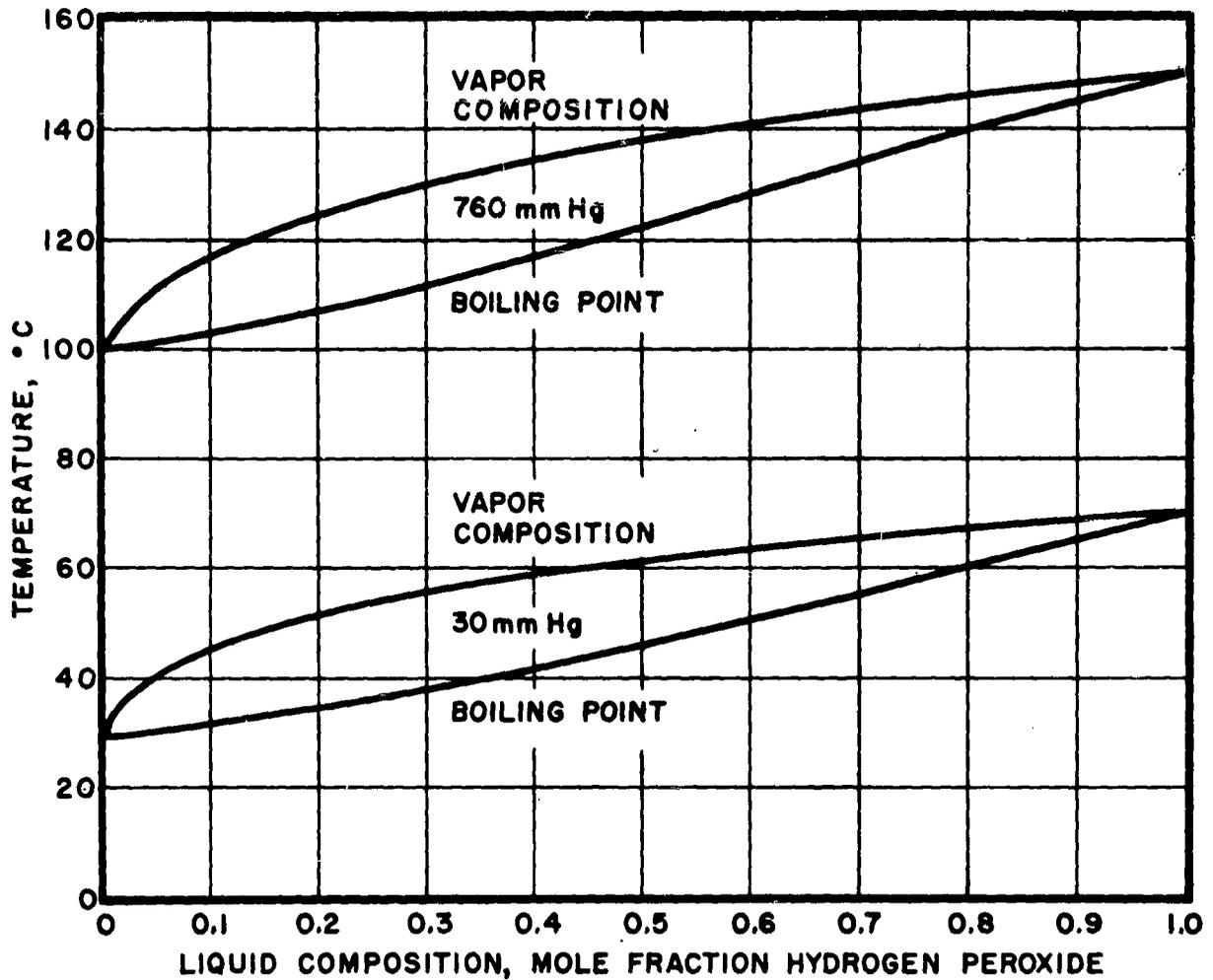


FIG. 7-BOILING POINTS OF AND VAPOR COMPOSITION OVER HYDROGEN PEROXIDE-WATER MIXTURES AT 30 AND 760 mm Hg TOTAL PRESSURE

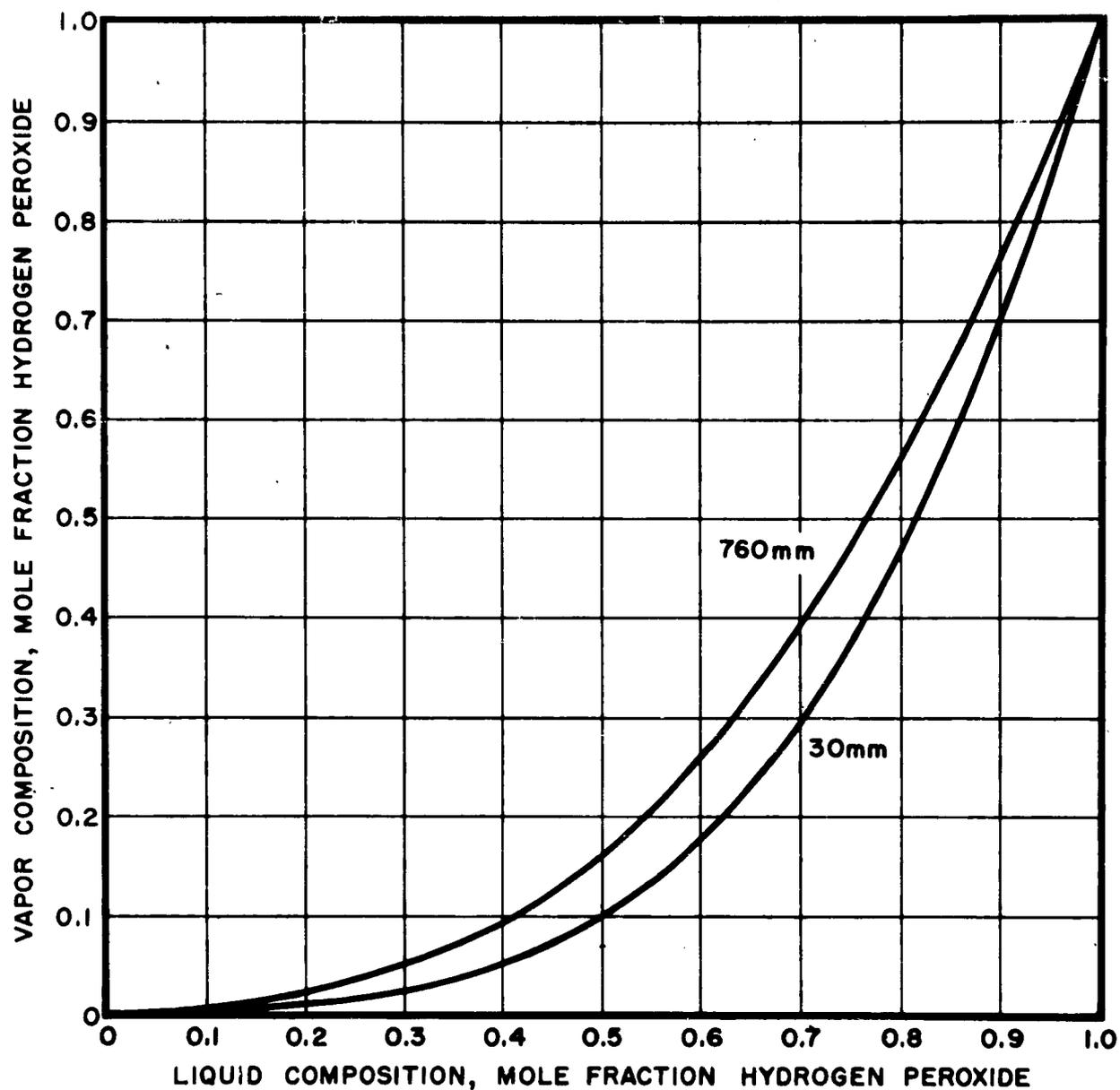


FIG. 8-VAPOR-LIQUID EQUILIBRIUM CURVES FOR HYDROGEN PEROXIDE - WATER MIXTURES AT 30 AND 760 mm Hg TOTAL PRESSURE

meter the values obtained from the equation recommended by Maass and Hiebert: $\log p_{\text{H}_2\text{O}}(\text{mm}) = 8.853 - 2534.7/T$. Similar agreement is obtained with the equation, $\log p_{\text{H}_2\text{O}}(\text{mm}) = 8.63 - 2469/T$, obtained for anhydrous hydrogen peroxide by Egerton, Emte, and Minkoff. At temperatures above 75° the divergence increases; Scatchard, Kavanagh, and Tickner discuss the reasons for this and suggest that for greatest accuracy the more detailed equation (19) be used to obtain the vapor pressures of anhydrous hydrogen peroxide. Dependence on this equation only is recommended here.

From the data given above the relative volatility, water to hydrogen peroxide, for hydrogen peroxide solutions is seen to be large, particularly so for water-rich solutions and at lower temperatures. An estimate of the hygroscopicity of hydrogen peroxide solutions may also be gained from these data. If 50% humidity at an ambient temperature of 25°C is taken as a basis for comparison, it will be found that solutions more concentrated than about 60 wt. % hydrogen peroxide are likely to absorb water vapor from the air. This effect is generally not noticeable except with very concentrated solutions or with solutions or crystals at low temperatures. In the storage of concentrated solutions the slow evolution of oxygen tends to isolate the solution from the atmosphere and aids in maintaining an equilibrium vapor in the container ullage.

The boiling points of hydrogen peroxide solutions have been obtained by interpolation of vapor pressure-composition curves for various temperatures and are tabulated in Table 19. These values for the boiling points are, with the exception of those at the highest concentrations, greater than those obtained by Giguère and Maass (67) by application of the simplified Ramsay and Young rule to their data or those obtained from a Cox chart of the same data (1). The boiling point rise brought about by increasing concentration is about 1°C for each 0.02 mole fraction. The precision of the boiling

TABLE 19

ATMOSPHERIC BOILING POINTS
OF HYDROGEN PEROXIDE SOLUTIONS

| Hydrogen Peroxide Concentration | | Temperature °C |
|---------------------------------|--------|-------------------|
| mole fraction | wt. % | |
| 0.0 | 0 | 100.0 |
| 0.1 | 17.34 | 103.0 |
| 0.2 | 32.07 | 106.9 |
| 0.3 | 44.73 | 111.5 |
| 0.4 | 55.73 | 116.7 |
| 0.5 | 65.37 | 122.3 |
| 0.6 | 73.90 | 128.2 |
| 0.7 | 81.50 | 134.0 |
| 0.8 | 88.31 | 139.7 |
| 0.9 | 94.44 | 145.1 |
| 1.0 | 100.00 | 150.2 |

point data given probably does not warrant their use as an indication of concentration to a degree closer than about 0.1 to 0.3 wt. %. Furthermore, at all concentrations there will be more or less oxygen evolution due to decomposition, and the boiling point will be lowered to the extent of the effect exerted by the partial pressure of oxygen over the solutions.

The decomposition which attends the boiling of hydrogen peroxide solutions, whether under atmospheric pressure or not, will depend upon the purity of the solution and cleanliness of the container and upon the extent to which decomposition of the evolved vapor may occur. The early investigators despaired of conducting concentration procedures by boiling at any but the lowest of pressures, however, it has been more recently demonstrated that hydrogen peroxide solutions of concentrations at least up to 90%, and approaching 100%, may be boiled smoothly at atmospheric pressure and with a minimum of decomposition if very carefully cleaned and non-catalytic surfaces are used throughout the apparatus. In particular it should be noted that the explosive decomposition which has been reported to occur on boiling concentrated or anhydrous hydrogen peroxide is probably due to explosive decomposition of the vapor alone,

as discussed in Chapter 4. Under proper conditions this explosive decomposition may be prevented or caused to occur smoothly as described in the discussion of vapor phase decomposition in Chapter 8. The decomposition which occurs in the liquid aids in the smooth boiling of hydrogen peroxide solutions, the bubbles of oxygen so formed acting to prevent the bumping which is encountered in boiling water.

The Critical Constants of Anhydrous Hydrogen Peroxide

On the assumption of the same proportionality of critical to boiling temperature for hydrogen peroxide and water the critical temperature for hydrogen peroxide was calculated by Scatchard, Kavanagh, and Ticknor to be 457°C (730°K) compared with 374.2°C for water. By the same procedure Maass and Hiebert (66) obtained the value 459°C . By use of equation (14) the critical pressure is found to be 163,000 mm Hg or 214 atm compared with 218.2 atm for water. The accuracy of these estimates is unknown; experimental attainment of these conditions seems unlikely.

The Heat of Vaporization of Liquid Hydrogen Peroxide

In Table 20 are tabulated values reported for the heat of vaporization of anhydrous hydrogen peroxide. The values given by Lewis and Randall (70), Maass and Hiebert (66) and Egerton, Emte, and Minkoff (53) are temperature-independent, having been derived by application of the Clausius-Clapeyron equation to the differentiated form of a linear log p , $1/T$ vapor pressure equation. The data used by Lewis and Randall were from the fragmentary observations of Wolfenstein and Brühl (63). Giguère and Maass (67) applied the simplified form of the Ramsey and Young equation which assumes the ratio of the temperatures at which hydrogen peroxide and water have the same vapor pressures to be constant under all conditions. On the basis of this good assumption it can be shown by use of the Clausius-Clapeyron equation that the ratio of the heats of vaporization is directly proportional to the ratio of temperatures at which the vapor pressure is the same for both substances. This procedure introduces a temperature dependence for the heat of vaporization.

TABLE 20

THE HEAT OF VAPORIZATION REPORTED
FOR ANHYDROUS HYDROGEN PEROXIDE

| Temp. °C | Heat of Vaporization | | Source |
|-------------|----------------------|-------|---|
| | cal/mole | cal/g | |
| -- | 12300 | 362 | Lewis and Randall (70) |
| -- | 11610 | 341.5 | Maass and Hiebert (66) |
| -- | 11300 | 332 | Egerton, Emte, and Minkoff (53) |
| 18 | 11950 | 351 | Giguère and Maass (67) |
| 150 | 11084 | 326 | Giguère and Maass (67) |
| 25 | 10266 | 302 | Kelley (71) |
| 155 | 10200 | 300 | Becco (1) |
| 25 | 13010 | 382 | National Bureau of Standards (72) |
| 0 | 12593 | 370.2 | Foley and Giguère (8) |
| 25 | 12334 | 362.6 | Morissette and Giguère (73) |
| 26.9 | 12314 | 362.0 | Morissette and Giguère (73) |
| 0 | 12930 | 380.3 | Scatchard, Kavanagh and Ticknor (25) |
| 25 | 12588 | 370.1 | Scatchard, Kavanagh and Ticknor (25) |
| 150 | 11260 | 331.2 | Scatchard, Kavanagh and Ticknor (25) |

The data of Maass and Hiebert and Giguère and Maass were combined by the Buffalo Electro-Chemical Co. (1) to prepare a Cox chart of vapor pressures from which heats of vaporization were obtained by the method of Othmer (74). The only direct measurements of the heat of vaporization are those given by Foley and Giguère (8) and Morissette and Giguère (73). These values, obtained by measurement of the heat loss attending the vaporization of anhydrous hydrogen peroxide in ice and diphenyl ether (mp 26.9°) calorimeters, are probably the most accurate values available, since the precision of direct measurement is greater than that of determination of the slope of even the most precise vapor pressure data. The heats of vaporization given by the data of Scatchard, Kavanagh, and Ticknor (25) were obtained from

the equation:

$$\Delta H_v = 0.021066 T^2 - 25.817 T + 18412 \quad (24)$$

obtained by differentiation of equation (19) and application to the Clausius-Clapeyron equation.

The values for the heat of vaporization of anhydrous hydrogen peroxide calculated with equation (24) are larger by approximately 300 cal/mole than the experimentally determined values of Foley and Giguère and Morissette and Giguère. This divergence tends toward improvement as the temperature increases, indicating that the data upon which equation (24) is based are of best accuracy at temperatures moderately above 25°C. In the evaluation of the heat of vaporization at temperatures removed from, but in the range of, the experimental determinations at 0 and 26.9°C the expedient might be adopted of subtraction of a quantity of the magnitude just mentioned from values calculated with equation (24); somewhat more accurate values will be obtained by combination of the experimental heats of vaporization with heat capacity data. At more elevated temperatures equation (24) alone should be used.

The heats of total vaporization for hydrogen peroxide-water solutions have been estimated by Giguère and Naass (67) and by the Buffalo Electro-Chemical Co. (1) by the same procedures used by them to obtain the values for anhydrous hydrogen peroxide. Such procedures do not take into account the heat of mixing or departure from ideality of the solutions. Neglect of the heat of mixing may introduce error in the calculated heats of vaporization, although this uncertainty is often of no consequence. It is necessary in the calculation of exact heats of total vaporization of solutions to combine the heats of mixing given below with the heats of vaporization of water and anhydrous hydrogen peroxide. Such values are given in Table 21 for 26.9°C. Similarly the differential or partial heats of vaporization may be calculated by taking into account the appropriate heat of dilution.

The slope, dp/dT , of the liquid-vapor equilibrium curve

at the triple point (-0.461°C) for anhydrous hydrogen peroxide is calculated by the Clausius-Clapeyron equation to be $2.9 \times 10^{-5} \text{ atm}/^{\circ}\text{C}$. The corresponding value for water is $4.4 \times 10^{-4} \text{ atm}/^{\circ}\text{C}$.

TABLE 21

TOTAL HEAT OF VAPORIZATION
OF HYDROGEN PEROXIDE-WATER SOLUTIONS AT 26.9°C ,
FROM MORISSETTE AND GIGUÈRE (73)

| H ₂ O ₂ Concentration, wt. % | Heat of Vaporization of Pure Components, cal/g solution | | Heat of Mixing, cal/g sol'n | Total Heat of Evaporation, cal/g sol'n |
|---|---|------------------|--------------------------------|--|
| | H ₂ O ₂ | H ₂ O | | |
| 0 | 0 | 582.1 | 0 | 582.1 |
| 20 | 72.4 | 465.7 | 4.7 | 542.8 |
| 40 | 144.8 | 349.3 | 8.4 | 502.5 |
| 60 | 217.2 | 232.8 | 9.7 | 459.7 |
| 80 | 289.6 | 116.4 | 7.4 | 413.4 |
| 100 | 362.0 | 0 | 0 | 362.0 |

THE THERMODYNAMIC PROPERTIES OF HYDROGEN PEROXIDE

The irreversibility of the reactions for the formation and decomposition reactions for hydrogen peroxide under laboratory conditions and the uncertainties introduced by decomposition have prevented the accurate experimental determination of several of the thermodynamic properties of hydrogen peroxide. Measurement of the absolute entropy of hydrogen peroxide has likewise not been undertaken and would appear to present a difficult problem. Nevertheless, a sufficient number of direct measurements of thermodynamic properties and of measurements of other properties from which thermodynamic properties may be calculated have been made to allow the assembly of a useful and substantially complete tabulation of the thermodynamic properties of hydrogen peroxide in all phases.

In the order of presentation adopted here the properties discussed first are as far as possible independent of the properties presented in later sections. The enthalpies of phase change, which were discussed in preceding sections are only briefly tabulated here for convenience.

The Thermodynamic Functions of Anhydrous Hydrogen Peroxide Vapor

By observation of the infrared and Raman spectra of hydrogen peroxide vapor it is possible to determine the energy taken up by the vibrational and oscillatory motions of its constituent atoms. The contribution of these vibrations as well as the contributions of the translational and rotational motions to the energy of the molecule at various temperatures may then be summed up by equations developed from the quantum theory. This procedure, by which is determined the relation of the energy states of the molecule and the number of molecules in each energy state to the total energy possessed by the system, results in the formulation of the so-called partition functions and is developed in detail by the standard textbooks (75).

When the energy of the system is known, the thermodynamic properties may be calculated directly. It is customary to tabulate the results of such calculations in terms of "thermodynamic functions", the quantities S° , C_p° , $-(F^\circ - H_0^\circ)/T$, and $(H^\circ - H_0^\circ)/T$. In this symbolism S° is the absolute entropy, C_p° the constant pressure heat capacity, F° is the free energy, H_0° is the enthalpy at absolute zero, T is the absolute temperature, and H° is the enthalpy of the molecule in question. As a basis for this scheme, the energy of the elements in the standard state (ideal gas at 1 atmosphere pressure) is taken to be zero. The enthalpy at absolute zero, H_0° , is equivalent to the total energy at absolute zero since $E = H + PV = H + RT$ for the ideal gas. The enthalpy at absolute zero is then also equal to the heat or free energy of formation at absolute zero.

The relationships developed from the partition functions between these thermodynamic functions and the observed properties of a substance, explained in detail by Aston (76) and Herzberg (77), are as follows for the hydrogen peroxide molecule:

$$C_p^\circ = 4R + \sum \frac{Rx^2 e^x}{(e^x - 1)^2} + f\left(\frac{V}{RT}, \frac{n^2}{I_{red} V}\right) \quad (25)$$

$$\left(\frac{H_0 - H_0^0}{T}\right) = 4R + \sum \frac{Rx}{e^x - 1} + f\left(\frac{V}{RT}, \frac{n^2}{I_{red}V}\right) \quad (26)$$

$$\begin{aligned} -\left(\frac{F^0 - H_0^0}{T}\right) &= R \left[9/2 \ln T + 3/2 \ln M - \ln P + 1/2 \ln I_A I_B I_C - \right. \\ &\quad \ln \sigma - \sum \ln(1 - e^{-x}) + 1/2 \ln(I_{red} \times 10^{40}) - \\ &\quad \left. \ln n + 128.247 \right] - f\left(\frac{V}{RT}, \frac{n^2}{I_{red}V}\right) \quad (27) \end{aligned}$$

In these sums there are terms for the energy contributed by each of the motions of the hydrogen peroxide molecule; those of vibration are represented by the terms carrying summation signs, those for torsional oscillation are represented by the indicated functions of the parameters, V/RT and $n/I_{red}V$, (plus additional terms in the free energy function), and the remaining terms represent the contributions of translational and rotational motion, e.g., for the heat capacity there is a contribution $5R/2$ for translational motion and $3R/2$ for rotation. These equations do not contain terms for the contribution to the energy of the molecule by differing electronic states or by rotation of the nuclei, nor is the effect of the presence of isotopes considered. These effects are negligible or cancel out in use; for the justification of this, see Rossini (78).

Three approximations have been used in deriving the equations: it has been assumed that in rotation as a whole the molecule remains rigid, that the vibrations may be considered to be harmonic oscillations, and that the potential barrier which restricts the internal rotation of the OH groups about the O - O axis may be represented by a function:

$$V = (1/2)V_0(1 + \cos n\phi) \quad (28)$$

where V represents the potential against rotation of an OH group through the angle ϕ . V_0 is the maximum value of this

potential, and n is number of positions per rotation at which the potential is at a minimum. The relation between the wave number characterizing the internal rotation and the potential is:

$$N \sigma_0 = n(V_0)^{1/2} / 2\pi(2I_{\text{red}})^{1/2} \quad (29)$$

These approximations are well justified in the calculation of the thermodynamic functions of hydrogen peroxide, although they may not represent the true state of affairs; for example, evidence was cited by Lassettre and Dean (79) to show that a different potential function than that of equation (28) is actually required to represent the internal rotation or torsional oscillation in the hydrogen peroxide molecule.

The thermodynamic functions for hydrogen peroxide have been calculated, according to the methods outlined in the previous paragraphs, by Zeise (80), Mickley (81) and Giguère (82).^{*} Most recent are the calculations of Giguère, which are presented here, since they are based upon an evaluation of the latest available molecular data. The molecular data used by Giguère are presented in Table 22; the details of these measurements and the basis for their choice are discussed in later sections. The results of the calculation by Giguère are presented in Table 23. The vibrational contributions were obtained from the tables presented in reference (75), and the contribution of torsional oscillation was obtained from the tables of Pitzer and Gwinn (83). Giguère has followed the usual practice of reporting the results of the calculations to a greater accuracy than is justified by the assumptions made. Since the torsional oscillation makes an important contribution to the energy of the molecule, and, since at the same time there remains doubt regarding the exact magnitude of this contribution, the results in Table 23 have been reported both with and without the effect of torsional oscilla-

^{*} Calculations of thermodynamic functions have also been published by G. Ribaud, Publ. sci. et tech. ministere air (France) 1952, No. 266, p. 129.

TABLE 22

MOLECULAR DATA FOR HYDROGEN PEROXIDE,
FROM GIGUERE (82)

| Fundamental Vibration | Wave number, cm^{-1} |
|-----------------------------------|-------------------------------|
| ν_1 (a) O-H stretching | 3590 |
| ν_2 (a) symmetric bending | 1320 |
| ν_3 (a) O-O stretching | 877 |
| ν_4 (a) torsional oscillation | 500 |
| ν_5 (b) O-H stretching | 3590 |
| ν_6 (b) unsymmetric bending | 1255 |

Moments of Inertia, g cm^2

$$I_A = 2.786 \times 10^{-40}$$

$$I_B = 32.9 \times 10^{-40}$$

$$I_C = 34.8 \times 10^{-40}$$

$$I_{\text{red}} = I_A/4 = 0.696 \times 10^{-40}$$

Barrier restricting internal rotation, V_0 , = 5 kcal/mole.

tion. More accurate functions* may then be calculated when further information is available without the necessity of repeating the entire calculation. Data like that of Table 23 for hydrogen, oxygen and water vapor, necessary for calculation of certain other thermodynamic properties of hydrogen peroxide, are available from Rossini et al. (72) (Series III).

Heat Capacity of Anhydrous Hydrogen Peroxide

The heat capacities of liquid and solid, anhydrous hydrogen peroxide were determined by Maass and Hatcher (11) using

* The low temperature heat capacity of crystalline hydrogen peroxide has now been measured by Morrison and Dugdale of the National Research Council, Ottawa, Canada (36). With 99.97 wt. % hydrogen peroxide having a triple point of -0.42°C the third law entropy was found to be 55.72 ± 0.11 cal/mole $^\circ\text{C}$ in the standard state of ideal gas at 1 atm and 25°C ; no first or second order transitions were observed to take place.

TABLE 23
 THE THERMODYNAMIC FUNCTIONS FOR HYDROGEN PEROXIDE VAPOR AT 1 ATMOSPHERE
 FROM GIGUERE (82)*

| T , °K. | $F^{\circ} - H^{\circ}$ $-\left(\frac{H^{\circ} - H^{\circ}_0}{T}\right)$ cal/deg/mole | $H^{\circ} - H^{\circ}_0$ $\frac{H^{\circ} - H^{\circ}_0}{T}$ cal/deg/mole | S° , cal/deg/mole | C_p° , cal/deg/mole | $H^{\circ} - H^{\circ}_0$ cal/mole |
|--------------|--|--|-------------------------------|---------------------------------|---------------------------------------|
| 298.16 | (45.33) | (8.12) | (53.45) | (8.79) | (2421) |
| 300 | (45.38) | (8.13) | (53.51) | (8.81) | (2439) |
| 400 | (47.75) | (8.41) | (56.16) | (9.72) | (3364) |
| 500 | (49.67) | (8.76) | (58.43) | (10.58) | (4380) |
| 600 | (51.29) | (9.12) | (60.41) | (11.30) | (5472) |
| 700 | (52.73) | (9.48) | (62.21) | (11.90) | (6636) |
| 800 | (54.01) | (9.82) | (63.83) | (12.42) | (7856) |
| 900 | (55.20) | (10.14) | (65.34) | (12.89) | (9126) |
| 1000 | (56.27) | (10.43) | (66.70) | (13.32) | (10430) |
| 1100 | (57.28) | (10.71) | (67.99) | (13.70) | (11781) |
| 1200 | (58.22) | (10.97) | (69.19) | (14.06) | (13164) |
| 1300 | (59.13) | (11.23) | (70.36) | (14.38) | (14599) |
| 1400 | (59.96) | (11.47) | (71.43) | (14.68) | (16058) |
| 1500 | (60.75) | (11.69) | (72.14) | (14.94) | (17535) |
| | | | | | 2579 |
| | | | | | 2598 |
| | | | | | 3692 |
| | | | | | 4900 |
| | | | | | 6198 |
| | | | | | 7560 |
| | | | | | 8976 |
| | | | | | 10440 |
| | | | | | 11940 |
| | | | | | 13453 |
| | | | | | 15012 |
| | | | | | 16601 |
| | | | | | 18214 |
| | | | | | 19860 |

* The numbers in parentheses do not include the contribution of internal rotation.

a Richards' adiabatic calorimeter with an accuracy estimated by them to be 2 to 4%. The values obtained were 0.58 cal/g°C for the liquid over the temperature range 0 to 18.5°C, and 0.47 cal/g°C for the solid over the range -40 to 0°C. Just as with the value for the heat of fusion derived from these experiments made by Maass and Hatcher, Foley and Giguère (8) believe the results to have been affected by premelting due to the presence of some water.

Heat capacity measurements were made by Foley and Giguère (8) with an ice calorimeter. For the measurements on the solid, samples of the purity described in the section on heat of fusion were used to determine the change in heat content over the temperature range -25.1 to -9.6°C. The average of two determinations gave the value for the heat capacity of the solid: 0.41 ± 0.02 cal/g°C. Using the same technique with liquid, 99.8% hydrogen peroxide, they obtained the value 0.632 ± 0.003 cal/g°C for the heat capacity of the liquid over the temperature range 0 to 25°. A slight error in the calibration of the thermometer used in the latter work was found by Morissette and Giguère. By application of a correction and by extrapolation of their results for solutions, Morissette and Giguère (73) obtained the value 0.628 cal/g°C for the heat capacity of liquid anhydrous hydrogen peroxide over the temperature range 0 to 27°C.

No measurements have yet been made of the heat capacity of hydrogen peroxide vapor. Lewis and Randall (70) chose to apply to hydrogen peroxide vapor the expression $C_p = 7.5 + 0.0042T$ which had been obtained for ammonia by measurement; this was at the time the only experimentally determined heat capacity available for a tetratomic molecule.

The heat capacity of hydrogen peroxide vapor has been calculated from molecular data as detailed in the last section. These molal heat capacities as obtained by Giguère (82) are presented in Table 23. An equation of the form:

$$C_p^{\circ}(v) = a + bT + cT^2 + dT^3 \quad (30)$$

has been fitted to these data, and in Table 24 the coefficients for this equation are given along with the coefficients obtained (84) for similar equations for water vapor and oxygen.

TABLE 24
COEFFICIENTS FOR EQUATION 30 FOR THE
MOLAL HEAT CAPACITY OF HYDROGEN PER-
OXIDE VAPOR, WATER VAPOR AND OXYGEN

| | a | 10^2b | 10^5c | 10^9d | Deviation, % | | Valid Temp. Range, °K |
|-------------------------------|-------|---------|---------|---------|--------------|------|--------------------------|
| | | | | | Ave. | Max. | |
| H ₂ O ₂ | 5.154 | 2.16 | -1.60 | 4.44 | 0.34 | 0.68 | 273 - 1500 |
| H ₂ O | 7.256 | 0.2298 | 0.0283 | 0 | 0.45 | 0.74 | 298 - 1500 |
| O ₂ | 6.148 | 0.3102 | -0.0923 | 0 | 0.24 | 0.65 | 298 - 1500 |

Heat Capacity of Hydrogen Peroxide Solutions

Direct measurements of the heat capacity of hydrogen peroxide solutions were first made by Pike and Green (85), who obtained by simple experimental procedure near 20°C the values 0.874, 0.870, 0.708 and 0.775 cal/g°C for solutions of 28.30, 30.08, 58.87 and 86.33 wt. % respectively. More refined measurements of solution heat capacity were made by Morissette and Giguère (73) using an isothermal calorimeter with diphenyl ether as the fusion substance; the results of these experiments are given in Table 25. In Table 26 are given smoothed values of the heat capacity of solutions.

These data show that the heat capacity of hydrogen peroxide water solutions varies appreciably from ideal, mole fraction average heat capacity. The deviation from the ideal is negative, that is, hydrogen peroxide solutions have a heat capacity lower than that of the average of the unmixed components. It is a consequence of this deviation that there must be a variation with temperature of the heat of solution of hydrogen peroxide. In the later section dealing with the ther-

TABLE 25

HEAT CAPACITY OF HYDROGEN PEROXIDE-WATER SOLUTIONS
BETWEEN 0 AND 26.9°C, DETERMINED BY
MORISSETTE AND GIGUÈRE (73)

| Concentration, Wt. % | Heat Capacity, cal/(g sol'n)(°C) |
|----------------------|-------------------------------------|
| 0 | 1.002 ₃ |
| 21.2 | 0.893 ₀ |
| 41.0 | 0.817 ₅ |
| 60.1 | 0.757 ₁ |
| 79.1 | 0.696 ₃ |
| 98.6 | 0.632 ₂ |

TABLE 26

HEAT CAPACITY OF HYDROGEN PEROXIDE-WATER SOLUTIONS
BETWEEN 0 AND 27°C (73)

| Concentration, Wt. % | Molecular Wt., g/(mole sol'n) | Heat Capacity, | | ΔC_{pM}^* |
|-------------------------|-------------------------------------|-------------------|----------------------|-------------------|
| | | cal/(g sol'n)(°C) | cal/(mole sol'n)(°C) | |
| 0 | 18.02 | 1.002 | 18.06 | 8.9 |
| 10 | 18.91 | 0.945 | 17.87 | 6.72 |
| 20 | 19.89 | 0.899 | 17.88 | 4.84 |
| 30 | 20.97 | 0.860 | 18.04 | 3.41 |
| 40 | 22.19 | 0.823 | 18.27 | 2.50 |
| 50 | 23.56 | 0.790 | 18.61 | 1.71 |
| 60 | 25.10 | 0.757 | 19.00 | 1.18 |
| 70 | 26.86 | 0.725 | 19.48 | 0.73 |
| 80 | 28.88 | 0.692 | 19.99 | 0.46 |
| 90 | 31.24 | 0.660 | 20.62 | 0.20 |
| 100 | 34.02 | 0.628 | 21.36 | 0.00 |

$$* \Delta C_{pM} = C_{pH_2O_2} + M C_{pH_2O} - (1 + M) C_{p_{sol'n}} \text{ (see Fig. 10)}$$

thermodynamics of mixing of hydrogen peroxide and water these heat capacity data are used in the interpretation and calculation of heats of solution. A quantity necessary in these calculations is the difference, ΔC_{p_M} , between the heat capacities of the components of the solution and the solution itself, per mole of hydrogen peroxide contained. Values of ΔC_{p_M} have been given in Table 26.

Thermodynamic Quantities in the Phase Change of Anhydrous Hydrogen Peroxide

The enthalpies of phase change for anhydrous hydrogen peroxide tabulated in Table 27 have been selected from the data presented in the earlier sections dealing with this topic. The precision of these data is not sufficient to permit any distinction between values quoted for temperatures differing only to the extent separating the freezing points of hydrogen peroxide (-0.461°C) and water.

TABLE 27

ENTHALPIES OF PHASE CHANGE OF ANHYDROUS
HYDROGEN PEROXIDE

| Equilibrium | Temperature | ΔH_{v} cal/mole | Reference |
|--------------|------------------------|--------------------------------|-----------|
| solid-vapor | -0.461°C | 15510 | (8) |
| solid-liquid | " | 2920 | " |
| liquid-vapor | " | 12593 | " |
| " " | 25 | 12334 | (73) |
| " " | 50 | 12270 | (25) |
| " " | 100 | 11710 | " |
| " " | 150 | 11260 | " |

The Thermodynamics of the Mixing of Hydrogen Peroxide and Water

The mixing or separation of hydrogen peroxide and water or the change of the composition of hydrogen peroxide solutions, either by dilution or concentration, are processes accompanied by appreciable heat effects. For the processes of mixing or dilution the effect is exothermic for all concen-

trations when carried out at a temperature above 21°C. Some dilution processes are endothermic below this temperature. The magnitude of these heat effects has been determined by direct measurement, from measurements of the heat of decomposition at various concentrations, and from measurements of the vapor pressure of solutions. The free energy and entropy changes for the mixing process have also been determined.

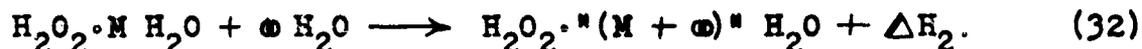
The terminology used in the discussion of these processes is sometimes confused, and it may be helpful to give exact definitions. The terms mixing and solution are applied only to the process of bringing together in solution anhydrous hydrogen peroxide and water. To the process of decreasing the concentration of a hydrogen peroxide solution by the addition of water is applied the term dilution. The heat effects* for these processes are given on a molal basis, that is, per mole of hydrogen peroxide undergoing the process, irrespective of the quantity of water involved. In this discussion hydrogen peroxide is considered to be the solute and water to be the solvent. All the values for the heat effects given here are integral quantities for finite changes of concentration of the solute, hydrogen peroxide. In the tabulation of recommended values are: a) the integral heat of solution for the process of mixing anhydrous hydrogen peroxide with water to form a given solution, and b) the heat of dilution to infinite dilution which is the heat effect for the dilution of a solution with an infinite amount of water.

These concepts may be represented by the following symbolism. The heat of solution for the case of forming a solution of infinite dilution from anhydrous hydrogen peroxide is ΔH_1 ,

* The "heat of solution" (or heat of other process) here has the same numerical value and sign as the enthalpy change of the process. Both will have a negative numerical value if heat is transferred from the system to the surroundings during the process described.



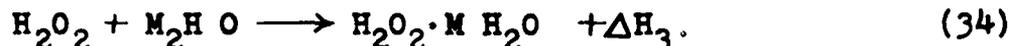
The value of ΔH may be either positive (heat absorbed) or negative (heat evolved) for certain of these processes. For the dilution of a solution containing M moles of water per mole of hydrogen peroxide to form an infinitely dilute solution the heat of dilution to infinite dilution is ΔH_2 ,



The difference between these equations yields the value:

$$\Delta H_3 = \Delta H_1 - \Delta H_2 \quad (33)$$

for the integral heat of solution for the process,



Until the appearance of the experimental determinations of the heats of dilution and heat capacities of hydrogen peroxide solutions by Morissette and Giguère (73) there existed considerable uncertainty regarding the values to be preferred among the several published heats of dilution or mixing. This uncertainty is now resolved and most of the previous recommendations can be reconciled in the light of their work. Their results were obtained by measuring the heat effect occurring in an isothermal calorimeter, using ice or diphenyl ether as the fusion substance, on diluting hydrogen peroxide of about 99 wt. % concentration. The technique was the usual one of allowing a glass tube containing one of the components to come to equilibrium while immersed in the other component in the calorimeter, the breaking of the tube serving to mix the components. Hydrogen peroxide samples of 0.6 to 5 g were used and the heat effects measured were between 8 and 34 cal. It was believed that any decomposition occasioned by the presence of the broken glass was so minor as to introduce a negligible heat effect. The experimental results obtained by Morissette and Giguère are given in Table 28.

TABLE 28

HEATS OF DILUTION OF HYDROGEN PEROXIDE SOLUTIONS
IN WATER AT 0 AND 26.9°C,*
FROM MORISSETTE AND GIGUERE (73)

| H ₂ O ₂ Concentration, wt. % | | Heat of Dilution, cal/g mole H ₂ O ₂ |
|--|-------|--|
| Initial | Final | |
| <u>At 26.9:</u> | | |
| 98.70 | 89.70 | -147.7 |
| " | 88.89 | -157.5 |
| " | 79.38 | -297.1 |
| " | 71.00 | -408.2 |
| " | 62.02 | -504.5 |
| " | 54.88 | -578.3 |
| " | 50.25 | -621.5 |
| " | 49.61 | -630.6 |
| " | 42.77 | -671.7 |
| " | 30.10 | -739.8 |
| " | 13.97 | -776.7 |
| " | 5.26 | -807.0 |
| <u>At 0°C:</u> | | |
| 98.70 | 85.97 | -195.0 |
| 99.40 | 70.22 | -417.3 |
| 99.40 | 60.50 | -515.1 |
| " | 46.27 | -593.6 |
| " | 45.92 | -597.3 |
| " | 38.07 | -669.4 |
| " | 37.24 | -669.9 |
| " | 19.69 | -671.9 |
| " | 19.05 | -671.6 |
| 24.5 | 9.34 | + 42.2 |

By graphical extrapolation it was determined from these data that the integral heat of solution of anhydrous hydrogen peroxide at 0°C to form a 99.40% solution was -10 cal/mole, to form a 98.7% solution was -21 cal/mole, and at 26.9°C to form a 98.70% solution was -22 cal/mole.

These results show that an appreciable temperature dependence exists for the heat of dilution of hydrogen peroxide solutions, as called for by the solution heat capacity data. The magnitude of this temperature dependence may be seen by reference to Figure 9 where these data are plotted as the

* See footnote on page 86.

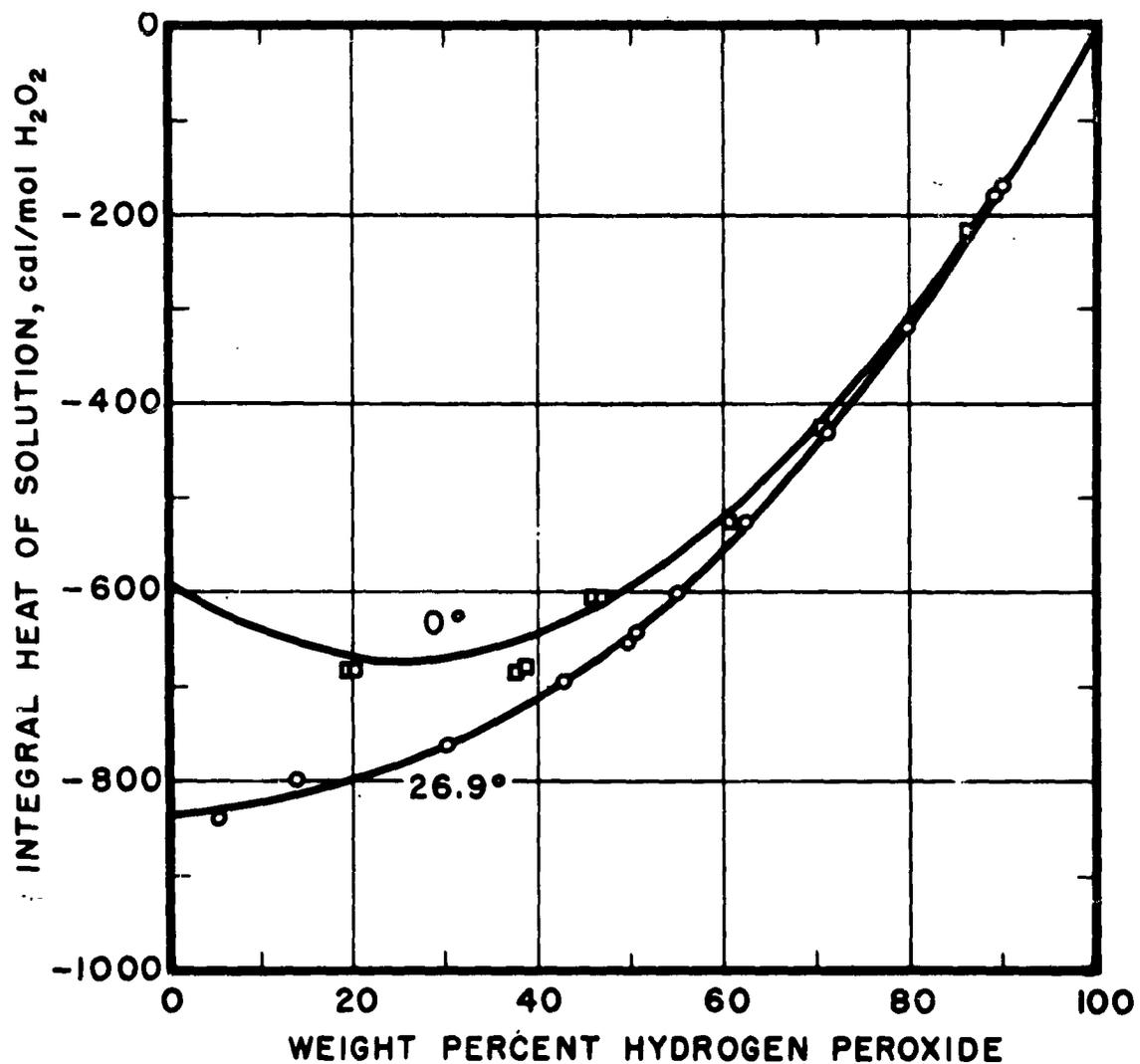


FIG. 9 - INTEGRAL HEAT OF SOLUTION OF HYDROGEN PEROXIDE, DATA OF MORISSETTE AND GIGUÈRE

integral heat of solution or mixing of anhydrous hydrogen to form a solution of the indicated composition. In Figure 9 the curve through the points at 26.9 is fitted to the data. The curve for 0°C has been calculated from these latter data and the solution heat capacities given in the last section. In addition to illustrating the temperature dependence of the heat of solution Figure 9 shows also that at lower temperatures the dilution of certain hydrogen peroxide solutions may become an endothermic process. An experimental verification of this is given by the last result shown in Table 28 where it is reported that the dilution of 24.5% hydrogen peroxide to 9.3% at 0°C required the addition of 42.2 calories per mole of contained hydrogen peroxide to maintain constant temperature.

It is recommended that the heat of dilution data at 26.9°C of Morissette and Giguère be accepted and combined with heat capacity data to establish the best values for the heat effects encountered in the mixing of hydrogen peroxide and water. The method of this combination will be outlined briefly and values given for the standard temperature of 25°C.

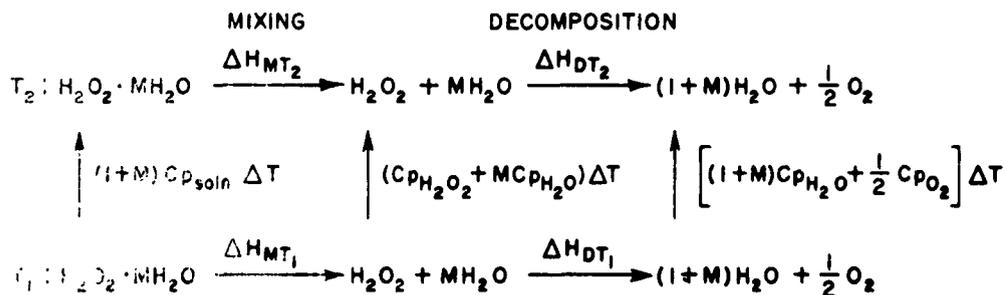


FIG. 10 - THE PROCESSES OF MIXING AND DECOMPOSITION FOR A MOLE OF HYDROGEN PEROXIDE

In Figure 10 is shown a diagram representing the processes of decomposing hydrogen peroxide and of mixing it with water. Considering only the mixing process, it is found that the difference between the heat effects upon separating hydrogen peroxide and water at two temperatures is equal to the difference between the heat capacities of the unmixed components and that of the solution multiplied by the temperature difference, i.e., $d(\Delta H_M)/dt = \Delta C_{p_M}$.

Values of ΔC_{p_M} were given in Table 26. Thus, if the integral heat of solution of hydrogen peroxide is known at temperature T_2 the integral heat of solution at T_1 is then:

$$\Delta H_{T_1} = \Delta H_{T_2} + \Delta C_{p_M}(T_2 - T_1) \quad (35)$$

In Table 29 are given the recommended integral heats of solution at 26.9°C obtained from the work of Morissette and Giguère, the integral heats of solution at 25° obtained from them by use of equation (35), and the heats of dilution to infinite dilution obtained by use of equation (33).

TABLE 29

INTEGRAL HEAT OF SOLUTION AND HEAT OF DILUTION TO INFINITE DILUTION FOR HYDROGEN PEROXIDE AND WATER*

| H ₂ O ₂ Concentration, Wt. % | Integral Heat of Solution cal/mole H ₂ O ₂ | | Heat of Dilution to Infinite Dilution, cal/mole H ₂ O ₂ , 25° |
|--|---|------|---|
| | 26.9° | 25° | |
| 0 | -834 | -817 | 0 |
| 10 | -822 | -809 | -8 |
| 20 | -799 | -790 | -27 |
| 30 | -763 | -757 | -60 |
| 40 | -711 | -706 | -111 |
| 50 | -643 | -640 | -177 |
| 60 | -551 | -549 | -268 |
| 70 | -442 | -441 | -376 |
| 80 | -312 | -311 | -506 |
| 90 | -162 | -162 | -655 |
| 100 | 0 | 0 | -817 |

* See footnote on page 86.

With an adequate basis at hand for evaluating the effect of temperature on the heat of dilution a comparison of other sources of data for this quantity may be made. In Figure 11 are plotted the values for the heat of dilution to infinite dilution obtained from the work of de Forcrand (62), Roth, Grau, and Meichsner (86), Pike and Green (85), Kubaschewski and Weber (20), and Scatchard, Kavanagh, and Ticknor (25). All these measurements were for 20°C with the exception of those of de Forcrand for 12 to 16° and those of Scatchard, Kavanagh, and Ticknor, which are without temperature specification as explained below. Not shown in Figure 11 are the data of Evans and Uri (87) (for which the conditions were not clearly specified) or the data which may be derived from heat of decomposition measurements. Heat of decomposition data are inherently less precise for this purpose and in the absence of a need for their consideration the clarity of the figure is improved without them. Reference to Figure 12 in the following section will, however, provide an estimate of the heats of dilution given by heat of decomposition data.

Since most of the above cited heat of dilution data do not extend to infinite dilution, appropriate heats of dilution to infinite dilution derived from the work of Morissette and Giguère were added to bring the data to a common basis. The agreement, with the exception of the data of de Forcrand, is seen to be good. The data of Morissette and Giguère are nevertheless depended upon solely to establish the heats of dilution since the procedure of the other workers involved adiabatic calorimetry and the use of uncertain heat capacities which did not allow proper recognition of the effect of temperature on the measurements. Previously the establishment of a recommended set of heat of dilution data had been hindered by the apparently large deviations indicated by data derived from heats of decomposition and from vapor pressure measurements, by the relatively minute heat of dilution below 30% hydrogen peroxide, and by the failure of any one set of data to extend over the entire range of composition.

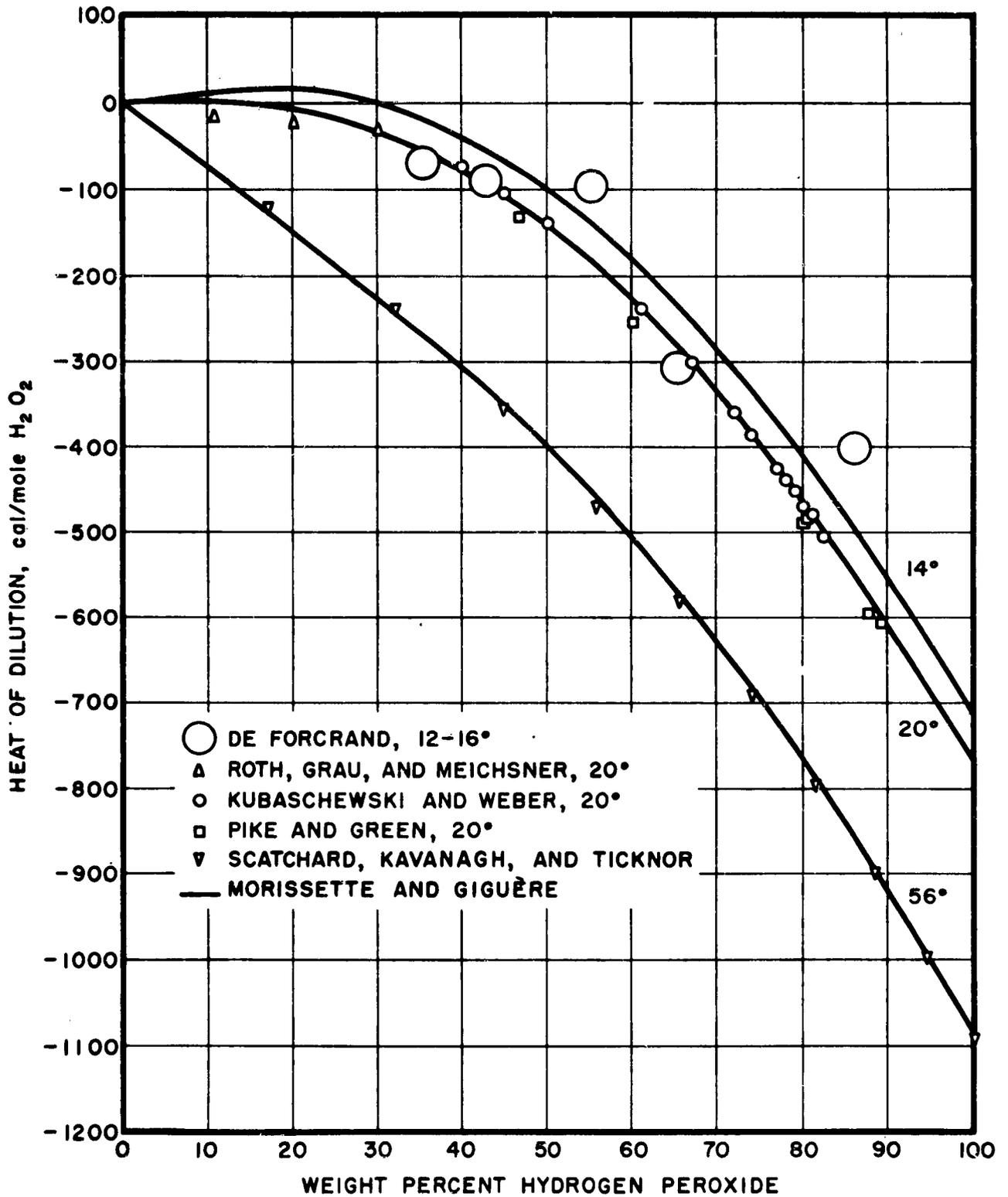


FIG. II - HEAT OF DILUTION TO INFINITE DILUTION OF INDICATED SOLUTION

Earlier evaluations of preferred heat of dilution data (and the heats of solution to infinite dilution given) were by Bichowsky and Rossini (89) (460 and 910 cal/mole), Mickley (81) (840 cal/mole), and Rossini et al. (72) (810 cal/mole). These values should now be replaced with values derived from Table 29 and containing a proper temperature correction.

The method by which the thermodynamic quantities for the enthalpy, entropy, and free energy of mixing were obtained by Scatchard, Kavanagh, and Ticknor (25) may now be outlined. In the discussion of vapor pressure there was presented equation (6) which expressed the assumed function for the excess free energy of mixing, F_X^E , of hydrogen peroxide and water. According to the relation, $S_X^E = -dF_X^E/dT$, the following equation is obtained after introduction of the constants:

$$S_X^E = -x_W(1 - x_W)(0.97) \quad (36)$$

Similarly, through the relation, $H_X^M = F_X^E + TS_X^E$, there is obtained the following equation for the excess heat of mixing per mole of solution:

$$H_X^M - x_W(1 - x_W) \left[-1017 + 85(1 - 2x_W) + 13(1 - 2x_W)^2 \right] \quad (37)$$

Since the heat effect upon mixing for an ideal solution is zero, the excess heat of mixing, H_X^M , represents the total heat effect for the process of mixing n moles of anhydrous hydrogen peroxide with $(1 - n)$ moles of water to make 1 mole of solution of x mole fraction water. The integral heat of solution to form a solution of mole fraction x_W in water is therefore $\Delta H = H_X^M/(1 - x_W)$.

Values of these thermodynamic mixing quantities as calculated by Scatchard, Kavanagh and Ticknor are given in Table 30. The deviation of these values for the free energy of mixing from the values calculated from experiments at individual temperatures had a maximum of 6 calories, and this occurred for the more con-

TABLE 30
 THERMODYNAMIC PROPERTIES FOR THE MIXING OF HYDROGEN PEROXIDE AND WATER
 FROM SCATCHARD, KAVANAGH, AND TICKNOR (25)

| Hydrogen Peroxide Concentration, mole fraction | Hydrogen Peroxide Concentration, wt. % | Excess Free En- ergy at 75°C, F^E , cal/mole | Excess En- tropy, S^E , cal/mole°C | Excess En- thalpy, H^E , cal/mole | Heat of Dilution to Infinite Dilution, cal/mole |
|--|--|--|--|---|---|
| 0.0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 17.34 | -66.5 | -0.087 | -97 | -119 |
| 0.2 | 32.07 | -116.1 | 0.155 | -170 | -239 |
| 0.3 | 44.73 | -149.3 | 0.204 | -220 | -356 |
| 0.4 | 55.73 | -166.9 | 0.233 | -248 | -469 |
| 0.5 | 65.37 | -169.8 | 0.243 | -254 | -581 |
| 0.6 | 73.90 | -158.8 | 0.233 | -240 | -689 |
| 0.7 | 81.50 | -135.1 | 0.204 | -206 | -795 |
| 0.8 | 88.31 | -99.7 | 0.155 | -154 | -897 |
| 0.9 | 94.44 | -54.2 | 0.087 | -85 | -995 |
| 1.0 | 100.00 | 0 | 0 | 0 | -1089 |

concentrated solutions having lower vapor pressures. The smoothed function for the free energy, equation (9), was also found to lie within the scatter of the individual values calculated from the vapor pressure measurements of Giguère and Maass (67). Because of uncertainty in the temperature variation of the free energy function no temperature dependence is introduced into the expressions for the entropy and enthalpy of mixing. The comparison made in Figure 11 shows that the heat of dilutions derived from vapor pressure data agree well with values obtained by extrapolation of the data of Morissette and Giguère to 56°C. This indicates that, just as with the heats of evaporation, the heats of dilution derived from the vapor pressure measurements are suited best to a temperature level near that (60 to 90°C) at which the measurements were made.

The partial molal heats of mixing have also been estimated by Giguère and Maass (67) from their vapor pressure measurements. Kubaschewski and Weber (20) utilized the activities obtained by Giguère and Maass to calculate partial molal free energies of mixing, which when combined with their measured heats of solution yielded values for the entropy of mixing. These results are not cited since it is believed that the data of Scatchard, Kavanagh, and Ticknor provide a sounder basis for evaluation of the thermodynamic mixing quantities. Although these data are recommended, it would be desirable to check and improve them by combining with them the heat of mixing data provided by Morissette and Giguère. The relation, $d(\Delta F/T)/dT = -\Delta H/T^2$, provides a means whereby the reliability of the temperature dependence of the free energy of mixing derived by Scatchard, Kavanagh and Ticknor may be reconciled with that implicit in the work of Morissette and Giguère.

Thermodynamic Quantities in the Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide according to the reaction $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ is accompanied by the evolution of heat, and a number of experimental determinations of

this heat of decomposition are available. The equilibrium for this reaction under ordinary laboratory conditions is quite favorable to the decomposition; the free energy and the equilibrium constant for the reaction have been calculated, using the measured heat of decomposition and the previously tabulated thermodynamic functions.

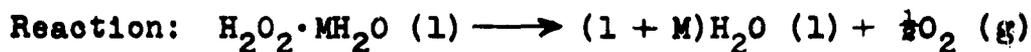
A group (89) of earlier determinations of the heat of decomposition will not be cited. These results are at some variance, and, although one or two values lie within the range of modern determinations, these early data are difficult to evaluate and probably do not conform to present-day standards of calorimetric accuracy. Similarly the value -24.3 kcal/mole for the heat of decomposition of 100% hydrogen peroxide at 1 atmosphere and 17°C obtained by Medard (90) is not in accord with the results of other measurements available. This value, computed from measurements made in a constant volume reactor, will not be considered here.

The remaining experimental values for the heat of decomposition of hydrogen peroxide at 1 atmosphere pressure have been brought to a common basis of 25°C by use of the heat capacity data (73) and are plotted in Figure 12. By reference to Figure 10 it may be seen that the difference in the heats of decomposition of a solution at two temperatures is equal to the difference in the heat capacity of the decomposition products and of the original solution multiplied by the temperature interval, i.e., $d(\Delta H_D)/dT = \Delta C_{p_D}$. Values for ΔC_{p_D} are given in Table 31.

Shown by the curve in Figure 12 and tabulated in Table 31 are values for the heat of decomposition of hydrogen peroxide solutions based on the recommended heat of solution data of the last section combined with the value, $23,560 \pm 30$ cal/mole, for the heat of decomposition of anhydrous hydrogen peroxide at 25°C taken from Morissette and Giguère (73). These values are the recommended ones; the justification for their selection is outlined in the following discussion of the experimental data.

TABLE 31

HEAT OF DECOMPOSITION
OF HYDROGEN PEROXIDE SOLUTIONS AT 25°C AND 1 ATMOSPHERE*
FROM MORISSETTE AND GIGUÈRE (73)



| Concentration, Wt. % H_2O_2 | Moles H_2O per mole H_2O_2 , M | Heat of Decomposition, cal/g mole H_2O_2 | C_{pD} * |
|--|---|--|------------|
| 0 | ∞ | -22,74 ₃ ± 30 | 9.1 |
| 10 | 16.98 | -22,75 ₁ | 6.90 |
| 20 | 7.55 | -22,77 ₁ | 5.02 |
| 30 | 4.40 | -22,80 ₄ | 3.59 |
| 40 | 2.83 | -22,85 ₄ | 2.68 |
| 50 | 1.89 | -22,92 ₁ | 1.89 |
| 60 | 1.26 | -23,01 ₂ | 1.36 |
| 70 | 0.809 | -23,12 ₀ | 0.91 |
| 80 | 0.472 | -23,24 ₉ | 0.64 |
| 90 | 0.210 | -23,39 ₉ | 0.38 |
| 100 | 0 | -23,56 ₀ | 0.18 |

$$* C_{pD} = (1 + M) C_{p\text{H}_2\text{O}} + \frac{1}{2}C_{p\text{O}_2} - (1 + M) C_{p\text{sol'n}} \quad (\text{See Figure 10})$$

Matheson and Maass (9) used an adiabatic calorimeter to determine the heat of decomposition of 10 g samples of hydrogen peroxide solution. Manganese dioxide was used as a decomposition catalyst, and it was stated that the decomposition terminated abruptly; no correction for residual hydrogen peroxide was made. A water vapor correction was made, but a part of the calorimeter equivalent was calculated. By linear extrapolation of the heat of dilution given by the average of four determinations, two each at 38.05 and 97.15 wt. %, the heat of decomposition of anhydrous hydrogen peroxide was computed to be -23,450 cal/mole.

* See footnote on page 86.

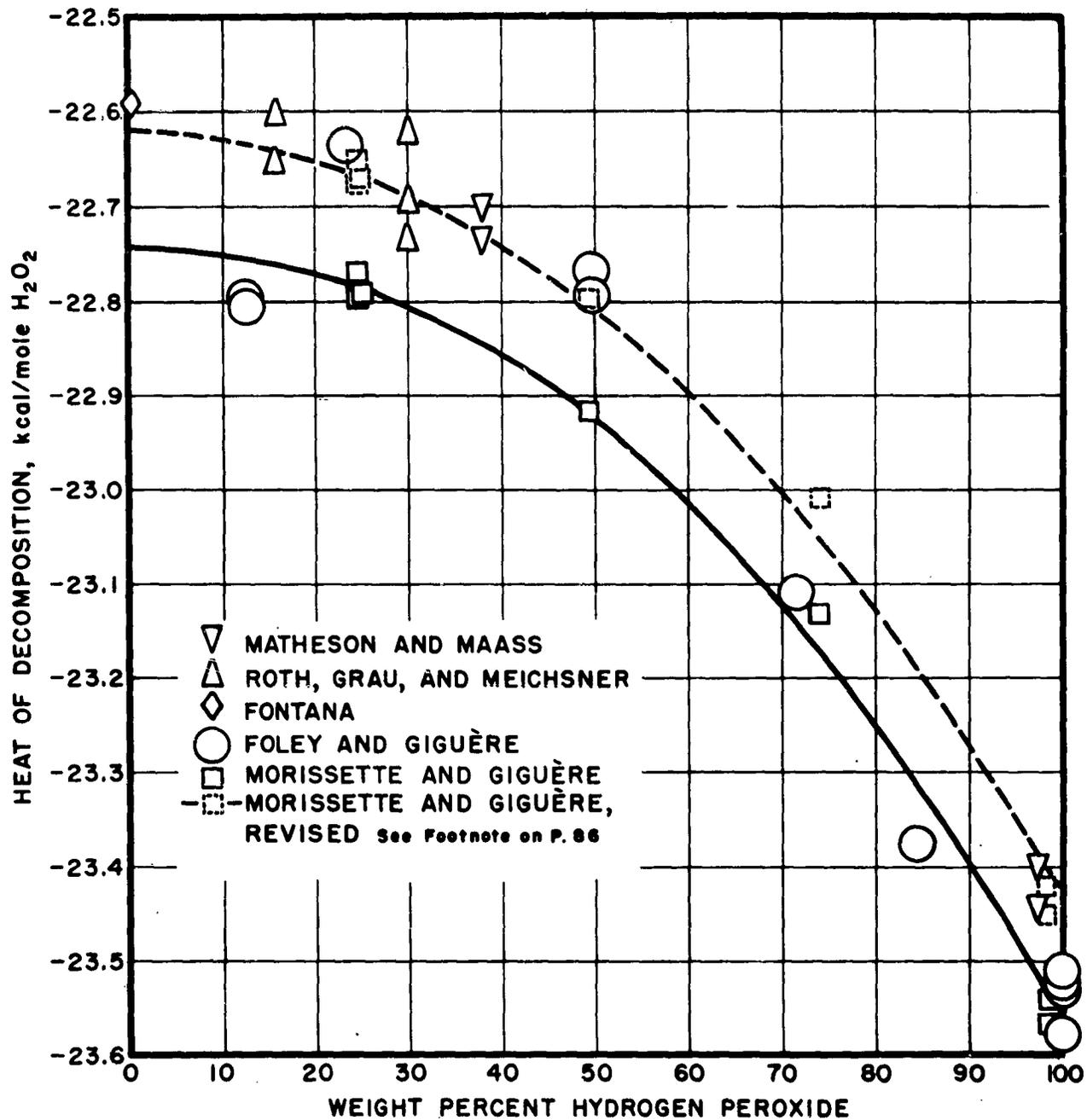


FIG. 12—THE HEAT OF DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS AT 25°C AND 1 ATM. REACTION: $H_2O_2 \cdot MH_2O(l) \rightarrow (1+M)H_2O(l) + 1/2 O_2(g)$

Roth, Grau, and Meichsner (86) used the same procedure as that of Matheson and Maass, only calibrating their calorimeter by electrical heating of the decomposition residue. Combining their data with that of Matheson and Maass, Roth, Grau, and Meichsner extrapolated to find the heat of decomposition of anhydrous hydrogen peroxide to be $-23,480$ cal/mole and of infinitely dilute hydrogen peroxide to be $-22,650$ cal/mole.

Fontana (91) measured the heat of decomposition of a quite dilute hydrogen peroxide solution ($H_2O_2 \cdot 8880 H_2O$). The calorimeter was electrically calibrated, about 2 g manganese dioxide were used as catalyst, and nitrogen was bubbled through the solution in the calorimeter at the rate of 125 cc/min to avoid uncertainty regarding the final state of the evolved oxygen. Appreciable differences in the results of trial measurements of the heat of dissolution of solid magnesium in hydrochloric acid had indicated that desirability of operating with the inert gas sweep of the solution. A correction of about 10 cal was applied by Fontana to his results to correct for decomposition occurring between the time of solution analysis and the calorimetric determination. Fontana obtained as the average of three determinations the value $-22,590 \pm 20$ cal/mole and considered this confirmation of the data of Roth, Grau and Meichsner.

The measurements of Foley and Giguère (8) were made with ca. 1 g samples in an ice calorimeter over the concentration range 12 - 100%. A length of platinized platinum wire was used to catalyze the decomposition over periods of 3 - 10 hours. The rapid reaction encountered at the beginning of an experiment was tempered by successively dipping and removing the catalyst wire from the solution until the reaction became less vigorous in the diluted solution. As the decomposition neared completion, the rate became irregular, ending in irregular periods of activity. Decomposition was not complete in these experiments, the unreacted hydrogen peroxide amounting to as much as 10% of the sample in some runs. The choice of the method of correcting for this rested on the decision as to the state of the remain-

ing hydrogen peroxide, that is, whether present as droplets of relatively concentrated hydrogen peroxide sprayed on the wall or as a residual solution of dilute composition. Foley and Giguère believed the total heat effect measured to be the sum of the heat of decomposition of the reacted portion and the heat of dilution from the original concentration of the unreacted portion; this correction ranged from zero to 96 cal/mole.

The isothermal diphenyl ether calorimeter was used by Morissette and Giguère (73) to obtain the heat of decomposition of 24.6 to 98.6 wt. % solutions at 26.9°C. A colloidal suspension of platinum was used as catalyst, small portions of this suspension being added to the calorimeter from time to time to maintain a steady, but slow rate of decomposition. Decomposition of the 0.7 to 1.8 g samples proceeded to completion over periods of about 2 to 4 hours; individual results obtained are given in Table 32.

TABLE 32
HEAT OF DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS,
EXPERIMENTAL VALUES AT 26.9°C*
FROM MORISSETTE AND GIGUÈRE (73)

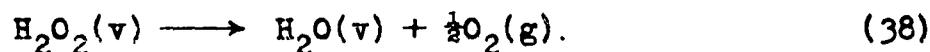
| H ₂ O ₂ Conc., Wt. % | Heat of Decomp., kcal/mole H ₂ O ₂ | Integral Heat of Solution, cal/mole | Heat of Decomp., of 100% H ₂ O ₂ , cal/mole |
|---|---|--|--|
| 24.64 | -22.78 ₆ | -784 | -23.57 ₀ |
| 24.72 | -22.76 ₂ | -784 | -23.54 ₆ |
| 25.10 | -22.78 ₄ | -783 | -23.56 ₇ |
| 49.58 | -22.91 ₄ | -647 | -23.56 ₁ |
| 74.23 | -23.12 ₉ | -390 | -23.51 ₉ |
| 98.52 | -23.56 ₇ | -25 | -23.59 ₂ |
| 98.62 | -23.54 ₁ | -24 | -23.56 ₅ |

mean -23.56₀ ± 0.03

* More recent evidence indicates that the calibration factor of the isothermal diphenyl ether calorimeter used in this work (73) was too high by 0.5%. Revision of the values quoted in this chapter would change the integral heat of solution for the formation of a 0 wt. % hydrogen peroxide solution from 834 cal/mole to 830 cal/mole and the heat of decomposition of anhydrous hydrogen peroxide from 23.56 kcal/mole to 23.44 kcal/mole. It was not possible to incorporate this change here, and the thermodynamic quantities presented are everywhere consistent with the higher values described in the text.

It may be seen from this discussion that several desirable features were included in the work of Morissette and Giguère, whereas one or another of these was lacking in earlier work. The use of an isothermal calorimeter avoids uncertainty regarding the exact temperature at which the reaction was conducted and requires no knowledge of heat capacity. A dilute, homogeneous catalyst insures slow, but complete decomposition, leaving no doubt regarding final concentration. The use of relatively concentrated hydrogen peroxide is also preferred, since at low concentrations uncertainties in concentration introduce relatively large errors.

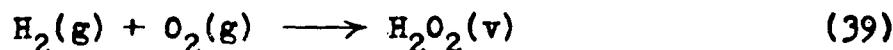
Having established a preferred value for the heat of decomposition of hydrogen peroxide, this datum may be combined with (a) the thermodynamic functions for hydrogen peroxide given in Table 23, (b) the thermodynamic functions for water vapor and oxygen given by Rossini *et al.* (72) (Series III), and (c) the value of 12,334 cal/mole for the heat of vaporization of anhydrous hydrogen peroxide to obtain values for the heat and free energy as a function of temperature for the reaction,



These values are given in Table 33. The values shown in Table 33 differ slightly from those published by Giguère (82) because of the adoption of more recent values for the heats of decomposition and vaporization.

Thermodynamic Quantities in the Formation of Hydrogen Peroxide

The heat, free energy, and equilibrium constant for the formation of hydrogen peroxide from the elements according to the reaction,



may be calculated in a fashion similar to that used in the last section. These quantities are tabulated in Table 34 and are based on the following: (a) heat of decomposition of liquid, anhydrous hydrogen peroxide at 25°C: 23,560 cal/mole; (b) heat

TABLE 33

HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT
FOR THE DECOMPOSITION OF
HYDROGEN PEROXIDE VAPOR

| Temp., °K | ΔH° , kcal/mole | ΔF° , kcal/mole | log K |
|-----------|------------------------------|------------------------------|-------|
| 0 | -26.17 | -26.17 | -- |
| 298.16 | -25.35 | -29.93 | 21.93 |
| 300 | -25.34 | -29.97 | 21.83 |
| 400 | -25.27 | -31.47 | 17.19 |
| 500 | -25.28 | -33.09 | 14.46 |
| 600 | -25.35 | -34.65 | 12.62 |
| 700 | -25.43 | -36.18 | 11.28 |
| 800 | -25.53 | -37.71 | 10.21 |
| 900 | -25.64 | -39.23 | 9.52 |
| 1000 | -25.75 | -40.72 | 8.90 |
| 1100 | -25.85 | -42.22 | 8.38 |
| 1200 | -25.96 | -43.71 | 7.96 |
| 1300 | -26.07 | -45.15 | 7.58 |
| 1400 | -26.18 | -46.64 | 7.28 |
| 1500 | -26.29 | -48.10 | 7.00 |

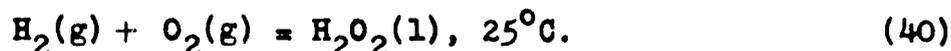
TABLE 34

HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT
FOR THE FORMATION OF HYDROGEN PEROXIDE VAPOR

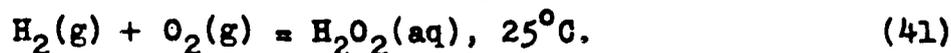
| Temp., °K | ΔH° , kcal/mole | ΔF° , kcal/mole | log K |
|-----------|------------------------------|------------------------------|-------|
| 0 | -30.94 | -30.94 | -- |
| 298.16 | -32.45 | -24.70 | 18.02 |
| 300 | -32.46 | -24.65 | 17.95 |
| 400 | -32.77 | -21.99 | 12.01 |
| 500 | -32.99 | -19.27 | 8.42 |
| 600 | -33.15 | -16.50 | 6.00 |
| 700 | -33.27 | -13.72 | 4.28 |
| 800 | -33.36 | -10.93 | 2.98 |
| 900 | -33.42 | -8.12 | 1.97 |
| 1000 | -33.46 | -5.31 | 1.16 |
| 1100 | -33.51 | -2.47 | 0.49 |
| 1200 | -33.54 | 0.35 | -0.06 |
| 1300 | -33.55 | 3.15 | -0.53 |
| 1400 | -33.56 | 6.00 | -0.94 |
| 1500 | -33.55 | 8.84 | -1.29 |

of vaporization of anhydrous hydrogen peroxide at 25°C: 12,334 cal/mole; (c) heat of formation of water vapor at 25°C (72): -57,798 cal/mole; (d) thermodynamic functions of hydrogen peroxide: Table 23; (e) thermodynamic functions of hydrogen and oxygen: Rossini, *et al.* (72) (Series III). The values shown in Table 34 differ slightly from those published by Giguère (82) because of the adoption of more recent values for the heats of decomposition and vaporization.

These values for the free energy of formation of hydrogen peroxide vapor also may be utilized to calculate the standard free energy of formation of hydrogen peroxide in the liquid phase--as anhydrous hydrogen peroxide and at unit molal activity in solution at 25°C. For the condensation of hydrogen peroxide vapor at 25°C, the free energy is calculated to be -3,530 cal/mole through use of the value for the vapor pressure of 1.95 mm Hg at 25°C in the relation, $\Delta F = -RT \ln (p_{H_2O_2}/760)$. Combining this with the free energy of formation of hydrogen peroxide vapor at 25°C from Table 34, the value, $\Delta F^\circ = -27,930$ cal/mole is obtained for the reaction:



Again making use of the vapor pressure data, the molal activity of anhydrous hydrogen peroxide as solute is calculated to be 214.1 (See Table, Chapter 7). The free energy of solution of anhydrous hydrogen peroxide to form a solution of unit activity at 25°C is then $\Delta F = -RT \ln(214.1/1) = -3,180$ cal/mole. This result may be combined with that for reaction (40) to obtain the value, $\Delta F^\circ = -31,110$ cal/mole for the reaction:



Although the values just calculated are based upon much more reliable data, they can be considered only a confirmation of the values given by Latimer (92), which were derived by Lewis and Randall (70) from fragmentary data. For example, Latimer gives for reaction (40), $\Delta F^\circ = -28,230$ cal/mole, and

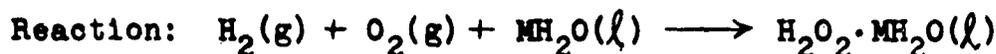
90.

for reaction (41), $\Delta F^{\circ} = -31,470$ cal/mole.

Table 35 has been prepared in the same fashion and gives the heat and free energy of formation of hydrogen peroxide in the solution phase as a function of concentration.

TABLE 35

HEAT AND FREE ENERGY OF FORMATION OF
HYDROGEN PEROXIDE IN SOLUTION AT 25°C



| Concentration Wt. % H_2O_2 | Heat of Formation ΔH° , cal/mole H_2O_2 | Free Energy of Formation ΔF° , cal/mole H_2O_2 |
|---|---|---|
| 0 | -45,600 | -- |
| 10 | -45,590 | -30,340 |
| 20 | -45,570 | -29,800 |
| 30 | -45,540 | -29,430 |
| 40 | -45,490 | -29,130 |
| 50 | -45,420 | -28,860 |
| 60 | -45,330 | -28,630 |
| 70 | -45,220 | -28,410 |
| 80 | -45,090 | -28,220 |
| 90 | -44,940 | -28,060 |
| 100 | -44,780 | -27,930 |

The Standard Electrode Potentials of Hydrogen Peroxide

The free energies of formation obtained in the last section may be used to calculate directly the electrode potentials of hydrogen peroxide. For the hydrogen peroxide-oxygen couple:



the standard (92) electrode potential, E° , is calculated to be -0.675 volts by substitution of the free energy of formation of hydrogen peroxide at unit molality of -31,120 cal/mole into the relation $\Delta F = nFE$.

By the addition of the equation for reaction (41) to the equation for the water-oxygen couple (92):



there is obtained the value $E^\circ = -1.78$ for the water-hydrogen peroxide couple:



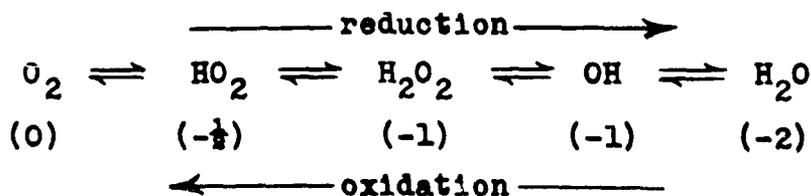
Just as with the values for the free energy of formation from which they were obtained, these electrode potentials* must be considered to constitute confirmation of those derived by Lewis and Randall (70), which have been long in use.

The electrode potentials given above are for the standard condition of unit molal acid solution. The value, $\Delta F^\circ = -15,230$ cal/mole, for the free energy of formation of perhydroxyl ion, O_2H^- , may be borrowed from the following section on dissociation and with this the electrode potentials in unit molal base solution may be calculated:



A useful diagram of the electrode potential of hydrogen peroxide as a function of concentration and pH has been published by Delahay, Pourbaix, and Van Rysselberghe (93).

* It will be recalled that hydrogen peroxide contains oxygen in a state of oxidation midway between that exhibited in molecular oxygen and water as indicated in the diagram:



Thus the hydrogen peroxide-oxygen couple (reaction (42)) may be regarded as the oxidation of hydrogen peroxide if equation (42) is read from left to right or as the reduction of oxygen if read from right to left. This ambiguity is further confused by regarding reaction (42) when going from left to right as repre-

A number of experiments have been undertaken with the aims of measuring the electrode potentials of hydrogen peroxide directly and establishing the exact reactions which are responsible for the potential (94). Much of this work has been concerned with study of the effect of the nature of the electrode and the history of its surface treatment on the potential assumed in hydrogen peroxide solution. The effects of the variation of the concentration of hydrogen peroxide and hydrogen ion and of the presence of additives have also been studied. The least ambiguous of these studies is perhaps that of Bornemann (95). Bornemann took as a hypothesis that the most positive potential with respect to the oxygen electrode (i.e., reaction (43)) which could be measured in hydrogen peroxide and which obeyed the proper concentration dependence would represent the nearest possible approach to the value of the potential of the hydrogen peroxide-oxygen couple (i.e., reaction (42)). The most suitable electrode was found to be platinum, and a procedure of chemical and electrolytic pretreatment was developed which gave, through alteration of the catalytic activity of the surface, the most positive and reproducible static potential in dilute hydrogen peroxide solutions of unit normal acidity. The results of this work gave a potential of -0.69 volts by extrapolation to a hydrogen peroxide concentra-

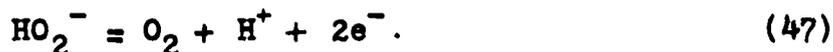
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 representing the "reduction potential" of hydrogen peroxide because there must be a concomitant reduction of some substrate as reaction (42) proceeds left to right.

Likewise, the water-hydrogen peroxide couple (reaction (44)) may be regarded as the oxidation of water if read left to right, as the reduction of hydrogen peroxide if read right to left, and as the "oxidation potential" of hydrogen peroxide if read right to left with regard to the action of the hydrogen peroxide upon some reactant.

All these usages will be found in the literature according to the habits of or emphasis intended by the various authors. Reference to the "hydrogen peroxide-oxygen couple" or the "water-hydrogen peroxide couple" probably introduces the least confusion, but it may be necessary to use one of the other designations to indicate the direction of the reaction. The direction in which the half-cell reactions are written and the signs attached to the potentials are established by convention; that of Latimer (92) is used here.

tion of one molar. Bornemann combined with this the value, -0.63 volts, determined earlier to be the potential of formation of hydrogen peroxide on an oxygen saturated electrode to obtain the average value, $E^{\circ} = -0.66 \pm 0.03$ volts, for the potential of the hydrogen peroxide-oxygen couple. By addition of reaction (43) he obtained $E^{\circ} = -1.80$ volts for the potential of the water-hydrogen peroxide couple. In the light of the experimental difficulties this result appears to be a considerable achievement.

The potential of the hydrogen peroxide-oxygen couple in basic solution was measured by Berl (96). A porous carbon electrode through which oxygen was bubbled was found to attain a standard potential, $E_B^{\circ} = 0.0416$ volts, corresponding to reaction (45), for which the value, $E_B^{\circ} = 0.084$ volts, was calculated above. This appears to constitute a reasonable confirmation. Berl determined that the reacting entity was in fact perhydroxyl ion, O_2H^- , and that the cell was truly reversible. These results were confirmed by Hickling and Wilson (97) in the course of a study of the anodic decomposition of hydrogen peroxide on several electrode materials. They prefer to write the reaction as:



A discussion of the individual steps resulting in reaction (47) and of the significance of this reaction in the phenomenon of oxygen overvoltage was given by Hickling and Wilson (97) and by Hickling (98).

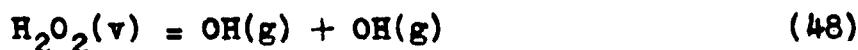
It was found by Kalousek (99) that the hydrogen peroxide-oxygen couple was reversible on a mercury electrode in acid, basic, or neutral solution. Novak and Heyrovsky (100) found that the potential of reduction of oxygen to hydrogen peroxide was unchanged in heavy water solution, but that the potential for the reduction of hydrogen peroxide to water was changed in heavy water to the same extent that the hydrogen overvoltage changed. There is no evidence to suggest that the

reduction of hydrogen peroxide (i.e., reaction (44)) occurs in any but an irreversible manner. Additional discussion of electrode processes involving hydrogen peroxide is given in Chapter 2 on Formation and Chapter 8 on Decomposition Processes.

Thermodynamic Quantities in the Dissociation of Hydrogen Peroxide

A number of monomolecular reactions of hydrogen peroxide are grouped together under the heading of dissociation. Not included under this heading are the dissociation into molecular hydrogen and oxygen, which has been discussed in the section on formation, or the decomposition, a term reserved for the reaction of hydrogen peroxide to form water and molecular oxygen. One particular distinction between these dissociation reactions and decomposition lies in the fact that hydrogen peroxide can be in equilibrium with only small concentrations of its dissociation products.

The heat, free energy and equilibrium constant for the reaction,



are given in Table 36. The values shown in Table 36 differ slightly from those published by Giguère (82) because of the adoption of more recent values for the heats of decomposition and vaporization of hydrogen peroxide.

Four other non-ionic dissociation reactions may be written for which thermodynamic quantities may be calculated (72) with considerable certainty. These reactions and their heats and free energies at 25° are:

| | ΔH° | ΔF° (kcal/mole) | |
|--|------------------|------------------------------|------|
| $\text{H}_2\text{O}_2(\text{v}) = \text{H}_2\text{O}(\text{v}) + \text{O}(\text{g})$ | + 33.81 | + 25.06 | (49) |
| $\text{H}_2\text{O}_2(\text{v}) = 2\text{H}(\text{g}) + \text{O}_2(\text{g})$ | + 136.63 | + 121.84 | (50) |
| $\text{H}_2\text{O}_2(\text{v}) = \text{H}_2(\text{g}) + 2 \text{O}(\text{g})$ | + 150.77 | + 134.68 | (51) |
| $\text{H}_2\text{O}_2(\text{v}) = 2\text{H}(\text{g}) + 2 \text{O}(\text{g})$ | + 254.95 | + 231.82 | (52) |

TABLE 36

HEAT, FREE ENERGY, AND EQUILIBRIUM CONSTANT
FOR THE DISSOCIATION OF HYDROGEN PEROXIDE INTO HYDROXYLS

| Temp., °K | ΔH° , kcal/mole | ΔF° , kcal/mole | log K |
|-----------|------------------------------|------------------------------|--------|
| 0 | 50.9 | 50.9 | -- |
| 298.16 | 52.57 | 42.56 | -31.19 |
| 300 | 52.59 | 42.51 | -30.96 |
| 400 | 52.91 | 39.18 | -21.40 |
| 500 | 53.11 | 35.60 | -15.56 |
| 600 | 53.22 | 32.08 | -11.67 |
| 700 | 53.28 | 28.56 | -8.91 |
| 800 | 53.29 | 25.03 | -6.83 |
| 900 | 53.26 | 21.50 | -5.22 |
| 1000 | 53.21 | 17.97 | -3.92 |
| 1100 | 53.17 | 14.43 | -2.87 |
| 1200 | 53.12 | 10.91 | -1.99 |
| 1300 | 53.05 | 7.42 | -1.25 |
| 1400 | 52.98 | 3.89 | -0.60 |
| 1500 | 52.90 | 0.37 | -0.05 |

Formally, to complete the list of possible non-ionic dissociation reactions there remains the reaction:



Only an estimate can be given for the heat of this reaction, since it involves knowledge of the thermodynamic properties of the perhydroxyl radical. The sum of the heats of reaction (53) and the reaction,



must be 137 kcal/mole according to the value obtained for the heat of reaction (50). As a first approximation it might be assumed, as Urey, Dawsey and Rice (101) did, that the heat effect for the abstraction of a hydrogen atom from both hydrogen peroxide and perhydroxyl radical is the same, leading to an estimate of 68 kcal/mole for the heats of reactions (53) and (54). However, just as with water, it seems likely that the abstraction of the first hydrogen from hydrogen peroxide may well require more energy than is required for the removal of the second.

In Table 37 are given the values cited for these dissociations. The values suggested by Walsh (102) on the basis of theoretical reasoning have received the least support. At the other extreme in magnitude are the values of Evans, Hush and Uri (105) derived by an interesting procedure which will not be described here. None of the intermediate values (103) appears to have

TABLE 37

VALUES REPORTED FOR HEATS OF
H₂O₂ AND HO₂ DISSOCIATION

| Reference | Heat of Dissociation kcal/mole | |
|------------------------------|---|---------------------------------|
| | H ₂ O ₂ , reaction (53) | HO ₂ , reaction (54) |
| Urey, Dawsey, and Rice (101) | 68 | 68 |
| Walsh (102) | 66 - 76 | 70 - 60 |
| Several Estimates (103) | 86 - 96 | 50 - 40 |
| Robertson (104) | 90 | 46 |
| Evans, Hush, and Uri (105) | 102 | 36 |

been derived on a more certain basis (those given by Heitler (103) are said to have been obtained by experiment, but no details are given). Robertson (104) obtained a measure of the heat of dissociation of reaction (53) through electron impact experiments, giving as an upper limit the value 90 kcal/mole. There remains considerable uncertainty in this value, but it will be accepted here along with the concomitant value of 46 kcal/mole for reaction (54). Further experiment to establish these values more accurately would be highly desirable.

Among the various possible ionic dissociation reactions of hydrogen peroxide the most important is the acid dissociation according to the reaction:



A discussion of this reaction is given in Chapter 7, Chemical Properties, where the results of Evans and Uri (106) are taken

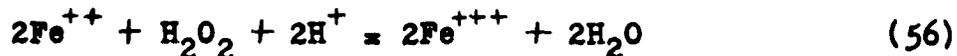
to establish the equilibrium constant and heat of this reaction. At 25°, $K = (H^+)(O_2H^-)/(H_2O_2) = 2.24 \times 10^{-12}$, $\Delta H^\circ = +8.2$ kcal/mole, and $\Delta F^\circ = +15.89$ kcal/mole. From these data the free energy of formation of perhydroxyl ion, O_2H^- , in solution at unit molality at 25°C is calculated to be -15.23 kcal/mole.

The dissociation of hydrogen peroxide vapor under electron impact to form the ions $H_2O_2^+$, H_2O^+ , HO_2^+ , OH^+ , O_2^+ and O^+ has been studied by Robertson (104). It was shown that H_2O^+ , O_2^+ , and O^+ ions appeared in the experiments only through the ionization of water and oxygen present because of decomposition of the hydrogen peroxide. The relative intensities of the ions $H_2O_2^+$, HO_2^+ , and OH^+ were 100, 10, and 20; their appearance potentials were 12.1, 16.1, and 16.0 electron volts, respectively.

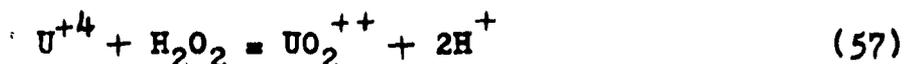
A number of reaction schemes in which hydrogen peroxide participates require knowledge of thermodynamic quantities for the dissociation of hydroxyl and perhydroxyl radicals derived from the dissociation of hydrogen peroxide. Calculations and estimates of the thermodynamic properties of these radicals and their dissociation products are given by Latimer (92), Evans, Hush and Uri (105), and Uri (107). The free energies of formation of the species OH , O_2H , and O_2^- in aqueous solution are given by Latimer as +8.53, +3.0 and +13.0 kcal/mole, respectively.

Thermodynamic Quantities in the Reaction of Hydrogen Peroxide

Aside from the possibility of calculating the thermodynamic quantities for reactions involving hydrogen peroxide through use of the above data and standard thermodynamic data (72, 92), there exist a number of direct measurements and tabulations of measured or calculated values. The heat of the reaction,



was measured to be -65.5 ± 2 kcal by Evans, Baxendale, and Uri (108) and to be -71.78 ± 0.12 kcal by Fontana (91). The heat of the reaction:



was measured to be -58.00 ± 0.02 kcal by Fontana (91). The calculated thermodynamic quantities for a number of reactions have been tabulated by Evans, Hush, and Uri (105) and Uri (107).

THE ELECTRICAL PROPERTIES OF HYDROGEN PEROXIDE

Conductivity

Since hydrogen peroxide is a very weak electrolyte, the electrical conductivity of its solutions in water approaches that of water alone, and the measurement of this property is complicated by the necessity for excluding traces of impurities. Like water too, hydrogen peroxide is an excellent ionizing solvent. The reactivity of hydrogen peroxide introduces a restriction on the metals which may be used for electrodes for conductivity measurements; block tin appears to be the practical choice for this purpose. Commercial solutions of hydrogen peroxide are nevertheless available which possess a conductivity comparable to that of ordinary distilled water, e.g., 10^{-5} ohm⁻¹ or less, and by careful distillation of such solutions, material may be obtained which yields conductivities very near to that which must be ultimately obtainable.

Calvert (109) measured the specific conductance of a 4.5% solution to be 2.89×10^{-8} ohm⁻¹, using platinum electrodes, in the course of his dielectric constant measurements. From later measurements of the conductivity of solutions of alkali hydroxides neutralized with hydrogen peroxide, using tinned electrodes at 25°C, Calvert (110) determined the equivalent ionic conductance of perhydroxyl ion, O_2H^- , at infinite dilution to be 48.5 (ohm equivalent)⁻¹. Although this value probably warrants redetermination, it indicates that the equivalent conductance of hydrogen peroxide at infinite dilution is about 400 (ohm equivalent)⁻¹. Joyner (111) found much larger conductances, about 10^{-5} ohm⁻¹, on tinned electrodes for 20 - 30 wt. % solutions at 25°, in an attempt to measure the dissociation constant of hydrogen peroxide. The

specific conductance of essentially anhydrous hydrogen peroxide was first measured by Cuthbertson and Maass (112), using tin electrodes and direct current, to be about $2 \times 10^{-6} \text{ ohm}^{-1}$, apparently at 0°C . Values for the conductivity of highly purified hydrogen peroxide-water solutions over the entire concentration range were published by Schumb (113). These measurements were made at 25°C and 1000 cycles in a cell with tin electrodes (cell constant 0.08037) and closed to the atmosphere, using water of specific conductance $5 \times 10^{-7} \text{ ohm}^{-1}$ to dilute 98.5 wt. % hydrogen peroxide of specific conductance $8.2 \times 10^{-7} \text{ ohm}^{-1}$. The results of this work are plotted in Figure 13, showing the maximum conductance of $5.8 \times 10^{-6} \text{ ohm}^{-1}$ occurring for 50 wt. % hydrogen peroxide. Gross and Taylor (114), in the course of their measurements of dielectric constant, using a cell with electropolished stainless steel electrodes and hydrogen peroxide in equilibrium with the air, confirmed Schumb's results, finding only a slightly lower conductance of $4 \times 10^{-7} \text{ ohm}^{-1}$ for their most concentrated solution (99.2%).

The shape of the curve in Figure 13 is found to be maintained for solutions of lesser purity and thus of higher conductance until values of the order of 10^{-5} ohm^{-1} are attained. When the conductance rises above this level the conductance is generally found to increase continuously as measurements are made on successive dilutions of concentrated hydrogen peroxide. This is interpreted to be due to gradual assumption of the control of the shape of the conductance curve by impurities, presumably, although not necessarily, added in increasing quantity as the successive dilutions are made. At the lower conductances it is assumed that the shape of the curve is determined by the varying concentrations and state of the dissociation products of water and hydrogen peroxide. The effect of specific additives upon the conductance of hydrogen peroxide solutions has been considered in work referred to in the later section dealing with the properties of multicomponent systems containing hydrogen peroxide.

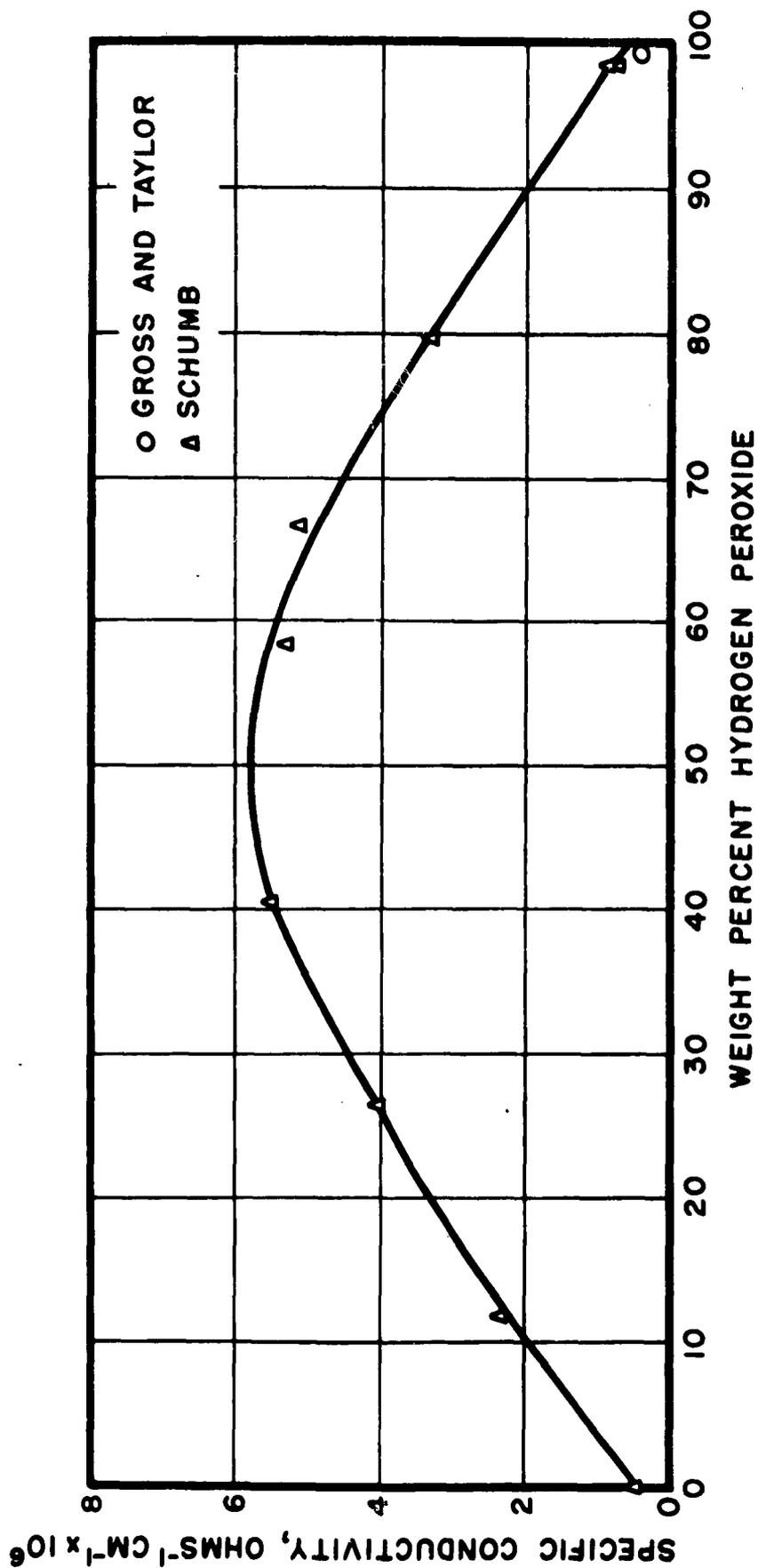


FIG. 13—SPECIFIC CONDUCTIVITY OF HYDROGEN PEROXIDE—WATER SOLUTIONS AT 25°C

The use of tin electrodes for the measurement of the conductance of hydrogen peroxide solutions at 0°C was found by Young (115) to lead to unreasonably low values. It was also found that tin electrodes gave values about 7% higher than electropolished stainless steel electrodes. These effects were not investigated. The addition of alkali to make 90% hydrogen peroxide about 0.0015 N in sodium hydroxide before distillation was found to be an effective method of decreasing conductance to the magnitude reported by Schumb. In the work of Gross and Taylor the distillation of alkaline hydrogen peroxide to prepare the solutions studied was conducted by quiet evaporation without ebullition to avoid contamination by entrainment.* It is probable that a possible closer approach to ultimate purity will not yield hydrogen peroxide of appreciably lower conductance than that demonstrated in Figure 13:

Dielectric Constant

Early evaluations of the dielectric constant of hydrogen peroxide solutions are confined to the measurements by Dewar and Fleming (116) on frozen 6 wt. % hydrogen peroxide and 5% sodium peroxide solutions at liquid air temperature and the measurement of Calvert (109), who found the dielectric constant of 37 wt. % hydrogen peroxide to be 84.7 at 18°C and by a doubtful extrapolation gave 92.8 for anhydrous hydrogen peroxide. Guthbertson and Maass (112) measured the dielectric constant at 0°C by a resonance method over the entire range of solution compositions, discovering that a maximum value of 120 existed for 35 wt. % hydrogen peroxide with values of 84.4 and 89.2 for water and anhydrous hydrogen peroxide, respectively. In answer to objections, Linton and Maass (117) reinvestigated the technique used and, on the basis of improvements, recommended revision of the value for the dielectric constant of anhydrous hydrogen peroxide to 93.5. Later measurements by Linton and Maass (118) of the dielectric constant of hydrogen peroxide-ether mixtures yielded the values 93.7 and 91 for the dielectric constant at 0°C of 100 wt. % hydrogen peroxide, confirming the previous work.

*Roth and Shanley (Ind. Eng. Chem., 45, 2343 (1953)) recently reported a conductance of 3.9×10^{-7} ohm⁻¹ in 99.9% hydrogen peroxide prepared by this method.

The dielectric constant of hydrogen peroxide solutions of all compositions over the temperature range -65° to 30°C was re-examined by Gross and Taylor (114). These authors believed the results of Cuthbertson and Maass to have been in error because of the effect of conductivity on the measurements. This is confirmed by the failure of the data of Cuthbertson and Maass for water to reproduce the accepted values of Wyman (119). Gross and Taylor used a bridge circuit of new design. Their cell was constructed of electropolished stainless steel, quartz, and Teflon (polytetrafluoroethylene) and was so designed that the measured capacitance was independent of the liquid volume contained. Their results for equilibrium conductivity water checked those of Wyman with a deviation of less than 0.2% and were unaffected by conductance as high as $2.5 \times 10^{-4} \text{ ohm}^{-1}$. Measurements were carried out at about 200 kilocycles, although frequency variation between 100 kilocycles and 1.5 megacycles produced no perceptible change in bridge balance with a 97% hydrogen peroxide sample at -9°C ; evidence was cited that indicates that dispersion effects are not to be expected in the range of frequencies used for measurement. The care used in preparation of hydrogen peroxide samples and construction of the cell permitted measurements to be made at temperatures up to $30 - 35^{\circ}\text{C}$ before traces of decomposition became apparent; the tendency to supercool allowed investigation at temperatures 20 to 40° below the freezing point of the solutions.

The results obtained by Gross and Taylor are summarized by the dielectric constant-composition isotherms given in Table 38 and Figure 14; these were taken from smoothed curves of dielectric constant-temperature plots. Values for the dielectric constant of anhydrous hydrogen peroxide were obtained by a short extrapolation and are expressed by the equation,

$$\epsilon = 84.2 - 0.62t + 0.0032t^2. \quad (58)$$

Equation 58 represents the data with a standard deviation of 0.13 and a maximum deviation of 0.2. Talât-Erben (120) has used these

TABLE 38
DIELECTRIC CONSTANT-COMPOSITION ISOTHERMS FOR HYDROGEN PEROXIDE-WATER SOLUTIONS,
FROM GROSS AND TAYLOR (114) *

| H ₂ O ₂ Concentration | 30° | 20° | 10° | 0° | -10° | -20° | -30° | -40° |
|---|--------|--------|--------|--------|--------|-------|-------|---------|
| Mole fr. | 30° | 20° | 10° | 0° | -10° | -20° | -30° | -40° |
| 0.0 | 76.7 | 80.4 | 84.1 | 88.0 | 93.7 | 103.7 | 113.3 | --- |
| .0406 | 76.3 | 80.7 | 85.0 | 89.4 | (93.7) | --- | --- | --- |
| .0638 | (76.9) | 81.3 | 85.7 | 90.4 | (95.3) | --- | --- | --- |
| .1582 | (77.6) | 81.9 | 87.3 | 92.8 | 98.2 | 103.7 | --- | --- |
| .1602 | --- | (82.4) | 87.7 | 93.1 | 98.4 | --- | --- | --- |
| .2241 | (77.5) | 83.1 | 88.8 | 94.6 | 100.6 | 106.7 | 113.3 | --- |
| .3151 | (76.8) | 82.6 | 88.6 | 94.7 | 101.2 | 108.0 | 115.4 | 124.7 |
| .3626 | (77.7) | 83.3 | 88.9 | 95.3 | 102.3 | 109.9 | 117.0 | 125.0 |
| .3785 | (78.6) | 83.9 | 89.8 | 95.9 | 102.6 | 109.6 | 116.9 | (125.0) |
| .4947 | --- | --- | (89.5) | (95.0) | 101.7 | 109.0 | 117.1 | 126.5 |
| .6187 | (75.9) | 81.3 | 87.3 | 93.5 | 100.1 | 107.7 | 115.9 | 125.3 |
| .7529 | (73.6) | 78.8 | 84.3 | 90.4 | 104.5 | 112.0 | 122.0 | --- |
| .9377 | (69.9) | 74.7 | 80.1 | 85.9 | 92.4 | --- | --- | --- |
| .9813 | (69.5) | 73.2 | 78.7 | 84.7 | 91.3 | 98.7 | 106.3 | --- |
| .9850 | (68.6) | 73.6 | 79.0 | 84.9 | (91.4) | --- | --- | --- |

* Parentheses indicate extrapolated values.

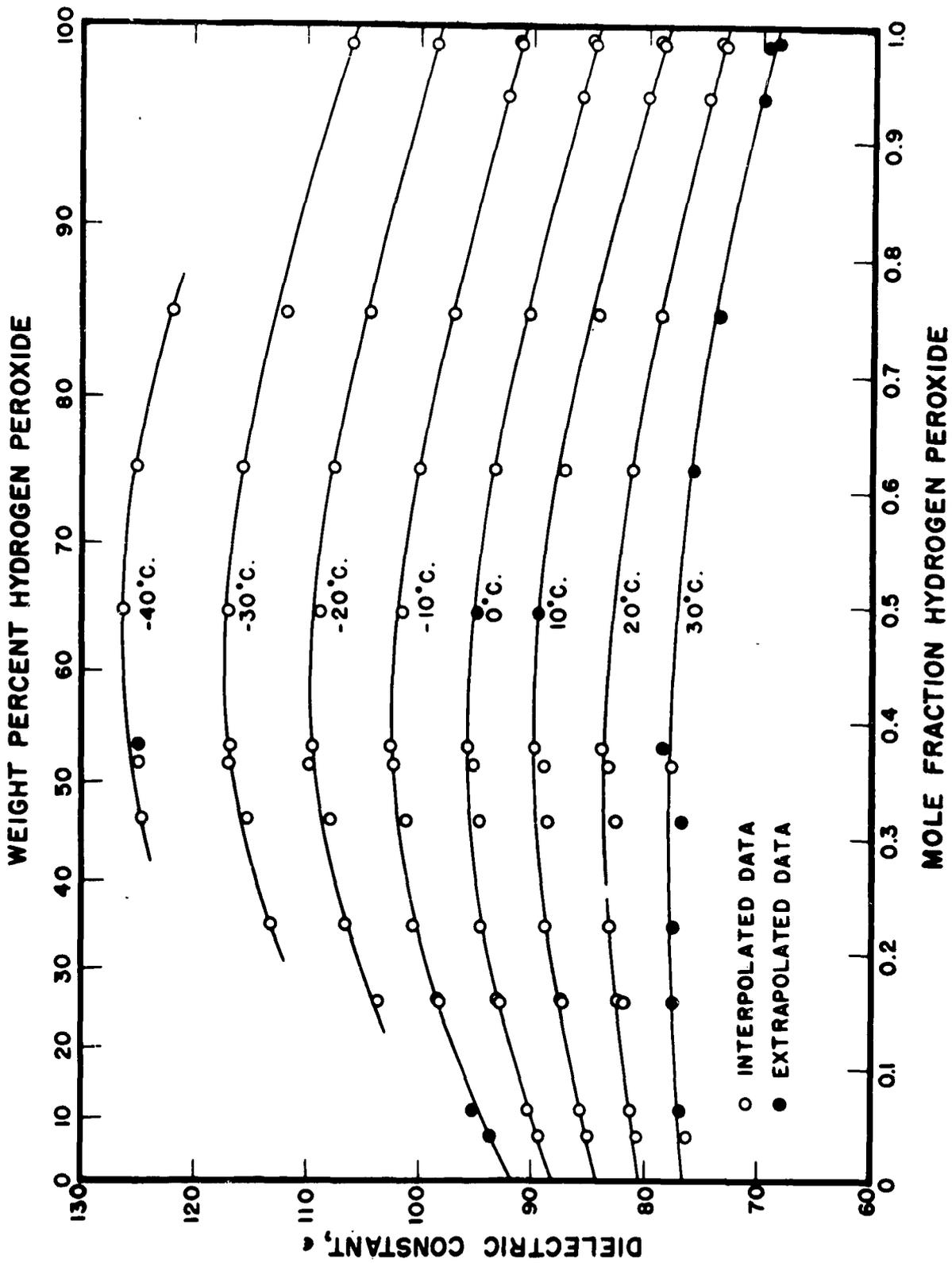


FIG. 14--DIELECTRIC CONSTANT-COMPOSITION ISOTHERMS FOR HYDROGEN PEROXIDE - WATER SOLUTIONS

data to demonstrate his proposed form of dielectric constant-temperature relationship, deriving the equation

$$\log (\epsilon T) = 4.78792 - 0.001558T, \quad (59)$$

which matches well the values obtained with equation (58).

It may be seen that the values determined by Gross and Taylor are lower than those of Cuthbertson and Maass, and that the dielectric constant of anhydrous hydrogen peroxide is less than that of water at all temperatures. The occurrence of the maximum is confirmed, but it is found to appear at about 55 wt. % hydrogen peroxide at 0° and the value is only 8 - 9% greater than that for water. The maximum becomes more pronounced and shifts to higher hydrogen peroxide concentrations as the temperature is decreased. The highest value, 157, was found for the dielectric constant of 75.4% hydrogen peroxide at -67.1°C .

Magnetic Susceptibility

When a substance is placed in a magnetic field the intensity of the field which passes within the substance may be either larger or smaller than the intensity of the field in the space surrounding the substance. A quantity termed the permeability is defined which is a measure of the tendency of a magnetic field to pass through a substance as compared to the tendency to pass through a vacuum. Those substances, such as oxygen, which are more permeable than a vacuum and in which a magnetic field becomes concentrated are termed paramagnetic. Those substances, such as water and hydrogen peroxide, which are less permeable than a vacuum and in which a magnetic field is weakened are termed diamagnetic. Paramagnetic substances possess a permanent magnetic moment and are attracted to the more intense region of an inhomogeneous magnetic field, whereas diamagnetic substances acquire an induced magnetic moment when placed in a magnetic field and tend to be expelled from an inhomogeneous field.

The permeability of a substance differs from that of a vacuum (permeability unity) by a quantity $4\pi k$; thus $P = 1 + 4\pi k$. The quantity k is termed the volume magnetic susceptibility and if positive denotes paramagnetism while if negative denotes diamagnetism. Other expressions for the magnetic susceptibility are the mass susceptibility, $\chi_g = k/\rho$, and the molar susceptibility, $\chi_m = M\chi_g$.

Four sources of data on the magnetic susceptibility of hydrogen peroxide and its water solutions are available. Maass and Hatcher (121) measured the susceptibility of anhydrous hydrogen peroxide using the Quincke method at 10°C and obtained the value 8.8×10^{-7} cgs emu/cc for the volume susceptibility. Gray and Farquharson (122) derived the value $\chi_m = (16.73 \pm 0.20) \times 10^{-6}$ cgs emu/mole for anhydrous hydrogen on the basis of measurements with a Curie-Cheneveau balance at 18°C on solutions containing up to 99.78 wt. % hydrogen peroxide; the individual data were not published. Savithri and Rao (123) measured the susceptibility of 6 to 32 wt. % hydrogen peroxide by the Gouy method, temperature unspecified. The most complete investigation was that of Neĭding and Kazarnovskii (58) who made measurements by the Gouy method over the entire composition range at 10 to 12°C , as well as making measurements on 96 to 98 wt. % hydrogen peroxide in the liquid, supercooled, and solid states over the temperature range $+18$ to -183°C .

The data of all these investigators is plotted in Figure 15 in terms of the mass susceptibility; for the datum of Maass and Hatcher the recent density value of 1.459 g/cc was used to convert to this basis. Judging from Figure 15 two consistent groups of data exist, that of Savithri and Rao and Maass and Hatcher and that of Neĭding and Kazarnovskii and Gray and Farquharson. It is believed that the choice lies with the latter. The evidence for this choice is as follows: Savithri and Rao measured the density of their solutions, but these densities are not in accord with accepted values, being (assuming "room temperature" of 10° to 25°C) high at the low concentrations and low at

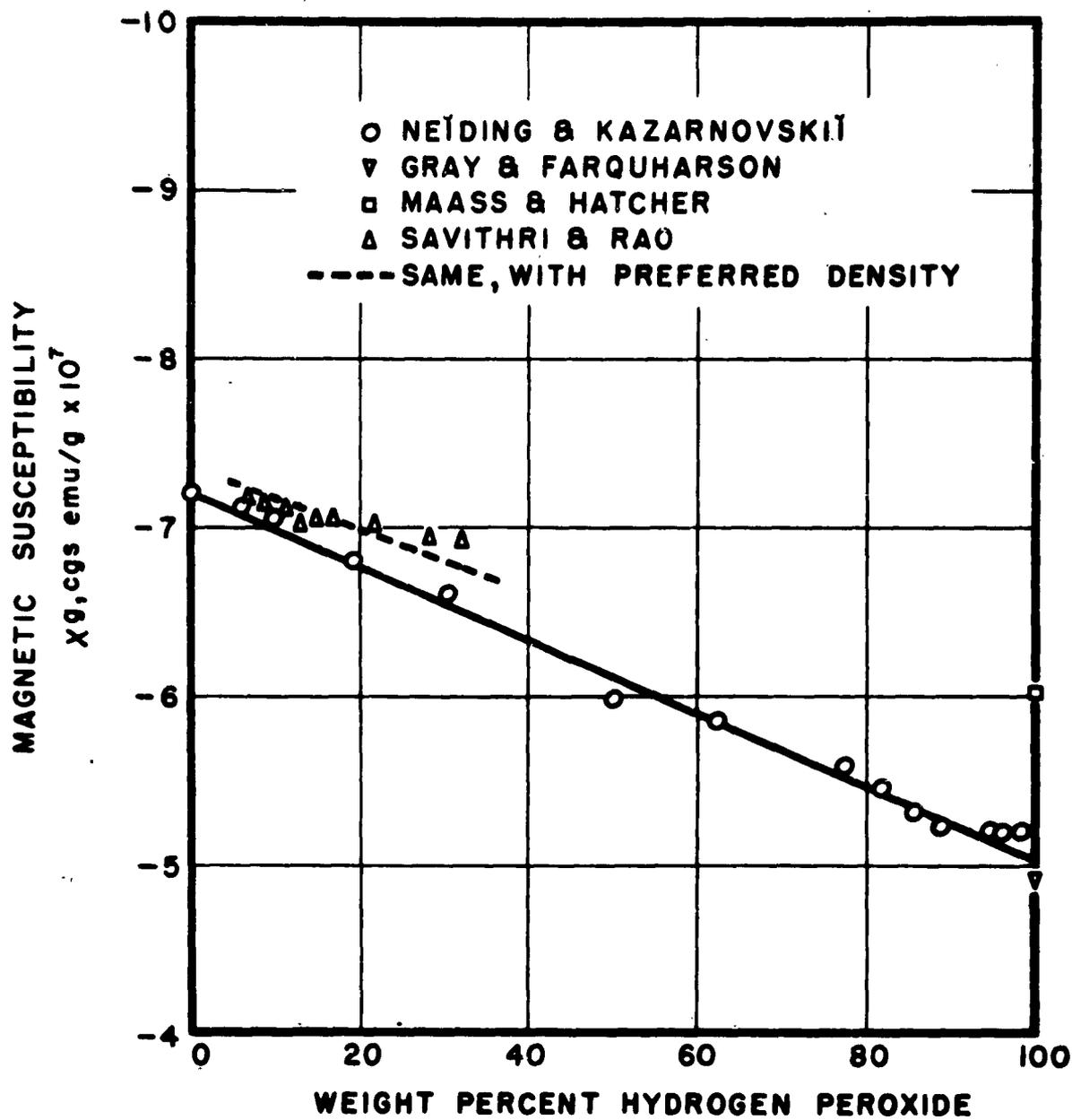


FIG.15- MAGNETIC SUSCEPTIBILITY OF HYDROGEN PEROXIDE - WATER SOLUTIONS

the higher concentrations. Recalculations of their data using accepted densities produces data paralleling that of Neĭding and Kazarnovskii very closely. There is no apparent reason for the departure of the single point given by Maass and Hatcher; however, the evidence of the three other investigators appears to outweigh it. Reduced consideration should be given to the value of Gray and Farquharson since they did not publish original data. The density values used by Neĭding and Kazarnovskii were those for 18° and thus introduce some error into their calculations based on data obtained at 10 to 12°C--about five parts in a thousand or within the precision of their data. In none of the work has the necessity for the avoidance of bubble formation in the sample tube been mentioned. Furthermore, in working with hydrogen peroxide there would appear to be increased opportunity for supersaturation with oxygen. The occurrence of both these effects would yield more positive susceptibility values.

There is disagreement at present in the literature as to whether susceptibility is a linear function of the composition of solutions. With no indication of a real deviation from linearity at hand for hydrogen peroxide solutions the following equation has been obtained by least squares from the data of Neĭding and Kazarnovskii,

$$10^6 \chi_g = -0.724 + 0.218w. \quad (60)$$

Comparison of this equation with the accepted value for water at room temperature, -0.720×10^{-6} cgs emu/gm, indicates that the quantity 0.004 cgs emu/gm, which closely represents the quoted precision of the data, might be reasonably added to the values calculated by equation (60) to bring them in accord with the accepted value for water. On this basis the various susceptibilities of anhydrous hydrogen peroxide are: $k(10^\circ) = -0.73 \times 10^{-6}$ cgs emu/cc, $\chi_g = -0.50 \times 10^{-6}$ cgs emu/gm, $\chi_m = -17 \times 10^{-6}$ cgs emu/mole. The permeability of anhydrous hydrogen peroxide is seen to be $(1 - 6.3 \times 10^{-6})$ cgs emu/cc or

very nearly the same as that of water, and the two substances are diamagnetic to the same degree.

The mass susceptibility of a diamagnetic substance is, according to theory, independent of temperature. For water the observed temperature effect has been found to be slight, and the effect for hydrogen peroxide may be presumed to be negligible within the precision of the data available. The measurements of the susceptibility of concentrated hydrogen peroxide as a function of temperature made by Neĭding and Kazarnovskii are recorded in Table 39. There is no indication of real change,

TABLE 39

MAGNETIC SUSCEPTIBILITY OF HYDROGEN PEROXIDE
AT VARIOUS TEMPERATURES
FROM NEĬDING AND KAZARNOVSKII (58)

| Temp., °C | State | $-\chi_g \times 10^6$, cgs emu/g | |
|-----------|--------------------|--------------------------------------|--------------------------------------|
| | | 98.15% H ₂ O ₂ | 96.66% H ₂ O ₂ |
| 18.2 | liquid | 0.520 | --- |
| 17.0 | " | --- | 0.526 |
| 9.8 | " | 0.523 | --- |
| -5.0 | " | --- | 0.523 |
| -6.0 | frozen | --- | 0.511 |
| -12.2 | supercooled liquid | 0.523 | --- |
| -12.2 | frozen | 0.505 | --- |
| -28.7 | " | 0.508 | --- |
| -78.5 | " | --- | 0.508 |
| -183.0 | " | 0.503 | 0.510 |

even in the supercooled liquid. On freezing, the susceptibility becomes more positive by about 2.4%, this is very close to the decrease for water on freezing of 2.2%. The density values used to obtain the values given in Table 39 were not given.

No measurements of the magnetic susceptibility of hydrogen peroxide vapor have been made. It is presumed that, as with other diamagnetic substances, there is no change of mass susceptibility upon vaporization.

EFFECT OF HYDROGEN PEROXIDE UPON RADIATION

Knowledge of the effects of hydrogen peroxide upon incident radiation, such as refraction, absorption, and scattering, is useful in analysis, in the deduction of structure, and in calculation of the magnitude and modes in which hydrogen peroxide may take up energy. In this division of the chapter the experimental results of measurements of the refraction of visible light, the magneto-optic rotation, the absorption for wave lengths extending from the microwave to the ultraviolet regions, the scattering in the visible region, and the diffraction of x-rays and electrons by hydrogen peroxide and its solutions are considered. Considerable literature is available in this field, and much excellent work has been done, but it may be expected that much more will be forthcoming particularly in the field of absorption spectroscopy as improving techniques make finer resolution possible. The interpretation and evaluation of the effects of hydrogen peroxide upon radiation is to some extent dependent upon information about the structure of the molecule for most of these properties. It has been attempted, however, to leave as much as possible of the discussion of structure for the subsequent chapter.

The experimental procedures used in some of these measurements do not permit concise description and it will be necessary to refer to the originals for such details as descriptions of radiation sources, types of film and recording instruments, etc. The usual techniques of this field are quite adequately introduced in the monograph edited by Weissberger (124).

Refractive Index

The usefulness of refractive index measurements as a precise and easy method of analysis for the concentration of hydrogen peroxide solutions makes the careful determination of this property of particular importance. The experimental techniques are straightforward, but in working with hydrogen peroxide particular care must be taken to prevent changes of concentration

from occurring in the small samples ordinarily used. Evaporation must not occur, and the sample holder or prism must be non-catalytic. The presence of bubbles formed through decomposition also interferes with the measurements.

A resumé of the published data on the refractive index of hydrogen peroxide water solutions is given in Table 40. The early measurements were probably of good precision, but the accuracy of the determination of the concentration of the samples is considered uncertain. The carefully conducted simultaneous measurements of concentration and refractive index of Giguère and Geoffrion (126) bear out this conclusion. Consideration of the experimental technique and comparison with the accepted data of Giguère and Geoffrion indicates that the samples of Cuthbertson and Maass (112) and Giguère (125) suffered decrease in concentration during measurement. Published measurements for anhydrous hydrogen peroxide, *i. e.*, by Brühl (63), Maass and Hatcher (11), and Egerton, Emte, and Minkoff (53), appear by this standard to have been made with slightly less than anhydrous material.

The experimental data for the sodium D line of Giguère and Geoffrion, given in Table 41, were obtained with a Precision Abbé refractometer, an instrument generally conceded (127) to provide precision of 5×10^{-5} or better. For these measurements exposed areas of prism cement were coated with ceresin wax, temperature was controlled to 0.02° , and the auxiliary lens was used to check the samples for evidence of decomposition. The samples, prepared by dilution of a quite stable, concentrated solution prepared by distillation of 90% material, showed evidence of instability at the lower concentrations, and a trace of stannate was therefore added. A detailed study was made of the permanganate analysis used to establish the concentration of the samples.

In Table 42 are given the coordinates of a smooth curve passed through the experimental data of Table 41. The

TABLE 40
SUMMARY OF MEASUREMENTS OF
REFRACTIVE INDEX OF HYDROGEN PEROXIDE

| Concentration Range, Wt. % | Method | Wave Lengths | Tempera- tures, °C | Quoted for Anhydrous Hydrogen Peroxide | | References |
|----------------------------------|----------------------|---|-----------------------|---|-----------|-----------------------------------|
| | | | | n | λ | |
| 8 - 25 | Minimum deviation | H _C , F, G; Na _D | 23 - 25 | - | - | Carrara (5) |
| 100 | -- | L ₁ ; H _C , F, G; Na _D ; T ₁ | 14 - 20 | 1.4062 | 20.4 | Brühl (63) |
| 96 - 100 | Minimum deviation | Na _D | 22 - 24 | 1.4139* | 22 | Maass and Hatcher (11) |
| 14 - 89 | Minimum deviation | H _C , F, G | 24.5 | 1.3910 | 24.5 | Cuthbertson and Maass (112) |
| 0 - 99 | Pulfrich | H _C , F, G; Na _D | 16 - 28 | 1.4087 | 20 | Giguère (125) |
| 0 - 99 | Precision- Abbé | Na _D | 20 - 25 | 1.4067 | 25 | Giguère and Geoffrion (126) |
| 100 | Hilger- Abbé | Na _D | 15 - 20 | 1.4058 | 20 | Egerton, Emte and Minkoff (53) |

*later (112) corrected to 1.4063

TABLE 41
 EXPERIMENTAL VALUES FOR THE REFRACTIVE INDEX OF
 HYDROGEN PEROXIDE-WATER SOLUTIONS,
 FROM GIGUÈRE AND GEOFFRION (126)

| Wt. % H_2O_2 | n_D | | Wt. % H_2O_2 | n_D | |
|----------------|---------------------|---------------------|----------------|---------------------|---------------------|
| | 25°C | 20°C | | 25°C | 20°C |
| 0.00 | 1.3325 ₁ | 1.3329 ₉ | 60.66 | 1.3738 ₉ | 1.3750 ₈ |
| 10.10 | 1.3388 ₁ | 1.3394 ₆ | 70.15 | 1.3815 ₁ | 1.3828 ₄ |
| 19.98 | 1.3452 ₁ | 1.3460 ₃ | 79.86 | 1.3892 ₇ | 1.3907 ₂ |
| 30.11 | 1.3520 ₃ | 1.3529 ₆ | 92.36 | 1.3999 ₈ | 1.4015 ₇ |
| 40.03 | 1.3588 ₅ | 1.3598 ₆ | 96.26 | 1.4033 ₃ | 1.4049 ₅ |
| 50.10 | 1.3661 ₁ | 1.3672 ₄ | 99.30 | 1.4060 ₇ | 1.4077 ₄ |

refractive index of hydrogen peroxide and its solutions may be seen to be greater than that of water, and the curve relating refractive index to composition (as wt. %) is concave upward. The temperature coefficient of refractive index is greater for hydrogen peroxide and its solutions than for water. The equation,

$$10^5 \alpha_n = 7.7 + 16.5 w \quad (61)$$

yields the temperature coefficient of refractive index, α_n , for the interval 25° down to 20°C adequate for the calculation of refractive index values within $\pm 10^{-4}$ unit or better. From a measurement with an immersion refractometer on carefully prepared anhydrous hydrogen peroxide Giguere and Geoffrion obtained $34 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ for the average temperature coefficient of refractive index between 15 and 25°C. If Table 42 is to be used to ascertain composition from refractive index measurements it is convenient to have a table of temperature corrections such that the listed values of refractive index may be matched with composition for other temperatures. Table 43 provides such corrections.

A number of constants of refraction and dispersion calculated from refractive index measurements are given in Table 44. The specific refraction for sodium D light is calculated from the relation $r_D = (n_D^2 - 1)/(n_D^2 + 2) \rho$ and the molar refraction, $[R]_D = Mr_D$. The molar refraction of solutions is generally equivalent to the mole fraction average of the molar refraction of the unmixed components, i.e., $[R]_m = x_1 [R]_1 + x_j [R]_j$. This relation holds within about one part in a thousand for hydrogen peroxide-water solutions. It is assumed that the molar refraction of hydrogen peroxide vapor is the same, or at the most, only a few percent greater than the molar refraction of the liquid. Other constants given in Table 44 are the polarizability, $\alpha = 3 [R]_D / 4\pi N$, the molar dispersion, $[R]_G - [R]_C$, and the dispersion constant, a , and characteristic frequency, ν_0 , calculated from

TABLE 42 (continued)

| H ₂ O ₂ % | 1.3 | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 | H ₂ O ₂ % | 1.3 | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 |
|---------------------------------|-----|-----|-----|-----|-----|-----|---------------------------------|-----|-----|-----|------|------|------|
| 60 | | 734 | 736 | 737 | 739 | 740 | 80 | | 894 | 896 | 897 | 899 | 901 |
| 61 | | 742 | 744 | 745 | 747 | 748 | 81 | 1.3 | 903 | 904 | 906 | 908 | 909 |
| 62 | | 750 | 752 | 753 | 755 | 756 | 82 | | 911 | 913 | 915 | 916 | 918 |
| 63 | | 758 | 760 | 761 | 763 | 764 | 83 | | 920 | 921 | 923 | 925 | 927 |
| 64 | | 766 | 768 | 769 | 771 | 772 | 84 | | 928 | 930 | 932 | 933 | 935 |
| 65 | | 774 | 776 | 777 | 779 | 780 | 85 | | 937 | 939 | 940 | 942 | 944 |
| 66 | | 782 | 784 | 785 | 787 | 788 | 86 | | 945 | 947 | 949 | 950 | 952 |
| 67 | | 790 | 792 | 793 | 795 | 796 | 87 | | 954 | 956 | 957 | 959 | 961 |
| 68 | | 798 | 800 | 801 | 803 | 804 | 88 | | 962 | 964 | 966 | 968 | 969 |
| 69 | | 806 | 808 | 809 | 811 | 812 | 89 | | 971 | 973 | 974 | 976 | 978 |
| 70 | 1.3 | 814 | 816 | 817 | 819 | 820 | 90 | 1.3 | 880 | 981 | 983 | 985 | 986 |
| 71 | | 822 | 824 | 825 | 827 | 828 | 91 | | 988 | 990 | 992 | 993 | 995 |
| 72 | | 830 | 832 | 833 | 835 | 836 | 92 | | 997 | 999 | *000 | *002 | *004 |
| 73 | | 838 | 840 | 841 | 843 | 844 | 93 | 1.4 | 006 | 007 | 009 | 011 | 013 |
| 74 | | 846 | 848 | 849 | 851 | 852 | 94 | | 014 | 016 | 018 | 020 | 021 |
| 75 | | 854 | 856 | 857 | 859 | 860 | 95 | | 023 | 025 | 027 | 028 | 030 |
| 76 | | 862 | 864 | 865 | 867 | 868 | 96 | | 032 | 034 | 035 | 037 | 039 |
| 77 | | 870 | 872 | 873 | 875 | 876 | 97 | | 041 | 042 | 044 | 046 | 048 |
| 78 | | 878 | 880 | 881 | 883 | 884 | 98 | | 049 | 051 | 053 | 055 | 056 |
| 79 | | 886 | 888 | 889 | 891 | 892 | 99 | 1.4 | 058 | 060 | 062 | 063 | 065 |
| | | | | | | | 100 | | 067 | | | | |

TABLE 43
TEMPERATURE CORRECTIONS TO BE SUBTRACTED FROM THE
PERCENTAGE OF HYDROGEN PEROXIDE IN TABLE 42

| Temperature, °C | Approximate concentration | | | | | | | | | |
|--------------------|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 20 | 0.9 | 1.2 | 1.3 | 1.4 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 |
| 21 | 0.8 | 0.9 | 1.0 | 1.1 | 1.1 | 1.2 | 1.2 | 1.3 | 1.4 | 1.5 |
| 22 | 0.6 | 0.7 | 0.8 | 0.9 | 0.9 | 1.0 | 1.0 | 1.0 | 1.1 | 1.1 |
| 23 | 0.4 | 0.4 | 0.5 | 0.6 | 0.6 | 0.6 | 0.6 | 0.7 | 0.7 | 0.8 |
| 24 | 0.2 | 0.2 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 0.4 |

TABLE 44
CONSTANTS DERIVED FROM REFRACTION DATA (125, 126)

| Constant | Hydrogen Peroxide | Water |
|---|-------------------|--------|
| Specific refraction, r_D , cc/g, 25° | 0.1705 | 0.2060 |
| Molar refraction, $[R]_D$, cc/mole, 25° | 5.801 | 3.712 |
| Polarizability, $\alpha \times 10^{24}$, cc/molecule, 25° | 2.30 | 1.47 |
| Molar dispersion, $[R]_G - [R]_D$, cc/mole, 20° | 1.3576 | 0.9285 |
| Dispersion constant, $a \times 10^{-30}$, sec ⁻² , 20° | 8.479 | 6.532 |
| Characteristic frequency, $\nu_0 \times 10^{-15}$, sec ⁻¹ , 20° | 2.979 | 2.945 |

the simplified Sellmeier formula (128), $n^2 - 1 = a/(\nu_0^2 - \nu^2)$, where ν is the frequency at which the refractive index is measured. These two latter constants were evaluated from the refractive indices at 20°C measured by Giguère (125) with the C (red) and F (blue) lines of hydrogen. These two constants and the molar dispersion calculated from the same work may be slightly inaccurate since, as explained above, the precision of the refractive index measurements of Giguère was affected by uncertainty in the determination of composition. The dispersion or difference in refractive index at different frequencies for hydrogen peroxide and its solutions is normal, that is the refractive index increases regularly with decreasing wavelength in the visible spectrum, e.g., the refractive indices at 20° determined by Giguère (125) for the three hydrogen lines C(6562.8 Å), F(4861.33 Å) and G(4340.46 Å) were $n_C = 1.4066$, $n_F = 1.4136$, and $n_G = 1.4175$ for anhydrous hydrogen peroxide.

Magneto-optic Rotation in Hydrogen Peroxide

Hydrogen peroxide and its solutions and water are not optically active, that is, there is no rotation of the plane of polarization on passing light through them. When placed in a magnetic field, however, rotation of the plane of polarization does occur; this is the Faraday effect or phenomenon of magneto-optic rotation. This effect is given quantitative expression by the equation:

$$\alpha = V\mu H \cos \theta_0 \quad (62)$$

The values of the Verdet constant at 0°C for light of wavelength 5460 Å were determined by Andersen and Rasmussen (129) to be 0.0154, 0.0154 and 0.0152 min/gauss cm for solutions of hydrogen peroxide of concentration 10.52, 15.67, and 30.42 wt. %, respectively.

Comprehensive measurements of the value of the Verdet constant for hydrogen peroxide were made by Giguère and Feeny (130).

Their results, obtained at $10 \pm 2^\circ\text{C}$ in a magneto-polarimeter calibrated with water, are summarized in Table 45 along with the values for refractive index of the solutions used to establish the concentrations. Within the precision of these data, about 1%, the Verdet constant of hydrogen peroxide-water solutions is found to be a linear function of mole fraction composition at each wavelength. Some small changes in the values of the data given in Table 45 might be made on the basis of improved values of the refractive index of hydrogen peroxide and recent measurements (131) of the Verdet constant of water, but such changes are probably not warranted. Giguère and Feeny found the dispersion with wavelength of the Verdet constant of hydrogen peroxide to parallel that of water and have presented values calculated for the dispersion constants. Calculation of the molecular magnetic rotation of hydrogen peroxide on the basis of the atomic equivalents of Perkins was found to yield a value lower than that found by experiment.

The magnetic rotary power of 20 to 80 wt. % hydrogen peroxide solutions at 20°C was measured by Gallais and Wolf (132) using light of wavelengths 5780, 5460 and 4360 Å. These data are in substantial agreement with those of Giguère and Feeny with regard to magnitude and composition dependence.

The precision of these three sets of data is not sufficiently good to allow the calculation of the temperature coefficient of the Verdet constant for the wavelength 5460 Å investigated in common. It is indicated that the Verdet constant decreases with temperature, but the effect, as with water (131), is very small.

Microwave Absorption Spectrum

The absorption by hydrogen peroxide vapor of radiation in the microwave region (wavelength 1 m to 1 mm) has been investigated by Massey and Bianco (133). The frequency region from 9,000 Mc/sec to 40,000 Mc/sec was searched; nine absorption lines were found for H_2O_2 and about one hundred lines were found for D_2O_2 and HDO_2 . The results for hydrogen peroxide are given in

TABLE 45

THE VERDET CONSTANTS OF HYDROGEN PEROXIDE-WATER SOLUTIONS AT 10°C,
FROM GIGUERE AND FEENEY (130)

| H ₂ O ₂ Conc., | | Refractive Index | Verdet Const., V, min/gauss cm x 10 ³ | | |
|--------------------------------------|----------|---------------------|--|--------|--------|
| wt. % | mole fr. | | 5893 | 5780 | 5461 |
| 0 | 0 | 1.3330 | 13.09 | 13.64 | 15.40 |
| 18.1 | 0.105 | 1.3447 | 12.91 | 13.38 | 15.13 |
| 38.1 | 0.246 | 1.3585 | 12.69 | 13.15 | 14.86 |
| 50.9 | 0.354 | 1.3680 | 12.53 | 12.98 | 14.60 |
| 62.0 | 0.463 | 1.3766 | 12.30 | 12.80 | 14.43 |
| 78.5 | 0.659 | 1.3899 | 11.98 | 12.45 | 14.07 |
| 96.0 | 0.927 | 1.4052 | 11.60 | 12.03 | 13.64 |
| 100.0 | 1.00 | 1.4112 | 11.48* | 11.90* | 13.52* |

*extrapolated

Table 46, where J represents the angular momentum quantum number, J^* being the larger of the two quantum numbers involved in the transition. The accuracy of these results is not as high as is normally obtained in the microwave region. This was caused by experimental difficulties in manipulating the hydrogen peroxide vapor. Massey and Bianco found it necessary to devise a flow system, even so, rapid decomposition in the waveguide made it impossible to operate at pressures sufficiently low for high accuracy. The quadratic Stark splitting of these lines was studied and the following equations relate the observed separation of lines to the electrical field strength, E , for four of the lines. $\Delta\nu'$ represents the frequency deviation of the m th component from the original line frequency, m being the magnetic quantum number.

TABLE 46

MICROWAVE SPECTRUM OF HYDROGEN PEROXIDE,
FROM MASSEY AND BIANCO (133)

| Line** | Frequency, Mc/sec | |
|--------|--------------------|--|
| 1 | 14,829.5 \pm 0.2 | quadratic Stark effect $J^* = 1$ |
| 2 | 37,517.6 \pm 0.2 | " " " $J^* = 2$ |
| 3 | 22,054.5 \pm 0.2 | " " " $J^* = 7, \Delta J = 1$ min |
| 4 | 27,639.6 \pm 0.2 | " " " $J^* = 7, \Delta J = 1$ min |
| 5 | 11,072.4 \pm 0.5 | " " " probably high J |
| 6 | 35,916 \pm 2 | " " " high $J, \Delta J = 1$ |
| 7 | 39,033 \pm 2 | probably high J |
| 8 | 39,495 \pm 2 | " " " |
| 9 | 39,760 \pm 2 | " " " |

** all lines of medium or strong intensity, except 5, 6 and 7, which are relatively weak.

$$\text{Line 1 } \Delta\nu' = 29.09 E^2 \times 10^6 \quad (63)$$

$$\text{Line 2 } \Delta\nu' = (6.88 - 4.25m^2) E^2 \times 10^6 \quad (64)$$

$$\text{Line 3 } \Delta\nu' = (5.65 - 0.0874m^2) E^2 \times 10^6 (J^* \geq 8) \quad (65)$$

$$\Delta\nu' = (6.07 - 0.0727m^2) E^2 \times 10^{-6} (J^* \geq 9) \quad (66)$$

$$\Delta\nu' = (6.47 - 0.0623m^2) E^2 \times 10^{-6} (J^* \geq 10) \quad (67)$$

$$\text{Line 4 } \Delta\nu' = (4.18 - 0.0537m^2) E^2 \times 10^{-6} (J^* \geq 8) \quad (68)$$

$$\Delta\nu' = (4.49 - 0.0459m^2) E^2 \times 10^{-6} (J^* \geq 9) \quad (69)$$

$$\Delta\nu' = (5.10 - 0.0356m^2) E^2 \times 10^{-6} (J^* \geq 10) \quad (70)$$

It was not found possible to determine J^* unambiguously for lines 3 and 4, thus several equations are presented with the minimum allowable value of J^* corresponding to each.

Infrared Absorption Spectrum

It was shown by Friedel (134) in 1895, that the absorption of infrared radiation by hydrogen peroxide was large and of the same magnitude as that for water. The total transmitted radiation only was measured and the success of the demonstration that absorption occurred was due to the fact that the radiation source used, a metal block heated to 393°C , emitted maximum intensity at a wavelength of 4.4 microns, near the most intense infrared absorption bands of water and hydrogen peroxide. The study of the location in the spectrum of the infrared absorption bands of hydrogen peroxide was not begun until 1935, when Malone (135) compared the intensity of absorption of liquid 36% hydrogen peroxide with that of water for radiation of wavelength 1.0 to 6.0 microns. Malone found the absorption bands at 1.5 and 2.0μ of water to be increased in intensity in the hydrogen peroxide solution, found an absorption band of water at 3.0μ to become more intense and shifted toward longer wavelengths in hydrogen peroxide and observed a water absorption band at 4.6μ to be replaced in hydrogen peroxide with two distinct bands having maxima at 4.4 and 4.85μ . Ganz (136) presented the result of brief measurements of the effect of temperature on the infrared absorption of liquid 30% hydrogen peroxide for radiation of wavelength 0.7 to 0.9μ . Absorption was found to occur in water and hydrogen peroxide near 0.77μ ; increasing the

temperature of hydrogen peroxide from 12° to 55° noticeably increased the intensity of absorption.

An extended examination of the infrared absorption of hydrogen peroxide was first made by Bailey and Gordon (137) who measured the absorption of 95 wt. % liquid in the range 2 to 12μ and of vapor at a pressure of about 18 mm Hg in the range 2.5 to 13μ . The liquid was held as a film between mica sheets in the examination of the region 2.0 to 8.8μ . For the region beyond 8.8μ the liquid was held between rock salt plates; rapid work was necessary because of chemical reaction. The values of the frequencies of the centers of the absorption bands observed by Bailey and Gordon are presented in Table 47. Bailey and Gordon stated that they did not observe the absorption reported by Maione at 4.4 and 4.85μ .

Absorption in the infrared near the wavelength of one micron was studied by Zumwalt and Giguère (138) with the liquid and by Giguère (139) with the vapor. Zumwalt and Giguère examined the region from 0.95 to 1.05μ , passing hydrogen peroxide at 90 mm pressure and 100°C through a 6 m cell illuminated by a carbon arc, using a high dispersion grating instrument and recording the spectrum photographically. A pair of absorption bands at 0.972μ was found. A microphotometer trace of the photograph of these bands made with the 21 ft concave grating spectrograph was presented. The individual frequencies of the absorption lines were identified and an analysis made of the band structure. Giguère found the absorption of 99.6% liquid hydrogen peroxide in this region of the spectrum to occur as a wide band with the center at 1.01μ .

The region of infrared absorption studied by Bailey and Gordon was re-examined and extended by Giguère (140). The liquid, 99.5 wt. % hydrogen peroxide, was examined in the region 2 to 21μ , and the vapor, at 90°C and 5, 10, and 15 mm pressure, was examined in the region 1.4 to 15μ . The liquid was manipulated as a film pressed between silver chloride plates, and difficulty due to decomposition was encountered. Silver chloride windows were also used in the absorption cell used with the vapor.

TABLE 47

 INFRARED ABSORPTION SPECTRUM
 OBSERVED BY BAILEY AND GORDON (137)

| Location of Band Centers | | | Relative Intensities* | |
|-----------------------------------|--|---|-----------------------|-------|
| Liquid Wavelengths, microns | Liquid Wave number, cm ⁻¹ | Vapor Wave number, cm ⁻¹ | Liquid | Vapor |
| 11.40 | 877 | 870 | 33 | 17.8 |
| 7.50 | 1341 | 1370 | 87 | 22.2 |
| 3.48 | 2869 | 2870 | 55 | 15 |
| 2.93 | 3418 | 3418 | 78 | 59 |

*on an arbitrary basis for intercomparison

For work beyond 15 μ potassium bromide optics were used in the spectrometer, and the spectrometer case was specially dehydrated to avoid interference due to absorption by water vapor. The values of the frequencies of the centers of the absorption bands and the absorption coefficients observed by Giguère (140) are presented in Table 48. The band at 18.3 μ in the liquid was

TABLE 48

 INFRARED ABSORPTION SPECTRUM
 OBSERVED BY GIGUÈRE (140)

| Location of Band Centers | | | Extinction Coefficient,* K, (atm cm) ⁻¹ |
|----------------------------------|--|---|---|
| Liquid Wavelength, microns | Liquid Wave number, cm ⁻¹ | Vapor Wave number, cm ⁻¹ | |
| 18.2. | 550 | --- | --- |
| 11.4 | 880 | 877 | 0.025 |
| 7.4 | 1350 | 1255 | 0.70 |
| 3.6 | 2780 | 2630 | 0.05 |
| 2.1 | 4720 | --- | --- |
| 1.4 | --- | 7036.6 | 0.085 |
| 1.4 | --- | 7041.8 | --- |

* K = (1/pd) log(I₀/I_x)

poorly defined and the band at 2.1μ in the liquid was quite weak and considered uncertain since it did not appear on all the photometer tracings. The dispersion of the spectrometer was sufficiently high to show clearly with the vapor that the band at 8μ contained two maxima with indications in some tracings of the presence of a Q branch. The 1.4μ band was examined under high dispersion with the vapor; the individual frequencies of the two bands resolved were identified and an analysis made of the band structure.

Supercooled (-30°C) liquid hydrogen peroxide (99.2 wt. %) and crystalline hydrogen peroxide, at -30° and -78° , were subjected to infrared examination by Taylor (141) over the range 2 to 25μ . Measurements at -30° of the absorption of liquid 82.5 wt. % deuterium peroxide in heavy water containing 8 - 10% hydrogen were also made. Samples were held in silver chloride cells with little difficulty from decomposition because of the low temperature. Fluorite, rock salt, or potassium bromide prisms were used and a photometer trace of the absorption bands obtained with solid hydrogen peroxide at -78° was presented. A summary of Taylor's data for hydrogen peroxide is presented in Table 49.

Recent improvement in infrared spectrometry has permitted some resolution of the fundamental infrared absorption bands. Bain (142) obtained the data shown in Table 50 and resolved the absorption band near 21 to 18 microns. This band was described as composed of two overlapping perpendicular bands with centers around 465 and 575 cm^{-1} .

Giguère and Bain (143) have reported briefly an investigation of the infrared absorption spectrum in the range 2 to 25 of deuterium peroxide vapor and of alkaline solutions of hydrogen peroxide. The results of spectroscopic measurements on deuterium peroxide are described in a later section.

TABLE 49

 INFRARED ABSORPTION SPECTRUM OF HYDROGEN PEROXIDE,
 OBSERVED BY TAYLOR (141)

| Liquid, Wavelength, microns | Location of Band Centers* | | |
|-----------------------------------|--|---|---|
| | Liquid, -30° Wave Number, cm ⁻¹ | Solid, -30° Wave Number, cm ⁻¹ | Solid, -78° Wave Number, cm ⁻¹ |
| 21.2 | -- | -- | 472 (vw) |
| 15.8 | 635 (m,br) | -- | 660 (s) |
| 12.6 | -- | -- | 792 (w) |
| 11.4 | 878 (vw) | -- | 878 (vw) |
| 7.4 | 1353 (ms) | 1365 (s) | 1378 (s) |
| 7.1 | -- | 1418 (w) | 1430 (w) |
| 3.6 | 2796 (mw,br) | 2743 (m) | 2733 (m) |
| 3.1 | -- | -- | 3218 (vs) |
| 2.1 | 4715 (vw) | 4640 (vw) | 4595 (vw) |

* see Table 51 for explanation of symbols

TABLE 50

 INFRARED ABSORPTION SPECTRUM OF HYDROGEN PEROXIDE,
 OBSERVED BY BAIN (142)

| Wavelength, microns | Vapor Wave Number, cm ⁻¹ | Liquid, 20°C Wave Number, cm ⁻¹ |
|------------------------|---|--|
| 20 - 15 | (490 - 660) (ms) | |
| | 1255 (w) | |
| 7.9 | 1266 (vs) | |
| 7.8 | (1280) (w) | |
| 2.7 | 3610 (s) | |
| 2.3 | | 4290 (vw) |
| 2.2 | 4465 (vw) | |
| 2.0 | 4835 (vw) | |
| 2.0 | 4955 (vw) | |
| 1.6 | | 6100 (vw) |
| 1.5 | | 6805 (vw) |
| 1.2 | | 8040 (vw) |

A summary of the observed absorption bands of hydrogen peroxide is presented in Table 51. This table includes all the subsidiary peaks reported, illustrates the temperature variations reported, and repeats bands probably identical but given different locations by various authors. The most probable values and frequency assignments of the principal bands are given in the next chapter, which deals with structure. It should be remembered that the infrared absorption of hydrogen peroxide is relatively weak, that certain of the reported bands have not been confirmed, and that the accuracy of the location of some of these band centers is not high. As indicated in the discussion, some of the bands have been studied under high dispersion; other bands could doubtless be resolved in greater detail. For comparison, the principal infrared absorption bands for water (2) may be listed as 0.85, 0.98, 1.18, 1.46, 1.98, 2.97, 4.70, and 6.1 μ .

Raman Spectrum

If a substance is illuminated with monochromatic radiation it may be found that the radiation scattered by the substance contains not only the exciting wavelength but also one or more other wavelengths. These other wavelengths differ in wavelengths from that of the exciting radiation by an amount which is independent (to a first approximation) of the wavelength of the exciting radiation. The spectrum consisting of these scattered wavelengths composes what is termed the Raman spectrum. Although the Raman spectrum, being a spectrum due to the emission of light, is the opposite of an absorption spectrum, the emission often arises through the same intra-molecular motions which are responsible for the infrared absorption spectrum. Thus the difference in wavelength of the exciting line and a Raman line is a measure of the energy, $h\nu$, extracted from the exciting radiation and applied to intra-molecular motion, the less energetic remainder of lower frequency being emitted and observed as the Raman line. An exact correspondence may then exist between the wave number, σ , characterizing an infrared absorption band and the magnitude of the difference in the wave numbers, $\Delta\sigma$, of a Raman line and its

TABLE 51

 INFRARED ABSORPTION SPECTRUM OF HYDROGEN PEROXIDE--
 SUMMARY OF REPORTED BANDS AND INTENSITIES

| Wavelength, | Wave Number, cm ⁻¹ | Intensity* | Temperature, °C** | Reference |
|----------------|----------------------------------|------------|----------------------|---------------|
| SOLID: | | | | |
| 21.2 | 472 | (vw) | -78 | 141 |
| 15.2 | 660 | (s) | " | " |
| 12.6 | 792 | (w) | " | " |
| 11.4 | 878 | (vw) | " | " |
| 7.3 | 1365 | (s) | -30 | " |
| 7.3 | 1378 | (s) | -78 | " |
| 7.1 | 1418 | (w) | -30 | " |
| 7.0 | 1430 | (w) | -78 | " |
| 3.6 | 2743 | (m) | -30 | " |
| 3.7 | 2733 | (m) | -78 | " |
| 3.1 | 3218 | (vs) | " | " |
| 2.2 | 4595 | (vw) | " | " |
| 2.2 | 4640 | (vw) | -30 | " |
| LIQUID: | | | | |
| 18.2 | 550 | (vw) | -- | 140 |
| 15.8 | 635 | (m) | -30 | 141 |
| 11.4 | 880 | (w) | -- | 137, 140, 141 |
| 7.4 | 1350 | (m) | -- | 137, 140, 141 |
| 4.85 | 2000 | (vw) | -- | 135 |
| 4.4 | 2300 | (vw) | -- | " |
| 3.6 | 2780 | (m) | -- | 140 |
| 3.6 | 2796 | (m) | -- | 141 |
| 3.48 | 2864 | (m) | -- | 137, 141 |
| 2.93 | 3418 | (s) | -- | 137 |
| 2.3 | 4290 | (vw) | 20 | 142 |
| 2.1 | 4720 | (vw) | -- | 135, 140, 141 |
| 1.6 | 6100 | (vw) | 20 | 142 |
| 1.5 | 6700 | (w) | -- | 135 |
| 1.5 | 6805 | (vw) | 20 | 142 |
| 1.2 | 8040 | (vw) | 20 | 142 |
| 1.01 | 9900 | (w) | -- | 139 |
| 0.77 | 13000 | (w) | 12, 55 | 136 |
| VAPOR: | | | | |
| 20 - 15 | 490 - 660 | (ms) | -- | 142 |
| 11.4 | 877 | (vw) | 90 | 137, 140 |
| 8.0 | 1255 | (vs) | 90 | 140, 142 |
| 7.9 | 1266 | (vs) | -- | 142 |
| 7.8 | 1280 | (w) | -- | 142 |
| 7.3 | 1370 | (w) | -- | 137 |
| 3.8 | 2630 | (w) | 90 | 140 |
| 3.5 | 2870 | (vw) | -- | 137 |
| 2.9 | 3418 | (m) | -- | " |
| 2.7 | 3610 | (s) | -- | 142 |
| 2.2 | 4465 | (vw) | -- | " |
| 2.0 | 4835 | (vw) | -- | " |
| 2.0 | 4955 | (vw) | -- | " |
| 1.4 | 7037 | (w) | 90 | 140 |

(Continued on page 129)

TABLE 51 (Cont.)

| Wavelength, | Wave Number, cm ⁻¹ | Intensity* | Temperature, °C** | Reference |
|-------------|----------------------------------|------------|----------------------|-----------|
| VAPOR: | | | | |
| 1.4 | 7042 | (w) | 90 | 140 |
| 0.972 | 10283.68 | (w) | 100 | 138 |
| 0.972 | 10291.08 | (w) | " | " |

* Symbols (??): (v.s.), very strong; (s.), strong; (m.), medium; (w.), weak; (v.w.), very weak. Intensity estimates are relatively valid only for bands in the same region of the spectrum.

**Absence of a value indicates data obtained at room temperature.

exciting line (the Raman Shift). Certain intra-molecular motions may give rise to a Raman line without causing infrared absorption and vice-versa, and this, along with various considerations of experimental convenience and precision dictates the desirability of the determination of Raman spectra.

Venkateswaran (144) published the earliest notice of the Raman spectrum in hydrogen peroxide, reporting the existence of Raman shifts of 875 and 903 wave numbers in 30% liquid hydrogen peroxide. The 875 cm⁻¹ line was found to be intense, the 903cm⁻¹ line was weak, and other bands of even weaker intensity were stated to appear. Damaschun (145) shortly confirmed the existence of a Raman shift of 873 cm⁻¹, but did not observe the 903 cm⁻¹ line. In a more detailed paper Venkateswaran (144) reported the occurrence in 30% liquid hydrogen peroxide of Raman shifts of 400, 875, and 903 cm⁻¹ as well as the water bands, presumably referring to the shift of about 3400 cm⁻¹, which is also to be observed in the Raman spectrum of water. The depolarization ratio of the line shifted 875 cm⁻¹ was measured by Venkateswaran and found to be 0.15.

Concentrated liquid hydrogen peroxide (99.5 wt. %) was examined for Raman scattering by Simon and Feher (146) who found shifts with band maxima removed by 877, 1421, and 3395 cm⁻¹ from

the exciting line of wavelength $4358 \overset{\circ}{\text{A}}$. These authors believed the shift of 903 cm^{-1} reported by Venkateswaran to have arisen from the glass container. Simon and Feher published a photometer trace of their Raman spectrum showing the following band limits and intensities: 877 cm^{-1} , sharp, relative intensity 15; 1421 cm^{-1} , band limits $1462 - 1345$, relative intensity 1; 3395 cm^{-1} , band limits $3410 - 3200$, relative intensity 3. The 1421 cm^{-1} shift appeared to have two maxima separated by 27 cm^{-1} , became weaker with dilution, and was shifted less at lower concentrations, *viz.*, the shift was 1399 cm^{-1} in 95% hydrogen peroxide and 1392 cm^{-1} in 80%. The 3395 cm^{-1} shift was found to be altered less on dilution. In 30% hydrogen peroxide this band was broadened to extend over 690 cm^{-1} , and while broadening was observed to split to give two maxima with individual shifts of about 3130 and 3430 cm^{-1} . The limit of the band was observed to move to 3630 cm^{-1} in 3% hydrogen peroxide, whereas it had been 3410 cm^{-1} in the 99.5% hydrogen peroxide. At this dilution the Raman shift of 1630 cm^{-1} ascribed to water was observed to appear. Simon and Feher also found that all the Raman lines with the exception of that at 3395 cm^{-1} disappeared on neutralizing the hydrogen peroxide with sodium hydroxide.

Kohlrausch (147) believed that the Raman shift given as 3395 cm^{-1} by Simon and Feher should have been reported as 3305 cm^{-1} . However, Bailey and Gordon (137) shortly published the results of the examination of the Raman spectrum of 95% liquid hydrogen peroxide made by Leckie, who reported the occurrence of a shift of 3418 cm^{-1} ; the difference between 3395 and 3418 was considered insignificant and to constitute a confirmation of Simon and Feher.

The Raman spectra of 99.3+ wt. % liquid hydrogen peroxide, water solutions, and crystalline hydrogen peroxide have been recently investigated thoroughly by Taylor (148). Various mercury lines were used for excitation, with suitable filters to suppress as nearly as possible all but the desired line. Exposures of 12 to 48 hours were recorded with a spectrograph having a dispersion of $15 \overset{\circ}{\text{A}}/\text{mm}$ in the blue. The hydrogen peroxide was distilled directly into the cell, and an analysis was made before and after each illumina-

tion. At 30°C some difficulty with decomposition was encountered due to the intense illumination used; particular care in pre-treatment of the Pyrex cell was necessary to minimize this decomposition.

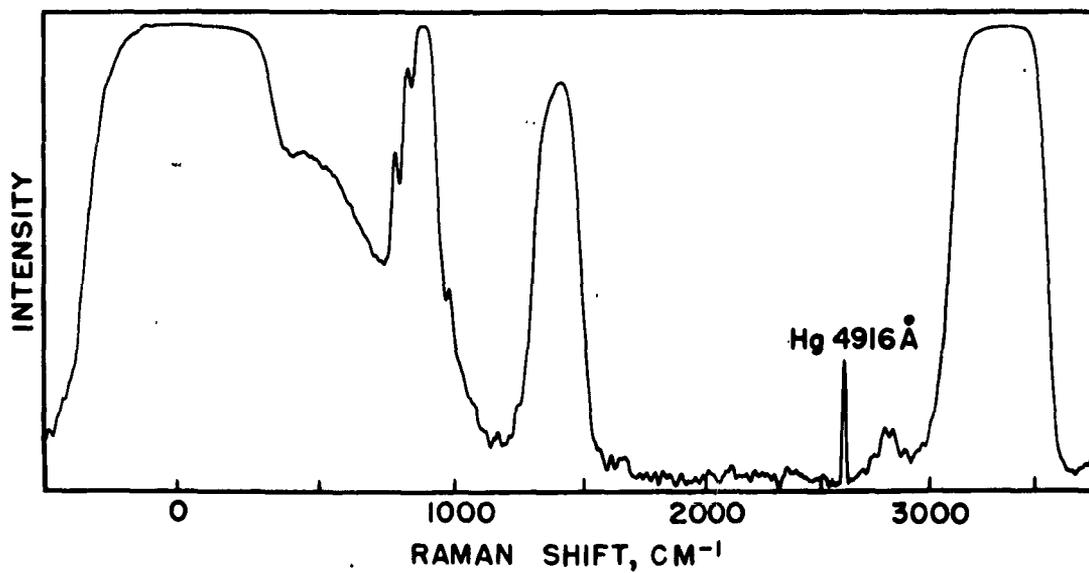
The spectra obtained by Taylor with 99.3% liquid hydrogen peroxide, using for the exciting lines radiation of wavelength 4358 Å, are shown in Figure 16 and summarized in Table 52. The traces shown in Figure 16a give clear evidence of Raman shifts at 525 and 2815 cm⁻¹ as well as those at about 880, 1400 and 3400 cm⁻¹ reported by previous workers.

The unsymmetrical intensity distribution about the exciting line which appears in the normal exposure must also be regarded as Raman scattering. However, the resolution is not sufficiently fine to allow characterization of the magnitude of the shift of this shoulder or wing of the exciting line.

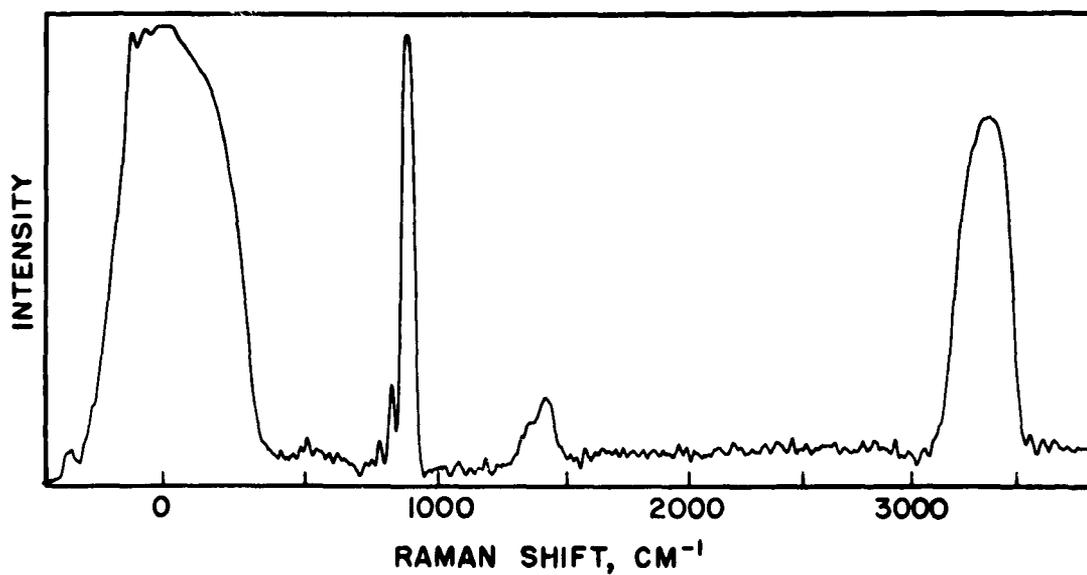
The 4358 Å mercury line used for excitation of the spectrum shown in Figure 16 is in fact a very closely spaced triplet. Evidence of this may be seen in the shape of the 880 cm⁻¹ shift. One other complication occurs with the 4358 Å excitation: there are several weak mercury lines removed some 2800 to 2900 wave numbers from 4358 Å. On long exposure the Rayleigh scattering* of such lines may become apparent even with efficient filtering. Some question might therefore arise regarding the origin of the Raman shift apparent at 2815 cm⁻¹ in Figure 16a. The results of the Raman spectroscopy of solutions described below appear to substantiate the conclusion that the shift at 2815 cm⁻¹ is real.

The record of the Raman spectrum of solutions of hydrogen peroxide in water at room temperature and near the freezing point, chiefly 30 and -40°, obtained by Taylor is summarized in

* Rayleigh scattering is that scattering by matter of molecular dimensions of incident radiation which occurs without change in wavelength.



a - HEAVY EXPOSURE TO SHOW WEAK BANDS AT 525 CM^{-1} AND 2800 CM^{-1}



b - NORMAL EXPOSURE

FIG. 16 - THE RAMAN SPECTRUM OF 99% LIQUID HYDROGEN PEROXIDE AT -40°C

TABLE 52

RAMAN SHIFTS OBSERVED IN 99.3 WT. % LIQUID HYDROGEN PEROXIDE,
FROM TAYLOR (148)

| Exciting Radiation, Wavelength, Å | Temperature, °C | Raman Shift, $\Delta\sigma$, cm^{-1} | Band Width at base, cm^{-1} |
|--------------------------------------|--------------------|---|---|
| 4358 | 30 | 880 | (s) |
| " | " | 1400 | 260 |
| " | " | 3411 | 470 |
| 4046 | " | 879 | (s) |
| " | " | 1397 | 250 |
| " | " | 3417 | 500 |
| 4358 | -40 | 525 | - |
| " | " | 882 | (s) |
| " | " | 1402 | 300 |
| " | " | 2815 | - |
| " | " | 3364 | 530 |
| 4046 | " | 879 | (s) |
| " | " | 1415 | 190 |
| " | " | 3382 | 470 |

Table 53 and the photometer traces of the spectrum in the 3000 cm^{-1} region obtained for solutions at -40° are shown in Figure 17. In order to eliminate as far as possible apparent changes in the position of the band maxima caused by differences in plate density, the tracings of Figure 17 were chosen from spectra in which the intensities of the 3400 cm^{-1} shift were approximately the same. Recordings at -8 and -25°C were necessitated by the failure of the solutions of 1:9 and 1:4 mole ratio of hydrogen peroxide to water to supercool to -40°C .

Two results of particular interest are brought out by the data of Table 53 and Figure 17: the definite occurrence of a Raman shift of about 2800 cm^{-1} and the splitting of the 3400 cm^{-1} shift into two components as dilution increases. Some uncertainty regarding the existence of the 2800 cm^{-1} shift might exist because of the fact that with 4358 Å excitation there occur mercury lines removed 2784 and 2866 cm^{-1} from the exciting line. The possibility of confusion from this fact was eliminated by Taylor through the expedient of determining the Raman spectrum excited by 4046 Å

TABLE 53
RAMAN SHIFTS OBSERVED IN LIQUID HYDROGEN PEROXIDE-WATER SOLUTIONS,
FROM TAYLOR (148)

| Mole Ratio H_2O_2/H_2O | Temperature $^{\circ}C$ | Raman Shift, ΔS , cm^{-1} | | | | | |
|-----------------------------|----------------------------|-------------------------------------|-------------------|----------------------|-------------------|-------|------|
| | | Region: 800 cm^{-1} | 1400 cm^{-1} | 1650 cm^{-1} ** | 2800 cm^{-1} | | |
| 8:1 | 30 | 800 | 1396 | -- | 2800b | -- | 3403 |
| 9:2 | -40 | 880 | 1411 | -- | 2850b | -- | 3373 |
| 4:1 | 30 | 881 | 1406 | -- | -- | -- | 3406 |
| 2:1 | -40 | 881 | 1422 | 1625 | 2840b | -- | 3377 |
| 3:2 | 30 | 878 | 1416 | 1650b | 2815b | -- | 3418 |
| 1:1 | -40 | 879 | 1431 | 1630 | 2825b | -- | 3395 |
| 1:1* | -40 | 877 | 1427b | -- | 2835 | 3207b | 3405 |
| 0.85:1 | 30 | 878 | 1430b | 1617b | 2815b | -- | 3430 |
| 1:2 | -40 | 879 | 1465b | 1638 | 2845b | 3260b | 3412 |
| 1:3 | 30 | 878 | 1445b | 1670b | -- | -- | 3430 |
| 1:4 | -25 | 878 | 1455b | 1640 | 2805b | 3240b | 3417 |
| 2:15 | 30 | 878 | 1450b | 1610b | -- | 3270 | 3430 |
| 1:9 | -8 | 878 | 1445b | 1630b | 2810b | 3345b | 3417 |
| 1:28 | 30 | 878 | 1440b | 1665b | -- | 3290b | 3429 |

b: Broad diffuse band, impairing accuracy of location.

* Exciting wavelength was 4046 \AA ; for all others the exciting wavelength was 4358 \AA .

** The 1650 cm^{-1} shift is due to water.

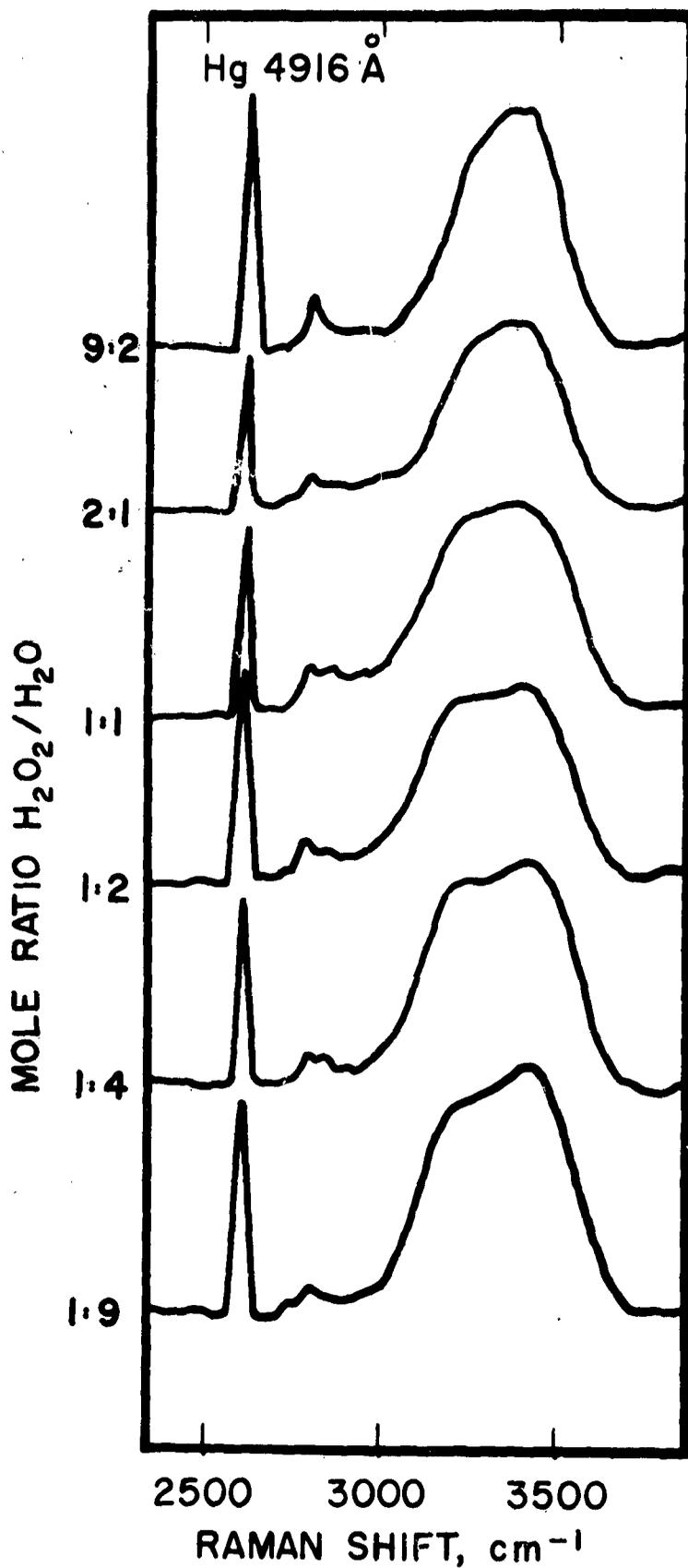


FIG. 17- THE OH BAND IN THE RAMAN SPECTRUM OF HYDROGEN PEROXIDE-WATER SOLUTIONS AT -40°C

radiation in a 1:1 mole ratio hydrogen peroxide-water solution. Here the region of the spectrum removed 2800 - 2900 cm^{-1} from the exciting line is completely free of Rayleigh scattering and the presence of the 2800 cm^{-1} shift in the solution was quite adequately confirmed.

The study of the Raman scattering produced by solid, nearly anhydrous hydrogen peroxide made by Taylor provides definite evidence of the 2800 cm^{-1} shift and shows sharp division of the 3400 cm^{-1} shift into two peaks. One experiment was carried out with a mass of fairly large crystals chiefly oriented so that the spectrum was observed looking along the longest axis of the crystals. The presence of the many crystal faces caused considerable reflection into the spectrograph with the result that any Raman scattering was obliterated which might have occurred in the region removed up to 2400 cm^{-1} from the exciting line. Beyond this region the spectrum was clear except for the enhanced intensity of certain of the mercury lines. The 3400 cm^{-1} Raman shift was clearly observed and found to occur as two lines with distinctly separated maxima. Comparison was made of the unfiltered mercury spectrum and the Raman spectrum of the solid to make sure that this splitting was real and not due to the appearance at this point of an enhanced mercury line. The Raman shifts for the mass of crystals observed by Taylor, using 4358 \AA radiation for excitation, may be summarized: at -10°C , maxima occurred at 3200 and 3334 cm^{-1} ; at -40°C , maxima occurred at 3198 and 3328 cm^{-1} .

The intermediate Raman shifts were observed by Taylor in the spectrum at -20°C obtained with a somewhat imperfect, single crystal. Sufficient reflected light was present to prevent detection of shifts of less than 600 cm^{-1} and to obscure details in the region between 600 and 2000 cm^{-1} , but the following shifts were clearly observed: 878 \pm 0.5, 1408 \pm 10, 2790 \pm 20, 3203 \pm 3, and 3331 \pm 4 cm^{-1} .

It is recommended that the data of Taylor (148) be accepted to establish the Raman spectrum of hydrogen peroxide. The discussion above should be referred to for details regarding the

effects of changes of temperature, phase, concentration, and wavelength of exciting line, but the shifts occurring in the anhydrous liquid may be summarized as 880, 1400, 2810 and 3410 cm^{-1} . As discussed in the chapter dealing with structure, the shift of 3410 cm^{-1} is believed to be composed of two fundamentals which overlap or coincide. This shift seems to be the most affected by concentration changes and by going from the liquid to the solid state. The most prominent Raman shifts occurring in water lie at $\Delta\sigma = 1650$ and 3400 cm^{-1} ; the many others which have been reported are tabulated by Dorsey (2).

The effect of the addition of alkali to hydrogen peroxide solutions upon Raman scattering was studied by Simon and Marchand (149). It was found that the presence of the alkali (hydroxides of lithium, sodium, and potassium but not ammonium hydroxide) caused the appearance of a Raman shift of 844 cm^{-1} in addition to the one occurring at 880 cm^{-1} . Complete neutralization brought disappearance of the shift at 880 cm^{-1} , leaving only that at 844 cm^{-1} . Giguère and Bain (150) were unable to detect this change in the infrared spectrum.

The Visible Spectrum

Hydrogen peroxide is generally stated to be colorless, and, indeed, it cannot be determined by visual inspection whether a flask contains anhydrous hydrogen peroxide, a solution of hydrogen peroxide in water, or water alone unless decomposition or reaction is occurring. In an early study of the absorption of visible radiation by various fluids it was stated, with qualifications, by Russell and Lapraik (151) that some absorption of the orange occurred in 6 wt. % hydrogen peroxide. If real, this was undoubtedly due to impurities, and it is believed that it may be stated for practical purposes that, as with water, hydrogen peroxide and its water solutions are transparent for radiation to which the eye is sensitive, i.e., having a wavelength between 4000 and 8000 Å. The limits of the region of non-absorption beyond the visible are not well defined on the infrared side; on the ultraviolet side it may be said that absorption begins to become appreciable very near the edge of the visible as reference to Figure 18 will show.

The Rayleigh scattering of visible radiation by concentrated hydrogen peroxide was studied by Spring (152). By observing the color of daylight reflected through a column of hydrogen peroxide and comparing this color with various copper sulfate solutions, Spring determined that nearly anhydrous hydrogen peroxide, acquired a color, through scattering, described as blue with a nuance of green, which was similar to but more intense than that observed in water. Spring found that when bubbles were being generated within the hydrogen peroxide the color was yellow to green.

Long columns of large containers of hydrogen peroxide in which the rather weak phenomenon of scattering may be observed are seldom encountered, but it appears from casual observation that Spring's conclusions may be well founded. On peering into a drum of concentrated hydrogen peroxide one obtains a definite impression of a weak, green to blue hue. This is undoubtedly influenced to some extent by the properties of the aluminum container wall, by bubbles in the liquid, and by the possible presence of suspended matter, but it seems reasonable to conclude that hydrogen peroxide may possess much the same scattering properties that water does. Dorsey (2) discusses this subject and the misunderstanding of it in some detail.

Ultraviolet Absorption Spectrum

In the course of his now-classical research in spectroscopy, it was determined by Hartley (153) that radiation in the ultraviolet of wavelength less than 2925 Å was completely absorbed in a hydrogen peroxide solution of concentration less than 1 wt. %. Interest in determining the applicability of the Einstein law of photochemical equivalence compelled Tian (154) and Henri and Wurmsler (155) to make the first quantitative measurements of the relative absorptive power of hydrogen peroxide for ultraviolet radiation of various wavelengths. Similarly, Resanov (156) determined the range of absorption of 3 wt. % hydrogen peroxide to lie between 3120 and 2480 Å in his study of the formation of hydrogen peroxide by the action

of radon on water. The ultraviolet absorption spectrum of hydrogen peroxide in the liquid and vapor states has now been investigated for the wavelength range lying between the edge of the visible near 4000 \AA up to the edge of the Schumann region near 2000 \AA . A summary of these investigations is given in Table 54.

The absorption of ultraviolet radiation by hydrogen peroxide results in dissociation of the molecule. This dissociation is discussed in Chapter 8, Decomposition Processes, but it may be stated here that the primary photochemical process results in the production of two OH radicals, although other reactions are possible and may occur to a smaller extent. The absorption spectrum is thus a continuous one as shown by Figure 18, where the data of the investigators listed in Table 54 is presented in terms of the molecular extinction coefficient.

Figure 18 shows that there is agreement within about 10% among the various data. The outstanding exceptions are the data of Urey, Dawsey, and Rice (101) and Fergusson, Slotin, and Style (163). In both of these cases, measurements were made of the absorption by the vapor. In one case (101) measurements were also made with the liquid and the results found to coincide, indicating no difference in the absorption by the two phases. In the other case (163) only the vapor was studied and the results were taken to indicate a difference in the absorptivity of the two phases. No particular reason is evident for the departure of these results, particularly those of Urey, Dawsey, and Rice at longer wavelengths, from the other results; both interpreted photographic records visually. It should be noted that work with the vapor involves additional difficulty in the accurate establishment of concentration. At the shorter wavelengths, too, the large absorption coefficients require the use of low concentrations or short absorption cells. Difficulty due to photochemical decomposition has not, however, been mentioned as severe. In only one investigation (164) has the small correction been made for the absorption by water.

TABLE 54

SUMMARY OF INVESTIGATIONS OF THE ULTRAVIOLET
ABSORPTION SPECTRUM OF HYDROGEN PEROXIDE

| Reference | Phase | Concentration H ₂ O ₂ | Wavelength, Å | Recording Method** |
|------------------------------------|-------|--|------------------|-----------------------|
| Henri and Wurmser (155) | L | 0.06% | 2980-2144 | -- |
| Kornfeld (157) | L | 0.04 to 0.8% | 3600, 3110 | T |
| Lederle and Rieche* (158) | L | -- | 3500-2000 | -- |
| Urey, Dawsey and Rice (101) | L | 0.02 to 0.6% | 3750-2150 | PG, V |
| " | V | 1.5 mm at 20° | 2750-2150 | " |
| Allmand and Style (159) | L | 0.02 to 35% | 3650-2540 | T |
| Sharma (160) | L | 3, 10, 30% | -- | -- |
| Bredig, Lehman and Kuhn* (161) | L | 0.2 to 5% | 3300-2400 | -- |
| Frost and Oldenberg (162) | V | 0.01 mm | 2900-2200 | PG |
| Fergusson, Slotin and Style* (163) | V | 10 ⁻⁶ mole/l | 2537 | PG, V |
| Holt, McLane and Oldenberg* (164) | L | -- | 2537-1850 | PC |
| " | V | -- | 3100-2100 | PG, PM, PC |
| Egerton, Harris and Young (165) | L | 0.0007 to 1% | 2260-2150 | -- |
| " | V | 5 to 20 mm | 2536 | -- |
| McLane (166) | V | 2 mm | 3800-2700 | PC |
| Taylor and Cross (167) | V | 50, 90% | 2100-2000 | PG, PM |
| Edse (168) | V | 2 mm | 4300-3000 | -- |
| Phibbs and Giguère (169) | L | 6, 55, 99% | | PC |

* Graphic presentation of results only

** T = thermopile, PG = photographic, V = visual interpretation, PC = photoelectric cell, PM = photometric interpretation

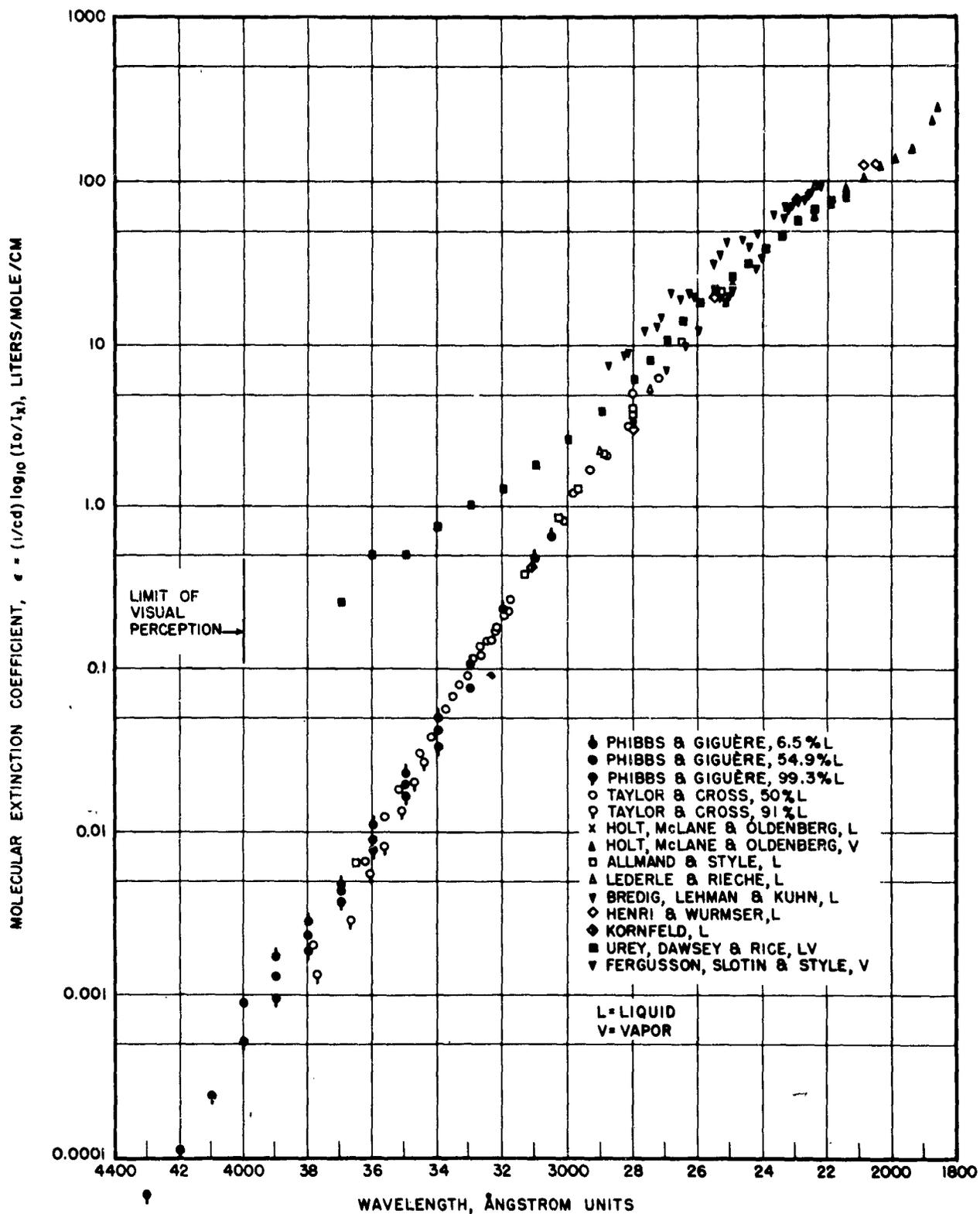


FIGURE 18 — ULTRAVIOLET ABSORPTION SPECTRUM OF HYDROGEN PEROXIDE-WATER SOLUTIONS

It is concluded that the absorption coefficient for both the liquid and vapor phases is the same within the precision of the results presently available. It is possible that a small difference exists, however, since recent data show that Beer's law is not obeyed by the solutions, a result believed (169) to be caused by the variations with concentration in the state of molecular association in the liquid. The data accepted here to establish the extinction coefficient for hydrogen peroxide vapor are those of Holt, McLane and Oldenberg (164). Aside from the results (101, 163) discussed above these are the only quantitative data available regarding absorption by the vapor. Others have made qualitative statements as follows: Frost and Oldenberg found that hydrogen peroxide vapor at a pressure as low as 0.01 mm could be detected in a 150 cm absorption cell at 2537 Å on the basis of the data of Urey, Dawsey, and Rice; Egerton, Harris, and Young (165) measured the wavelength at which complete absorption occurred for various concentrations of hydrogen peroxide in the vapor and the liquid, found no difference for the two phases, and stated their results to agree with others (155, 158, 101); McLane (166) found the absorption coefficient of the vapor at 2536 Å to agree within 1.5% of the value given by Holt, McLane and Oldenberg; Edse (168) stated that he confirmed the results of Holt, McLane and Oldenberg in the wavelength region 2100 - 2000 Å.

The shape of the curve relating the extinction coefficient to the wavelength is seen in Figure 18 to be parabolic. Over a considerable range of wavelength near the visible the curve might be represented by a linear relationship on a semilogarithmic plot. Holt, McLane and Oldenberg suggest that a maximum in the absorption curve may well exist at wavelengths much shorter than those which have been investigated. The data of Figure 18 indicate that two points of inflection occur on the curve, one at each of the extremes of the wavelength range investigated. It is believed that further investigation will be necessary before the reality of these inflections can be established. The indication of the presence of an inflection near 1920 Å by the data of Holt, McLane, and Oldenberg (164)

has been taken by Edse (168) to confirm the statement by Sharma (160) that a "sharp cut" exists in the absorption spectrum at 2055 Å. Sharma made this statement after an investigation of the absorption by 3 to 30% liquid hydrogen peroxide, but the meaning of the term "sharp cut" was not defined and no absorption coefficients were measured. There is no theoretical reason for the existence of a discontinuity or abrupt change in slope in the absorption curve (if this is taken to be the meaning of "sharp cut"), and the presently available data do not form an adequate basis for the demonstration of the occurrence of either a discontinuity or an inflection in the absorption curve.

The work of Taylor and Cross (167) and Phibbs and Giguère (169) has extended knowledge of the absorption coefficients to the range of concentration up to anhydrous hydrogen peroxide. These results show that Beer's law is not strictly obeyed by hydrogen peroxide solutions. As the concentration of hydrogen peroxide is increased the solutions are found to absorb to a greater extent than Beer's law would predict. This is shown in Figure 18 by the decrease of the molecular extinction coefficient with increasing hydrogen peroxide concentration. This decrease appears to be directly proportional to the hydrogen peroxide concentration. This departure from Beer's law cannot be demonstrated at wavelengths shorter than 3400 Å, since with the exception of the work of Taylor and Cross, the relatively large absorption encountered at the shorter wavelengths has not encouraged work with solutions more concentrated than 5 wt. %. The absorption coefficients observed by Taylor for 50 wt. % hydrogen peroxide in the region 3400 to 2700 Å do not differ, within the precision of the data, from the values obtained for more dilute solutions by others. It is concluded that the magnitude of the departure from Beer's law is less than the uncertainty in the accuracy of the absorption coefficients for solutions less concentrated than about 50 wt. %. This is further illustrated by the data of Allmand and Style (159), whose data at 3650 Å show no significant change in absorption coefficient for measurements on solutions up to 35 wt. % hydrogen

peroxide. In Table 55 are presented average values of the molecular extinction coefficient taken from Figure 18 and which may be used as a general guide. The one value at 2537 Å determined with a photoelectric cell by Holt, McLane and Oldenberg (164) and checked by McLane (166) is perhaps the best established value and at a convenient wavelength for analytical work* with dilute solutions or vapors.

TABLE 55

MOLECULAR EXTINCTION COEFFICIENTS FOR
ULTRAVIOLET RADIATION FOR LIQUID AND
VAPOR HYDROGEN PEROXIDE - WATER SOLUTIONS

| Wavelength, Ångstrom Units | Molecular Extinction Coefficient* ϵ , liters/mole cm |
|----------------------------|--|
| 4000 | 0.00066 |
| 3800 | 0.0022 |
| 3600 | 0.010 |
| 3400 | 0.47 |
| 3200 | 0.22 |
| 3000 | 1.0 |
| 2800 | 4.2 |
| 2600 | 13. |
| 2537 | 19.6 \pm 0.3 |
| 2400 | 35. |
| 2200 | 76. |
| 2000 | 140. |

* $\epsilon = (1/cd) \log (I_0/I_x)$. With the exception of the value for 2537 Å (164) these are average values interpolated from Figure 18 and do not represent the results of any one investigator.

The effect upon the absorption of ultraviolet radiation by hydrogen peroxide solutions brought about by the addition of alkali has been investigated by Lederle and Rieche (158) and by Bredig, Lehman, and Kuhn (161). It was found that the presence of alkali shifts the absorption curve toward the visible, i.e., increases the absorption coefficient. Bredig, Lehman and Kuhn varied the molecular ratio of sodium hydroxide to hydrogen peroxide from 0 to 11.2 in hydrogen peroxide solutions of 0.2 to 5 wt. % and found the shift in absorption coefficient to be nearly directly proportional

* The application of ultraviolet absorption by hydrogen peroxide to analysis has been described by Giguère in U.S. Patent 2,617,940 (Nov. 11, 1952).

to this molecular ratio up to a value of one. The shift is thus interpreted to be caused by the neutralization of hydrogen peroxide and to show that absorption by perhydroxyl ion, O_2H^- , is more intense than by hydrogen peroxide.

For the first neutralization step, i.e., at the ratio $(NaOH)/(H_2O_2) = 1$, a given value of the molecular extinction coefficient was obtained at a wavelength approximately 500 Å longer than the wavelength at which the same value of the coefficient is obtained with hydrogen peroxide solution without added alkali. There is some indication in the results of Bredig, Lehman, and Kuhn that the absorption continues to shift slightly as the molecular ratio is increased above one. This continued shift, which might be ascribed to the second neutralization of hydrogen peroxide, is relatively much smaller and of doubtful certainty. Sodium hydroxide solution alone does not absorb the ultraviolet under the conditions studied.

Emission Spectra in Hydrogen Peroxide Vapor

Urey, Dawsey and Rice (101) illuminated nearly anhydrous hydrogen peroxide vapor at a pressure of one millimeter of mercury with filtered radiation from a zinc spark and observed the presence of the 3064 Å water band (due to OH radical) in fluorescence.* This was interpreted to indicate simultaneous dissociation of hydrogen peroxide and excitation of hydroxyl radical. Oldenberg (170) has suggested that this interpretation of the experiment is not unique and that particles in addition to hydroxyl radical may be produced.

The effect of an electric discharge in hydrogen peroxide was also studied by Urey, Dawsey and Rice. On passing an uncondensed discharge in a cooled tube through which nearly anhydrous hydrogen

* A blue-green fluorescence of liquid hydrogen peroxide was observed by Allmand and Style (159). This was caused by impurities derived from the wax lining of the container. The fluorescence diminished and disappeared after continued insolation, with a concomitant rise in decomposition rate.

peroxide vapor was streamed rapidly, a faint blue color was observed. Spectroscopic examination showed this to be a continuous spectrum, showed atomic and molecular spectra of hydrogen to be absent, and demonstrated the presence of the water bands at high intensity. Frost and Oldenberg (171) found the emission by OH radicals in hydrogen peroxide vapor subjected to the discharge to be much stronger than the OH emission found in water vapor. The rate of disappearance of OH, as determined by absorption, was much faster in hydrogen peroxide than in water. The reactions to be observed in hydrogen peroxide vapor subjected to the electric discharge have been studied by Batzold, Luner, and Winkler (57).

X-Ray and Electron Diffraction by Hydrogen Peroxide

The diffraction of x-rays by crystalline hydrogen peroxide has been studied for the purpose of determining structural parameters by Feher and Klotzer (172), Natta and Rigamonti (54), Lu, Hughes, and Giguère (173), and Abrahams, Collin, and Lipscomb (12). The work of Feher and Klotzer and Abrahams, Collin, and Lipscomb was conducted with anhydrous hydrogen peroxide. Natta and Rigamonti studied concentrations of 82 and 90 wt. % and the compound $H_2O_2 \cdot 2H_2O$. Crystals of the addition compound urea hydroperoxidate, $CO(NH_2)_2 \cdot H_2O_2$ were used in the work of Lu, Hughes, and Giguère. Each of these papers presents photographs, tables of coordinates, dimensions and structure factors, or electron density maps calculated from the observed diffraction patterns.

Randall (174) has studied the scattering of x-rays by liquid anhydrous hydrogen peroxide. Electron diffraction by hydrogen peroxide vapor has been studied by Giguère and Schomaker (175).

Little that is useful can be given in the way of original data obtained in diffraction studies. The valuable result is the establishment of the dimensions and organization of the hydrogen peroxide molecule; these properties are discussed in the following chapter on structure.

THE PHYSICAL PROPERTIES OF MULTICOMPONENT SYSTEMS CONTAINING HYDROGEN PEROXIDE

Some physical properties of a few systems composed of hydrogen peroxide and substances other than water or in addition to water have been measured. These might be regarded as systems in which hydrogen peroxide or its water solutions play the part of solvent.

It cannot be emphasized too strenuously that the addition of substances other than water to hydrogen peroxide introduces the potential hazard of explosive decomposition or detonation. Inorganic additives may react with hydrogen peroxide or catalyze its decomposition at an explosive rate, sometimes after a deceptive induction period. Organic additives are capable of forming with hydrogen peroxide over wide ranges of composition, mixtures which can be detonated with a violence comparable to that of TNT. For example, the practice of concentrating hydrogen peroxide by ether extraction, much used in earlier times, has resulted in serious accidents (152). Suitable precautions should therefore be taken in handling such mixtures.

References to the available data on the physical properties of these mixtures are given in Table 56. Space does not permit the presentation of all the data. A number are of doubtful precision, and it should be borne in mind that the substances listed are the substances mixed with the hydrogen peroxide; in many cases immediate or ultimate reaction occurs between hydrogen peroxide and these substances, and the measured properties may be due to a different substance than that listed as the additive.

The purpose of most of these measurements has been to establish the solubility relationships of the various substances and hydrogen peroxide. Hydrogen peroxide and its water solutions possess, in general, the same solvent or solute relationships that water alone possesses. Important differences exist, but these have not been organized into a general scheme whereby the difference can be predicted. For example, the salts sodium flu-

TABLE 56

REFERENCES TO PHYSICAL PROPERTIES OF MULTICOMPONENT
SYSTEMS CONTAINING HYDROGEN PEROXIDE

| Substance | Freezing Point | Conductivity | Distribution Coefficient ⁶ |
|---------------------------------------|-----------------|-------------------------|---------------------------------------|
| Sodium Chloride | (121) | (176) | -- |
| Potassium Chloride | (9, 177, 178) | (112) | -- |
| Sodium Chlorate | -- | (109) | -- |
| Sodium Nitrate | (121, 178, 179) | (176) | -- |
| Potassium Nitrate | (177, 178) | (109) | -- |
| Sodium Fluoride | (9) | -- | -- |
| Sodium Sulfate | (121) | -- | -- |
| Potassium Sulfate | (180, 9) | -- | -- |
| Ammonium Sulfate | (177) | -- | -- |
| Potassium Peroxysulfate | (180) | -- | -- |
| Vanadium Salts | -- | (181) | -- |
| Ammonia | (121) | -- | -- |
| Hydroxides of Li, Na, K, Rb and Cs | -- | (110, 111) | -- |
| Sulfuric acid (sulfur dioxide) | (9, 177, 182) | (176) | -- |
| Nitric Acid | -- | (183, 176) | -- |
| Hydrochloric Acid | -- | (176) | -- |
| Perchloric Acid | -- | (176) | -- |
| Phosphoric Acid | -- | (176) | -- |
| Boric Acid | -- | (184) | -- |
| Formic Acid | -- | (185, 186) | -- |
| Acetic Acid | (182) | (112, 185, 186, 176) | -- |
| Trichloroacetic Acid | -- | (176) | -- |
| Propionic Acid | -- | (185, 186) | -- |
| Glycolic Acid | -- | (185) | -- |
| Oxalic Acid | (177) | -- | -- |
| Succinic Acid | -- | (186) | -- |
| Tartaric Acid | -- | (176) | -- |
| Citric Acid | -- | (176) | -- |
| Methyl Alcohol ¹ | (9) | -- | -- |
| Ethyl Alcohol ¹ | -- | -- | -- |
| Isobutyl Alcohol | -- | -- | (187) |
| Amyl Alcohol | -- | -- | (110, 111, 184, 188, 189, 190) |
| Acetone ¹ | -- | -- | -- |
| Chloroform | -- | -- | (187) |
| Ethyl Ether ^{1,2,3,4,5} | (9) | -- | (191, 192, 187, 188, 121) |
| Dioxane ^{3,4} | -- | -- | -- |
| Benzene | -- | -- | (187, 193, 121) |
| Nitrobenzene | -- | -- | (187) |

TABLE 56 (cont.)

| Substance | Freezing Point | Conductivity | Distribution Coefficient ⁶ |
|---------------------|----------------|--------------|---------------------------------------|
| Phenol | -- | -- | (187) |
| Aniline | -- | -- | (187) |
| Dimethylaniline | (9) | -- | -- |
| Piperidine | (9) | -- | -- |
| Diethylamine | (9) | -- | -- |
| Mono-n-butylamine | (9) | -- | -- |
| Tert-monobutylamine | (9) | -- | -- |
| Di-iso-butylamine | (9) | -- | -- |
| Tripropylamine | (9) | -- | -- |
| Sugar | (121) | -- | -- |
| Isoprene | -- | -- | (193) |
| Quinoline | -- | -- | (187) |
| Acetophenone | -- | -- | (187, 190) |
| Amyl Acetate | -- | -- | (187) |
| Propyl Formate | -- | -- | (187) |
| Iso amyl propionate | -- | -- | (187) |
| Propyl Butyrate | -- | -- | (187) |
| Ethyl-iso-valeriate | -- | -- | (187) |
| Iso-butyl butyrate | -- | -- | (187) |

1. Diffusivity of hydrogen peroxide in these substances measured by Stern (41)
2. Density of mixtures with hydrogen peroxide measured by Linton and Maass (117, 118)
3. Dielectric constant of mixtures with hydrogen peroxide measured by Linton and Maass (117, 118)
4. Effect of hydrogen peroxide on Raman spectrum determined by Simon and Feher (194)
5. Ultraviolet absorption spectrum of mixtures with hydrogen peroxide measured by Rieche and Sauthoff (195)
6. The distribution of hydrogen peroxide was measured between the solvents listed and either water or solutions of various salts or acids in water.

oxide, potassium chloride, and sodium or potassium sulfate are reported to be more soluble in hydrogen peroxide than in water whereas the salts sodium or potassium nitrate, sodium chloride, and silver nitrate are reported less soluble. Conductivity measurements indicate that the salts dissociate as in water, but the conductivity of acids in hydrogen peroxide is lower than in water, presumably indicating that the mobility of the hydrogen ion is lower in hydrogen peroxide than in water. Conductivity measurements have also been used as an indication of the reaction of acids or salts with hydrogen peroxide to form peroxy compounds. Evidence is given for the occurrence of a number of hydrogen peroxide addition compounds. Sulfuric acid, sodium sulfate, ammonia, and a number of amines were found to form hydroperoxides. Others of course exist, but phase diagrams have not been presented in the literature. Measurements of the solubility of hydrogen peroxide in organic substances show ether* and benzene to be practically insoluble in anhydrous hydrogen peroxide, and that methyl alcohol depresses the freezing point of hydrogen peroxide less than that of water. Hydrogen peroxide shows a relatively larger solubility in ether,* amyl alcohol, and quinoline than does water.

The properties of hydrogen peroxide-ethyl ether mixtures have received the most attention. Hydrogen peroxide and ether form non-ideal solutions with complete miscibility only above 80°C (critical solution temperature). Linton and Maass (117, 118) measured the density of hydrogen peroxide-ether and hydrogen peroxide-water-ether mixtures at 0 and 10°C. There is a volume decrease and an appreciable heat evolution on mixing hydrogen peroxide and ether. The dielectric constants of hydrogen peroxide and ether were found to be additive on forming solutions and represented by the formula

$$\epsilon = 4.6 + 0.608 c_{H_2O_2} \quad (70)$$

* These statements, apparently conflicting, refer of course to the conjugate solutions shown on the two different sides of the temperature-composition diagram for the hydrogen peroxide-ether system.

Stern (41) found the diffusion rate of hydrogen peroxide in ether to be enhanced over the rate in water, with a diffusion coefficient for 0.1 N hydrogen peroxide in ether at 20°C of 2.407 cm² per day. Simon and Feher (194) found the presence of hydrogen peroxide to change the Raman spectrum of methyl ether. The ultraviolet absorption spectrum of hydrogen peroxide in ether solution was found by Rieche and Sautheff (195) to be displaced somewhat toward the visible compared with that found in water solution.

THE PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE OF OTHER THAN NATURAL ISOTOPIC COMPOSITION

The mass and abundance of the isotopes of hydrogen and oxygen are shown in Table 57. Since both hydrogen and oxygen are relatively light atoms, a change in isotopic composition of a hydrogen peroxide molecule makes a relatively large percentage change in molecular weight. However, because the heavier isotopes are naturally present only in very small proportions, a sample of naturally-occurring hydrogen peroxide must be enriched many-fold in the heavier isotopes in order to increase the average molecular weight of a mixture significantly. The possibility of such enrichment during manufacture (as in the electrolysis or distillation) appears to be negligible.

Preparations of hydrogen peroxide having isotopic composition of both hydrogen and oxygen varying from the natural composition have been made. Hydrogen peroxide enriched in heavy oxygen (principally O¹⁸, since O¹⁷ is less abundant) to the extent of a few percent has been prepared and applied to studies of reaction mechanism, but no physical properties have been measured. Oxygen is not exchanged between hydrogen peroxide and water (196). Hydrogen, on the other hand, exchanges quickly and completely between hydrogen peroxide and water (197), making the preparation of enriched hydrogen peroxide by the solution of hydrogen peroxide in heavy water a simple process. This procedure has been applied to the study of the effect of deuterium on the reactions of hydro-

TABLE 57
 MASS AND ABUNDANCE OF ISOTOPES OF HYDROGEN AND OXYGEN

| Isotope | Atomic Number | Physical* Atomic Mass (198) | Abundance** Atom Fraction (199, 200) | Half-Life (201) |
|-----------------|---------------|-----------------------------------|--|--------------------|
| H ¹ | 1 | 1.00812 | 0.99985 | stable |
| H ² | 1 | 2.01471 | 0.00015 | stable |
| H ³ | 1 | 3.01402 | 10 ⁻¹⁸ | 10-12 yrs |
| O ¹⁴ | 8 | 14.013 | -- | 76 sec |
| O ¹⁵ | 8 | 15.0078 | -- | 2 min |
| O ¹⁶ | 8 | 16.0000 | 0.99759 | stable |
| O ¹⁷ | 8 | 17.0045 | 0.00037 | stable |
| O ¹⁸ | 8 | 18.0049 | 0.00204 | stable |
| O ¹⁹ | 8 | 19.0139 | -- | 30 sec |

* The ratio, physical scale/chemical scale = 1.000275 (202)

** Abundance may vary with source (203); for oxygen, abundances cited are for that derived from the atmosphere. The value for H³ represents the equilibrium between the continual formation and decay.

gen peroxide, but it is obviously not well suited for the study of physical properties, since there results a mixture of the species: H₂O, HDO, D₂O, H₂O₂, HDO₂, and D₂O₂. For the study of physical properties deuterium peroxide must therefore be prepared by more laborious procedures; these are described by Feher (204) (via peroxydisulfate) and Giguère, Secco, and Eaton (205) (via electric discharge in heavy water vapor). With anhydrous D₂O₂ at hand a mixture of HDO₂ with deuterium and hydrogen peroxides may be easily obtained through the exchange H₂O₂ + D₂O₂ = 2HDO₂. Feher (206) concluded that the equilibrium constant for this reaction was about four; thus an equimolar mixture of hydrogen and deuterium peroxides yields hydrogen, deuterium, and hydrogen-deuterium peroxides in the concentration ratio 1:1:2. The physical properties given below are, with one exception, for deuterium peroxide, D₂O₂, either anhydrous or in solution with heavy water, D₂O.

The density of deuterium peroxide solutions at 18°C was estimated by Feher (204), assuming D_2O_2 has the same molal volume as that of hydrogen peroxide. Feher then applied a microhydrometer technique to determine concentrations through use of these calculated densities. The density of deuterium peroxide at 0 and 20°C was measured directly by Phibbs and Giguère (27), using a pycnometer. These results, obtained with solutions containing less than 0.25% ordinary hydrogen, are given in Table 58. Measurements were also made by Phibbs and Giguère, using the same preparation of deuterium peroxide, of the refractive index (precision-Abbé refractometer), viscosity (Ostwald viscometer), and surface tension (capillary rise method). These results are given in Table 58.

The solid-liquid phase diagram of the deuterium peroxide-heavy water system has been determined by Giguère and Secce (207). Their freezing point curve, obtained by thermal analysis with samples containing less than 0.3% ordinary hydrogen, is represented by the data given in Table 59. This freezing point curve for the deuterium system lies parallel to and displaced vertically above that for the ordinary hydrogen system approximately as follows: on the water rich side, 4°C higher; between the eutectics, 0.6°C higher; on the hydrogen peroxide rich side, 2°C higher. The extrapolated value for the freezing point of anhydrous deuterium peroxide is found to be 1.6°C. The deuterium peroxide solutions were found to supercool even more markedly than those of ordinary hydrogen peroxide. On being cooled to liquid air temperatures a transparent glass could be formed of deuterium peroxide-rich solutions. At a time of about ten minutes after its formation the glass would revert to the crystalline form, the crystallization being accompanied by expansion.

Some thermodynamic properties of deuterium peroxide were measured by Morissette and Giguère (73). The values for the heat capacity of deuterium peroxide-heavy water solutions

TABLE 58

DENSITY, REFRACTIVE INDEX, VISCOSITY, AND SURFACE TENSION OF DEUTERIUM PEROXIDE SOLUTIONS,
FROM PHIBBS AND GIGUÈRE (27)

| Weight % | Conc. D ₂ O ₂ Mole Fraction | ρ , (g/ml) | | n _D 25°C | Viscosity, μ , centipoises | | Surface Tension, dynes/cm | |
|-------------------|--|--------------------|--------------------|------------------------|-----------------------------------|-------------------|------------------------------|------|
| | | 0°C | 20°C | | 0°C | 20°C | 0°C | 20°C |
| 0.00 | 0.0 | 1.104 ₆ | 1.105 ₆ | 1.32806 | 2.350 | 1.24 ₄ | 76.1 | 73.3 |
| 9.05 | 0.0524 | 1.141 ₄ | 1.137 ₀ | 1.3340 | 2.23 ₀ | 1.25 ₅ | 76.5 | 73.5 |
| 20.02 | 0.1222 | 1.185 ₇ | 1.178 ₀ | 1.3414 | 2.18 ₄ | 1.26 ₈ | 77.0 | 74.1 |
| 33.68 | 0.220 ₃ | 1.244 ₀ | 1.232 ₀ | 1.3510 | 2.18 ₂ | 1.30 ₀ | 77.9 | 75.2 |
| 43.2 ₅ | 0.297 ₉ | 1.286 ₀ | 1.270 ₁ | 1.3579 | 2.19 ₃ | 1.32 ₅ | 78.7 | 75.8 |
| 56.68 | 0.421 ₃ | 1.344 ₇ | 1.328 ₄ | 1.3678 | 2.19 ₂ | 1.37 ₂ | 79.8 | 77.0 |
| 73.78 | 0.610 ₂ | 1.423 ₆ | 1.403 ₃ | 1.3809 | 2.14 ₉ | 1.39 ₇ | 81.4 | 78.7 |
| 91.6 ₅ | 0.859 ₃ | 1.513 ₀ | 1.490 ₈ | 1.3955 | 2.04 ₇ | 1.37 ₉ | 82.7 | 80.0 |

TABLE 59

FREEZING POINT CURVE FOR THE SYSTEM
DEUTERIUM PEROXIDE-HEAVY WATER,
FROM GIGUERE AND SECCO (207)

| Concentration, wt. % D_2O_2 in D_2O | Freezing Point, $^{\circ}C$ | Eutectic |
|--|--------------------------------|--------------------|
| 0.00 | 3.80 ₀ | |
| 11.00 | -3.39 ₀ | |
| 20.6 ₂ | -11.6 ₂ | |
| 30.4 ₆ | -22.3 ₄ | |
| 38.5 ₁ | -35.4 ₁ | |
| 43.5 ₁ | -45.0 ₀ | |
| 44.68 | -47.0 ₀ | -51.3 ₇ |
| 45.8 ₄ | -50.1 ₀ | -51.3 ₂ |
| 46.5 ₁ | -51.5 ₂ | |
| 46.9 ₆ | -51.6 ₂ | |
| 48.8 ₄ | -51.5 ₃ | |
| 50.3 ₅ | -51.6 ₄ | |
| 56.0 ₃ | -53.2 ₈ | -55.1 ₀ |
| 61.1 ₇ | -- | -55.0 ₆ |
| -- | -- | -55.0 ₀ |
| 66.5 ₆ | -43.7 ₆ | |
| 77.5 ₄ | -25.8 ₁ | |
| 94.9 ₇ | -4.33 ₇ | |
| 95.8 ₅ | -3.07 ₀ | |
| 100.0 | 1.60 | |

between 0 and 26.9 $^{\circ}C$ are given in Table 60. These measurements were made in an isothermal diphenyl ether calorimeter using deuterium peroxide prepared from heavy water containing 99.7% D_2O . The total heat of evaporation of a 46.96 wt. % deuterium peroxide solution was similarly measured to be 454.96 cal/g at 26.9 $^{\circ}C$. The thermodynamic functions for deuterium peroxide given in Table 61 have been calculated by Liu and Giguère (208) from the spectroscopic data given in Table 62.

TABLE 60

HEAT CAPACITY OF DEUTERIUM PEROXIDE-HEAVY WATER
SOLUTIONS BETWEEN 0 AND 26.9°C,
FROM MORISSETTE AND GIGUÈRE (73)

| D ₂ O ₂ Concentration in D ₂ O wt. % | mele fr. | Solution Molecular Weight | Heat Capacity | |
|--|----------|------------------------------|---------------|----------|
| | | | cal/mole °C | cal/g °C |
| 0 | 0 | 20.03 | 20.35 | 1.016 |
| 30.46 | 0.1958 | 23.16 | 20.03 | 0.865 |
| 40.7 | 0.2762 | 24.45 | 20.17 | 0.825 |
| 74.2 | 0.6152 | 29.88 | 21.33 | 0.715 |
| 100.0 | 1.0 | 36.03 | 22.75* | 0.632* |

*extrapolated value

The microwave spectrum of D₂O₂ and HDO₂ has been studied by Massey and Bianco (133). More than one hundred absorption lines were observed in the region from 9000 to 40,000 Mc/sec, using a peroxide sample having a D₂O₂ to HDO₂ ratio of about three to one. It was not possible to make isotopic assignment of these lines. A qualitative study of the Stark effect indicated that Stark data might be obtained for about twenty-five of these lines and that transitions of the $|\Delta J| = 0$ type were present as well as those of $|\Delta J| = 1$ type.

The infrared absorption spectrum of deuterium peroxide has been measured by Taylor (141) and by Giguère and Bain (143, 150) and are summarized in Table 63. Taylor observed the spectrum of 82.5 wt. % liquid D₂O₂ at -30°C in a sample containing 8 to 10% ordinary hydrogen over the wavelength range of 3 to 19 microns. The spectrum of D₂O₂ vapor and solid D₂O₂ at -70°C was observed by Giguère and Bain over the range 2 to 25 microns. The rotational structure of the band at 2680 cm⁻¹ in D₂O₂ vapor was resolved by Giguère and Bain (208); eighteen sub-bands were noted.

The Raman spectrum of deuterium peroxide was observed by Feher (209). Raman shifts of 877, 1009, and 2510 cm⁻¹ were ob-

TABLE 61
 THERMODYNAMIC FUNCTIONS FOR DEUTERIUM PEROXIDE VAPOR AT 1 ATMOSPHERE,
 FROM LIU AND GIGUÈRE* (209)

| T °K | $-\left(\frac{F^{\circ} - H_0^{\circ}}{T}\right)$ cal/deg/mole | $\frac{H^{\circ} - H_0^{\circ}}{T}$ cal/deg/mole | S ^o cal/deg/mole | C _P ^o cal/deg/mole | H ^o - H ₀ ^o cal/mole |
|---------|---|---|--------------------------------|---|--|
| 298.16 | (46.36) | (8.26) | (54.62) | (9.34) | (2462) |
| 300 | (46.41) | (8.26) | (54.68) | (9.36) | (2479) |
| 350 | (46.69) | (8.46) | (56.17) | (9.95) | (2962) |
| 400 | (46.85) | (8.68) | (57.53) | (10.50) | (3474) |
| 500 | (50.83) | (9.15) | (59.98) | (11.45) | (4573) |
| 600 | (52.54) | (9.59) | (62.14) | (12.22) | (5757) |
| 700 | (54.05) | (10.02) | (64.07) | (12.88) | (7013) |
| 800 | (55.41) | (10.41) | (65.83) | (13.45) | (8330) |
| 900 | (56.66) | (10.78) | (67.44) | (13.96) | (9701) |
| 1000 | (57.82) | (11.12) | (68.94) | (14.40) | (11120) |
| 1100 | (58.89) | (11.44) | (70.33) | (14.79) | (12580) |
| 1200 | (59.90) | (11.73) | (71.63) | (15.12) | (14076) |
| 1300 | (60.85) | (12.00) | (72.85) | (15.41) | (15602) |
| 1400 | (61.75) | (12.25) | (74.00) | (15.67) | (17156) |
| 1500 | (62.60) | (12.49) | (75.09) | (15.89) | (18735) |
| | | | | | 2680 |
| | | | | | 2700 |
| | | | | | 3275 |
| | | | | | 3882 |
| | | | | | 5188 |
| | | | | | 6588 |
| | | | | | 8061 |
| | | | | | 9590 |
| | | | | | 11162 |
| | | | | | 12780 |
| | | | | | 14435 |
| | | | | | 16104 |
| | | | | | 17802 |
| | | | | | 19527 |
| | | | | | 21252 |

* The numbers in parentheses do not include the contribution of internal rotation.

TABLE 62
MOLECULAR DATA FOR DEUTERIUM PEROXIDE,
FROM LIU AND GIGUERE (208)

| Fundamental Vibrations | Wave Number, cm^{-1} |
|------------------------|-------------------------------|
| ν_1 (a) | 2680 |
| ν_2 (a) | 965 |
| ν_3 (a) | 885 |
| ν_4 (a) | 380 |
| ν_5 (b) | 3680 |
| ν_6 (b) | 947 |

Moments of Inertia, g cm^2

$$\begin{aligned} I_A &= 5.14 \times 10^{-40} \\ I_B &= 38.3 \quad " \\ I_C &= 37.9 \quad " \\ I_{\text{red}} &= I_A/4 = 1.29 \times 10^{-40} \end{aligned}$$

Barrier restricting internal rotation, $V_0 = 5 \text{ kcal/mole}$

TABLE 63
INFRARED SPECTRUM OF DEUTERIUM PEROXIDE*

| Wavelength, microns | Solid, cm^{-1} | Liquid, cm^{-1} | Vapor, cm^{-1} |
|------------------------|----------------------------|-----------------------------|--|
| 20.8 | 480 (m) (143)** | -- | -- |
| 18.6 | -- | 538 (m, br) (141) | -- |
| 11.4 | 880 (w) (150) | 878 (vw) (141) | -- |
| 10.6 | -- | -- | 923 (?) (150) 947 (vs) (143) 955 (150) |
| 9.6 | 1000 (s) (150) | 1004 (s) (141) | -- |
| 7.2 | -- | (1386) (w) (141) | -- |
| 5.1 | -- | -- | 1985 (w) (150) |
| 4.8 | 2090 (mw) (150) | 2087 (mw) (141) | -- |
| 4.0 | 2460 (vs) (150) | 2482 (vs) (141) | -- |
| 3.7 | -- | -- | 2680 (s) (143) |
| 3.0 | -- | (3368) (mw) (141) | -- |
| 2.9 | -- | 3430 (150) | -- |
| 2.0 | -- | 4980 (vw) (150) | -- |
| 1.9 | -- | -- | 5236 (vw) (143) |
| 1.6 | -- | 6110 (vw) (150) | -- |
| 1.4 | -- | 7215 (vw) (150) | -- |

* Sources of the data are given at each reported band.

**at -70°C

served in D_2O_2 . Hydrogen deuterium peroxide, DHO_2 , was prepared by making an equi-molal mixture of deuterium and hydrogen peroxides. Raman shifts of 877, 1009, 1406, 2510 and 3407 cm^{-1} were observed for this deuterium hydrogen peroxide. Feher cites convincing reasons for assuming that these shifts are due to the DHO_2 molecule itself and do not represent the additive contributions of deuterium and hydrogen peroxides separately. Taylor (148) observed a shift of 1990 cm^{-1} in a 90 wt. % solution of deuterium peroxide in heavy water.

The ultraviolet absorption spectrum of liquid containing 6.5 and 30.7 wt. % deuterium peroxide, essentially free of ordinary hydrogen, was observed over the wavelength range 3900 to 3050 \AA by Phibbs and Giguère (169). The absorption of the ultraviolet by deuterium peroxide was found to be less than that of hydrogen peroxide. Thus the extinction coefficient curve of deuterium peroxide is shifted toward shorter wavelengths relative to that for hydrogen peroxide. The magnitude of this shift, about 390 cm^{-1} , was calculated by Phibbs and Giguère to be of the magnitude to be attributed to the difference in the zero-point vibrational energy of the deuterium and hydrogen peroxide. A departure from Beer's law of the same degree as that observed for hydrogen peroxide was found for deuterium peroxide.

A summary of a number of physical properties of hydrogen and deuterium peroxides and of ordinary and heavy water has been assembled in Table 64 for the purpose of comparison. The authority for ordinary water is Dorsey (2), for heavy water, Kirshenbaum (203).

TABLE 64

SOME PHYSICAL PROPERTIES OF HYDROGEN AND DEUTERIUM PEROXIDES, AND ORDINARY AND HEAVY WATER

(Values are for 25°C and 1 atm unless otherwise noted)

| Property | H ₂ O ₂ | D ₂ O ₂ | H ₂ O | D ₂ O |
|--|-------------------------------|-------------------------------|------------------|------------------|
| Molecular Weight | 34.016 | 36.028 | 18.016 | 20.028 |
| Density of Solid, ρ_p , g/cc | 1.71 | -- | 0.917 | -- |
| Density of Liquid, 20°, g/cc | 1.450 | 1.534 | 0.998 | 1.106 |
| Viscosity of Liquid, 20°, centipoises | 1.245 | 1.354 | 1.002 | 1.25 |
| Surface Tension, 20°, dynes/cm | 80.4 | 81.2 | 72.75 | 72.73 |
| Diffusivity in Air, 60°, cm ² /sec | 0.188 | -- | 0.320 | -- |
| Heat of Sublimation, ρ_p , kcal/mole | 15.51 | -- | 12.17 | 12.60 |
| Melting Point, °C | -0.46 | 1.6 | 0 | 3.82 |
| Heat of Fusion, ρ_{mp} , cal/mole | 2920 | -- | 1436 | 1515 |
| Boiling Point, °C | 150.2 | -- | 100.0 | 101.4 |
| Heat of Vaporization, kcal/mole | 12.33 | -- | 10.51 | 10.85 |
| Critical Temperature, °C | 457 | -- | 374.2 | 371.5 |
| Critical Pressure, atm | 214 | -- | 218.2 | 218.6 |
| Heat Capacity of Solid, ρ_p , cal/g °C | 0.41 | -- | 0.50 | 0.53 |
| Heat Capacity of Liquid, cal/g °C | 0.628 | 0.632 | 0.998 | 1.016 |
| Heat Capacity of Vapor, cal/mole °C | 10.22 | 11.01 | 8.025 | -- |
| Heat Formation in Vapor, kcal/mole | -32.45 | -- | -57.80 | -59.56 |
| Free Energy of Formation in Vapor, kcal/mole | -24.70 | -- | -54.64 | -56.06 |
| Dielectric Constant, 20° | 73.1 | -- | 80.4 | 79.8 |
| Magnetic Susceptibility, 10 ⁶ cgs emu/g | -0.50 | -- | -0.720 | -0.647 |
| Refractive Index | 1.4067 | 1.4026 | 1.3325 | 1.3281 |

NOTATION*

Letter Symbols

- a Dispersion constant of Sellmeier formula, sec^{-2}
- a A coefficient of equation (4), g/cc
- a A coefficient of equation (26), cal/mole $^{\circ}\text{C}$
- B_0, B_1, B_2 Coefficients of excess free energy equation (9), cal/mole
- b A coefficient of equation (4), g/cc
- b A coefficient of equation (30), cal/mole $^{\circ}\text{C}$
- C_p Heat capacity at constant pressure, cal/mole $^{\circ}\text{C}$
- c Velocity of light in vacuum, 2.998×10^{10} cm/sec
- c Composition in molarity, moles solute per liter of solution
- c A coefficient of equation (4), g/cc
- c A coefficient of equation (30), cal/mole $(^{\circ}\text{C})^2$
- D Coefficient of diffusion in liquid, cm^2/day
- d Thickness of radiation absorption medium, cm
- d A coefficient of equation (4), g/cc
- d A coefficient of equation (30), cal/mole $(^{\circ}\text{C})^3$
- d Differential operator
- E Electromotive force or potential, volts; E_B in the standard state of basic solution of unit activity.
- E Internal energy, cal/mole
- E Electric field strength, volts/cm; in equations (63) to (70)
- e Base of natural logarithms, 2.718...
- F Free energy, cal/mole; F_x^E excess free energy of solution of mole fraction x
- F Faraday constant, 23,060 cal/volt equivalent
- H Enthalpy, cal/mole
- H Magnetic field strength, gauss
- h Planck's constant, 6.624×10^{-27} erg sec/molecule
- I Moment of inertia, g cm^2 ; I_A, I_B, I_C about axes A, B, and C;
 $I_{\text{red}} = I_A/4$

* The notation employed here follows in general the usages recommended by the American Standards Association and presented in their publications Z10.1-1941, Z10.6-1948, and Z10.12-1946.

| | |
|-----|---|
| I | Intensity of radiation; I_0 incident, I_x exit |
| J | A coefficient of equations (5), (6), and (7), g/cc |
| J | Angular momentum quantum number |
| K | A coefficient of equations (5), (6), and (7), g/cc ^{°C} |
| K | Equilibrium constant, quotient of product concentration over reactant concentration |
| K | Extinction coefficient, (atm cm) ⁻¹ ; ($K = (1/pd) \log (I_0/I_x)$) |
| k | Boltzmann constant, 1.380 erg/°C molecule |
| k | Volume magnetic susceptibility, cgs emu/cc |
| k | Force constant, dynes/cm |
| L | A coefficient of equations (5), (6), and (7), g/cc (°C) ² |
| l | Length, cm |
| M | Chemical molecular weight, g/mole |
| M | Number of moles of water per mole of hydrogen peroxide in a mixture |
| M | A coefficient of equations (5), (6), and (7), g/cc (°C) ³ |
| m | Composition in molality, moles solute per kg solvent |
| m | Magnetic quantum number, equations (64) to (70) |
| N | Avogadro number, 6.023×10^{23} molecules/mole |
| n | Number of moles |
| n | Refractive index, dimensionless |
| n | Number of potential minima in intramolecular rotation, 2 for hydrogen peroxide (equations (25, 26, 27)) |
| n | Number of equivalents |
| P | Total pressure, mm Hg |
| p | Partial pressure, mm Hg |
| p' | Partial pressure, atm |
| R | Gas constant, 1.987 cal/°C mole |
| [R] | Molar refraction, cc/mole |
| r | Specific refraction, cc/g |
| S | Entropy, cal/mole °C |
| T | Temperature, °K |
| t | Temperature, °C |
| V | Molal volume, cc/mole; \bar{V} partial molal volume = $\partial V / \partial n$ |
| V | Potential barrier hindering intramolecular rotation, cal/mole; V_0 maximum value (equations (25, 26, 27, 28, 29)) |

| | |
|-------------------|--|
| V | Verdet constant, min/gauss cm |
| \bar{V} | Volume strength, volumes oxygen at STP per volume hydrogen peroxide solution at STP |
| v | Specific volume, cc/g |
| W | Composition, weight percent hydrogen peroxide, dimensionless |
| w | Composition, weight fraction hydrogen peroxide, dimensionless |
| x | Mole fraction in liquid, dimensionless |
| x | A group, $hc\sigma/kT$, dimensionless (equations (25, 26, 27)) |
| y | Mole fraction in vapor, dimensionless |
| α_n | Coefficient of temperature for refractive index, $^{\circ}\text{C}^{-1}$ |
| α | Polarizability, cc/molecule |
| α | Angle of optical rotation, min of arc |
| β | Volumetric coefficient of expansion, $^{\circ}\text{C}^{-1}$ |
| β | Gas correction factor (26), cc/mole |
| γ | Activity coefficient, dimensionless |
| γ | Force constant, dynes/cm |
| Δ | Denoting a finite increment |
| δ | Force constant, dynes/cm |
| ϵ | Molecular extinction coefficient, l/mole cm; ($\epsilon = (1/cd)\log(I_0/I_x)$) |
| ϵ | Dielectric constant, dimensionless |
| θ_0 | Angle between magnetic field and path of light, degrees |
| θ | The angle QOH in the hydrogen peroxide molecule, degrees |
| λ | Wavelength, \AA ; ($\lambda = c/\nu$) |
| μ | Viscosity, micropoises |
| μ | Chemical potential = $\partial F/\partial n$, cal/mole |
| ν | Frequency, cycles/sec; ($\nu = c\sigma$) |
| ν' | Frequency, Mc/sec |
| π | 3.1416... |
| ρ | Density, g/cc; ρ_0 at STP |
| σ | Wave number, cm^{-1} ; ($\sigma = \nu/c = 1/\lambda$) |
| σ' | Symmetry number in equation (27), for hydrogen peroxide = 2 |
| ϕ | Azimuthal angle between planes containing the OH groups in the hydrogen peroxide molecule, degrees |
| χ_{M} | Mass magnetic susceptibility, cgs emu/g |
| χ_{m} | Molar magnetic susceptibility, cgs emu/mole |

Superscripts

- E Denotes excess quantity
 M Denotes quantity pertaining to mixing
 ° Referring to a quantity or a process with each substance in its standard state

Subscripts

- a Denoting the property of a general substance a
 b Referring to coefficient b of equation (4)
 C Referring to light of wavelength in air of 6562.8 Å[°]
 c Referring to coefficient c of equation (4)
 c Referring to a property at the critical point
 D Referring to the process of decomposition
 D Referring to light of wavelength in air of 5893 Å[°]
 d Referring to coefficient d of equation (4)
 F Referring to light of wavelength in air of 4861.33 Å[°]
 G Referring to light of wavelength in air of 4340.46 Å[°]
 H Denotes a property of hydrogen peroxide
 i Denotes a property of substance i
 j Denotes a property of substance j
 M Referring to the process of mixing
 m Denoting the property of a mixture
 T Denoting a property or process at temperature T
 t Denoting a property or process at temperature t
 V Referring to the process of vaporization
 W Denoting a property of water
 x Denoting a property at mole fraction x
 x A number
 y A number
 1,2,3 Referring to successive conditions or to different processes
 ° Denoting a property or process at 0°K
 ° Denoting the property of a pure component

Abbreviations

- ° Å Angstrom units (= 10⁻⁸ cm)
 atm Atmospheres
 aq In aqueous solution, generally in a standard state
 C Centigrade

| | |
|----------|--------------------------|
| c | cycles |
| ca. | circa |
| cal | calories |
| cc | cubic centimeters |
| cm | centimeter |
| conc. | concentration |
| const. | constant |
| cos | cosine |
| cgs | Centimeter gram second |
| decomp. | Decomposition |
| emu | Electromagnetic units |
| exp | "e raised to the power" |
| esu | Electrostatic units |
| F | Fahrenheit |
| fp | Freezing point |
| fr. | Fraction |
| ft | Feet |
| G | Gas |
| g | Gram |
| hr | Hour |
| K | Kelvin |
| kcal | Kilogramcalories |
| kg | kilograms |
| L | Liquid |
| l | Liquid |
| l | Liter |
| ln | Logarithm to the base e |
| log | Logarithm to the base 10 |
| <u>M</u> | Molar |
| Mc | Megacycles |
| m | Meters |
| mg | Milligrams |
| min | Minutes |
| ml | Milliliters |
| mm | Millimeter |
| mp | Melting point |

166.

| | |
|----------|--|
| <u>N</u> | Normal |
| n.s. | New series |
| STP | Standard temperature and pressure (0°C, 1 atm) |
| s | Solid |
| sec | Second |
| sol'n. | Solution |
| temp. | Temperature |
| V | Vapor |
| v | Vapor |
| v | Volts |
| wt. | Weight |
| yr | Year |
| μ | Micron ($= 10^{-4}$ cm) |
| ° | Degree |

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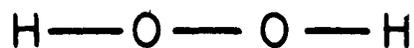
CHAPTER SIX

STRUCTURE

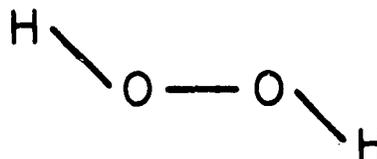
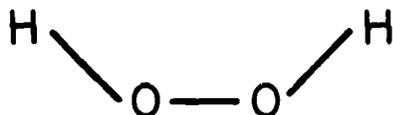
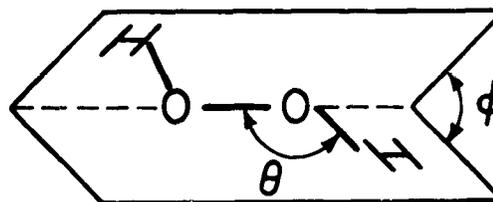
It is convenient to discuss the structure of hydrogen peroxide in parts, dealing separately with the architecture of the molecule and the nature of its associations in solution and with itself in the various phases. The establishment of the structure depends chiefly on the measurements of physical properties which have been gathered in the previous chapter. Some chemical properties have been borrowed from the following chapter for application to the determination of structure, but the implications or effects of structure upon chemical properties have been left for discussion later. A table has been given on page 211, summarizing the most probable values of various structural parameters.

STRUCTURE OF THE HYDROGEN PEROXIDE MOLECULE

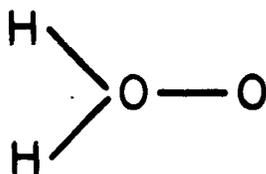
The determinations of the molecular weight and the stoichiometry of the reactions of hydrogen peroxide demonstrate clearly that the formula corresponds to H_2O_2 . Polymers, $(H_2O_2)_x$, do not exist in the usual sense of the term molecule. Similarly, a molecule having an oxygen-hydrogen ratio greater than one is not hydrogen peroxide, although it has been suggested repeatedly, even recently (1), that hydrogen peroxide has such a formula or occurs in mixture with significant concentrations of such molecules. Several reasonable configurations of the molecule H_2O_2 which have been suggested at one time or another are depicted in Figure 1 and will serve as a basis for discussion. These models are intended only to show the relative positions of the atomic nuclei; no particular type of bonding is implied. Two general structural forms have been the basis for discussion: in one, each hydrogen atom is attached to a different oxygen atom, as exemplified by models A through D in Figure 1; in the other form, both hydrogen atoms are attached to the same oxy-



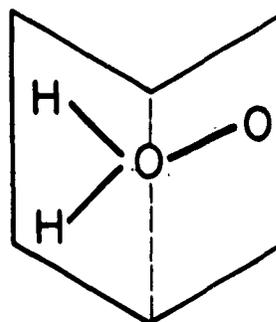
a. LINEAR CHAIN

b. TRANS PLANAR CHAINc. CIS PLANAR CHAIN

d. SKEW CHAIN



e. PLANAR TRIGONAL



f. PYRAMIDAL TRIGONAL

FIGURE 1—POSSIBLE CONFIGURATIONS OF THE HYDROGEN PEROXIDE MOLECULE

gen atom, as exemplified by models E and F. Some care is necessary to avoid ambiguity in making reference to these models. The distinction which models A through D bear is the catenate or chain arrangement of the atoms. Models E and F, on the other hand, are distinguished by the spoke-like disposition of two hydrogen atoms and an oxygen atom about a central oxygen atom, justifying the description trigonal. The possible variation within these two groups, chain and trigonal, is indicated by further description such as linear, planar, skew, or pyramidal.*

The first step in making a decision regarding the structure of hydrogen peroxide requires a decision between these two general forms; once this question has been resolved the details of dimensions and angles may be taken up for consideration.

Chemical Evidence

From a very elementary standpoint the chemical properties of hydrogen peroxide do not contribute much to the understanding of its structure. The decomposition of hydrogen peroxide results in the formation of water and oxygen, and an easily visualized mechanism for this decomposition is the breaking of the oxygen-oxygen bond in model E or F, leaving water and an oxygen atom free to combine with another oxygen atom derived similarly from another molecule. On the other hand, a dialkyl peroxide may be formed from hydrogen peroxide, and the dialkyl peroxide forms an alcohol on reduction, not an ether, leading to the conclusion (2) that hydrogen peroxide has one of the chain configurations represented by A through D. This dilemma remained unresolved for a long period, with the greatest weight of opinion in favor of the trigonal form (see Chapter 1; a purely geometric argument was offered in favor of the planar trigonal form by Raikow (3) as late as 1928). This opinion warrants the criticism that while the evidence given by the organic derivative seems sound there is no particular reason why the trigonal structure giving the most direct and obvious path to the formation

* The skew form might also be construed to be pyramidal, however, this term logically seems best reserved for a regular form such as model F.

of oxygen must be favored. Aside from the very reasonable possibility of more intricate, stepwise mechanisms of reaction, the implication that the oxygen in the planar structures is shielded from reaction does not seem warranted. A configuration of neighboring molecules of the planar chain structure in space or on a surface can be imagined which would appear to possess a directness of reaction, geometrically, equal to that of the trigonal form.

One more piece of evidence is available which has been interpreted in favor of the trigonal form. Geib and Harteck (4) found in 1932, that a glassy deposit could be condensed at liquid air temperatures from the products resulting from the reaction after mixture of atomic hydrogen and molecular oxygen. This glassy deposit partially decomposed on warming to -115°C ; further warming resulted in melting to hydrogen peroxide and water. Qualitative examination of the ultraviolet absorption spectrum of the glass and consideration of a material balance indicated that only hydrogen peroxide and water were present. To explain this appearance and behavior Geib and Harteck suggested that, as first formed, the glass might be composed of a mixture of "normal" hydrogen peroxide and "abnormal" hydrogen peroxide of the planar trigonal form. The decomposition at -115°C might then be ascribed to the abnormal form which might be presumed to be unstable. It is important to note, however, that the assumption of the presence of the planar trigonal form was given by Geib and Harteck only as a hypothesis.

For a long period no definite proof was available, and the interpretation as evidence for the existence of the trigonal form was only speculative. The experimental results of Geib and Harteck have now been confirmed and enlarged (5). In addition, Giguère and Secco (6) have now given a preliminary description of observations of the infrared absorption spectrum of this glassy deposit which they interpret to support the Geib and Harteck hypothesis. In the products obtained from the discharge in both heavy and ordinary water there was observed among the absorption bands one at 1300 cm^{-1} which was unaffected by the isotopic sub-

stitution. It was concluded that this might well arise from a coordinate oxygen-oxygen link.

This latter evidence does not establish the occurrence of the trigonal form uniquely; it only seems less well explained by other hypotheses. Additional work will be necessary before an adequate explanation can be advanced. The consideration of other possibilities such as gas absorption and the presence of radicals such as OH is doubtless still warranted. Whatever the outcome of such considerations it is worthwhile to emphasize that there is no evidence that the putative isomer exists in measurable concentrations at ordinary temperatures, or that, conversely, ordinary hydrogen peroxide can be converted to a different form by drastic reduction of temperature.

The recognition of the role of hydrogen ion concentration in hydrogen peroxide reactions led to the suggestion that the active entity is in fact the ion O_2H^- , but this might be in accord with any of the models. Similarly the recently available evidence of isotopic tracer experiments showing that the oxygen gas evolved in the catalytic decomposition or in reduction by hydrogen peroxide comes solely from the hydrogen peroxide might be interpreted in favor of several models. It must be concluded that chemical evidence is not adequate to establish the structure.

Additive and Constitutive Properties

The usual additive or constitutive properties of molecular structure do not contribute a great deal to the establishment of the structure of hydrogen peroxide. Under this heading may be considered the parachor, molar refractivity, magneto-optic rotation, molar volume, and magnetic susceptibility.

The parachor of hydrogen peroxide was calculated from measurements to be $69.6 \text{ g}^{1/4} \text{ cm}^3 / \text{sec}^{1/2}$ mole by Guthbertson and Maass (7) and considered by them to be evidence for the planar trigonal structure. The parachors of three models of hydrogen peroxide were calculated to have values between 72.5 and 97.7 on the basis of the atomic and structural contributions of Sugden.

Phibbs and Giguère (8) established the parachor at 70.0 on the basis of new surface tension and density measurements. The empirical nature of the parachor and the effects of molecular association upon it make it of doubtful value in the determination of the molecular structure of hydrogen peroxide.

The observed value for the molecular refraction, 5.801 cc/mole, is said to be "exalted" over that calculated from additive atomic equivalents. Brühl (9) and Strecker and Spitaler (10) interpreted this to signify the occurrence of multiple bonds between the oxygen in hydrogen peroxide. Linton and Maass (11) believed this evidence to favor the planar trigonal form. Giguère (12) pointed out that the "exaltation" is best considered to be caused by the presence of the two lone pairs of electrons on the O-O group. Thus the molecular refraction does not aid in establishing the structure on the basis of refractive equivalents determined from observation on other substances. At best it can only be said to establish a value for the contribution to refraction by the O-O group. The molecular refractivity does offer the opportunity to estimate the radius of the hydrogen peroxide molecule. In Chapter 5 the polarization of hydrogen peroxide was given as 2.30×10^{24} cc/molecule, from which the molecular radius is calculated to be 1.32 Å according to simple electrostatic theory. The dispersion constant, a , of the Sellmeier formula permits the calculation (13) of the number of electrons per molecule of hydrogen peroxide having a period of vibration corresponding to the characteristic frequency, ν_0 (which lies near 1000 Å in the far ultraviolet). The number of electrons per molecule is found to be four for hydrogen peroxide; for water the number is two. Presumably the lone pair of electrons on each oxygen atom is indicated here. A related optical property of hydrogen peroxide, the molecular magnetic rotation, fails to conform to the value calculated from accepted atomic equivalents (14).

Gray and his co-workers (15) have developed a theoretical interpretation of the structural magnetic susceptibility constants. This theory was applied to hydrogen peroxide, but apparently with

little success since in one case the planar chain molecule (form B or C) was favored and in another case the planar trigonal form was preferred. The simple additive magnetic factors of Pascal also fail to reproduce the recommended magnetic susceptibility. The chief contribution of the magnetic susceptibility to the determination of the structure seems to be to establish that hydrogen peroxide is not an "odd-electron" molecule (see below).

The Dipole Moment of Hydrogen Peroxide

The determination of the dipole moment of hydrogen peroxide by Linton and Maass (11) in 1932 by the dilution method using dioxane and ethyl ether as solvents, appeared to them to provide support for the planar trigonal form. These authors obtained for the dipole moment of hydrogen peroxide in dioxane, 2.13×10^{-18} esu and in ether, 2.06×10^{-18} esu. Some objections to the method of Linton and Maass were mentioned in the discussion of the dielectric constant, but these do not affect the values obtained for the dipole moment to an important degree. Experimental confirmation of these values for the dipole moment was obtained by Massey and Bianco (16), who found a value of 2.26×10^{-18} esu to be consistent with their observations of the Stark effect in the microwave spectrum of hydrogen peroxide. These values for the dipole moment certainly rule out of consideration the linear chain and trans planar chain models.

Smyth (17) had previously pointed to the high dielectric constant of hydrogen peroxide as likely evidence of a large dipole moment and had similarly interpreted this as evidence for the planar trigonal form. An objection to this was raised by Hunter and Partington (18) who suggested that the free rotation of the hydroxyl groups in hydrogen peroxide about the O-O axis (thus assuming during rotation all forms of the planar and skew chain models, B, C, and D) would result in a large dipole moment for the molecule. After the experimental dipole moments became available, Thielacker (19) made such a calculation for the molecule possessing free OH rotation. On the assumptions that the OOH angle in hydrogen peroxide is the same as the HOH angle in

water (then taken to be 110°) and that the moment of the OH group is the same in each molecule, Thielacker calculated the dipole moment of hydrogen peroxide to be about 2.1×10^{-18} esu, in good agreement with experiment.

The OH bond in hydrogen peroxide was calculated to have a moment of 1.71×10^{-18} esu by Rogers and Campbell (20), using the experimental dipole moment and the values 105° for the OOH angle and 100° for the azimuthal angle. This they compared with the value 1.51×10^{-18} esu for the OH bond moment in water.

The permanent dipole moment of the hydrogen peroxide molecule lies along its C_2 axis (i.e., axis C of Figure 4a). Higher moments, quadrupole, octupole, etc., have not been measured and have been calculated only approximately. This subject receives brief comment in a later section.

The discussion so far has not allowed any certain conclusion; for a satisfactory elucidation of the structure the evidence of spectroscopic measurements and quantum mechanical calculations must be considered. Although this evidence rules out the trigonal model and establishes the skew chain form, model D, as the correct one the viewpoint has persisted that hydrogen peroxide may consist of a tautomeric mixture of the planar trigonal form, model E, and the preferred skew chain form, model D. This viewpoint, as presented, for example, by Sidgwick (21), has been engendered chiefly by the Geib and Harteck hypothesis. Quartaroli (22), for example, interpreted a study of the reaction of hydrogen peroxide with cupric hydroxide to show that a tautomeric mixture indeed exists. The physical evidence now to be cited establishes clearly that the probability of the occurrence of the trigonal form is vanishingly small and that the true configuration of the hydrogen peroxide molecule is that of model D. This statement must be taken with a small reservation until the nature of the substance formed at low temperature is elucidated. As far as ordinary temperatures are concerned, however, the foregoing conclusion seems the only possible one.

Electronic Structure

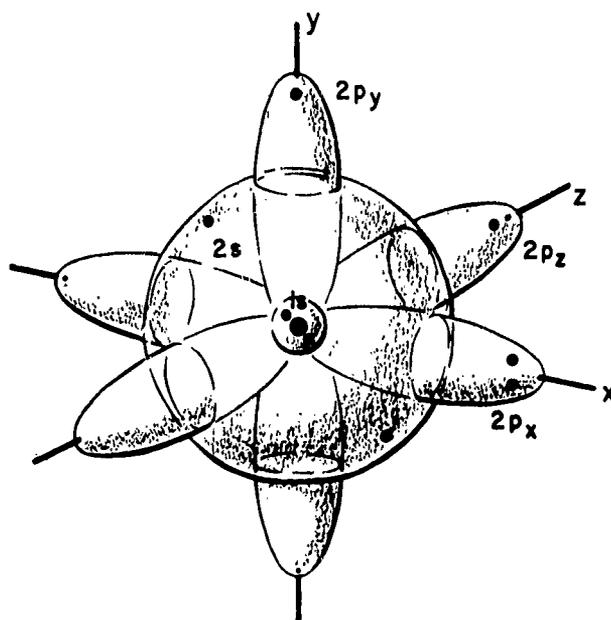
Consideration of the electronic organization of hydrogen peroxide permits a much more certain understanding of the structure. The oxygen atom is composed of a nucleus and eight electrons. These electrons are disposed in two shells, the first or K shell carrying two electrons and the second, M, or valence shell, carrying six electrons. The hydrogen atom likewise is composed of a nucleus and a single electron in its K shell. This description of hydrogen and oxygen and the development of the octet theory enabled Lewis (23) to represent hydrogen peroxide with the electronic configuration, $H:\ddot{O}:\ddot{O}:H$. This shows the completion of an octet of electrons on each oxygen atom by the sharing of the valence electrons of the participating atoms. Although this provides a structure recognized as stable, no definite orientation of the hydrogen atoms with respect to the oxygen atom is required. Lewis pointed out that the "mobile" hydrogen atoms might take any position around the pair of oxygens; thus any of the configurations shown in Figure 1 are possible and preserve the completed octet structure. The development of the quantum mechanical description of electronic structure has provided the additional detail which allows the choice of a particular orientation of the hydrogen atoms with respect to the oxygen atoms.

The quantum mechanical representation of electron structure emphasizes the individuality of pairs of electrons which may occupy successive and unique energy levels or orbitals within an atom. These orbitals are not thought of as fixed courses of motion, but are best described as regions of space around the nucleus in which the probability of finding an electron is high. Each orbital may contain two electrons, but no more. Certain of these orbitals must possess definite orientation with respect to others. Appreciation of this directional characteristic provides the essence of an understanding of the structure of hydrogen peroxide. An elementary description may therefore be given. For a more complete exposition of this subject in general there may be recommended the concise description by Noller (24) and the books by Pauling (25) and Coulson (26).

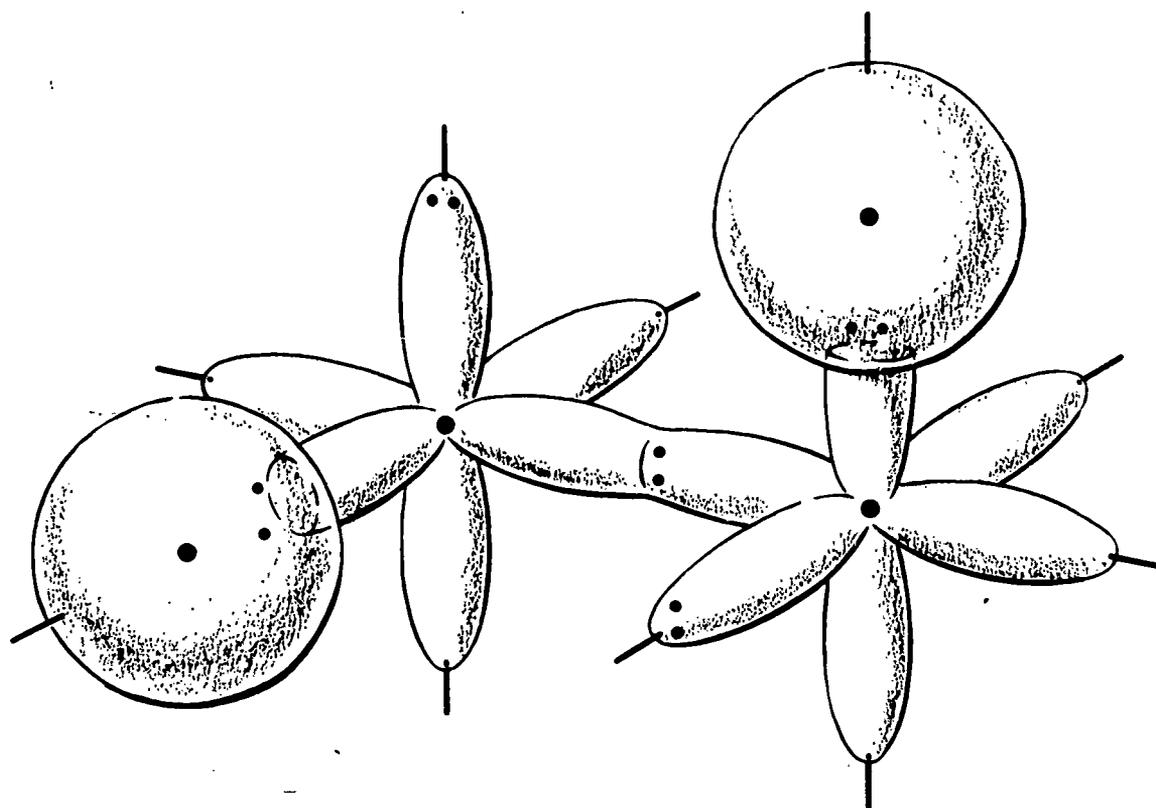
The electronic structure of the oxygen atom is given representation by Figure 2a. The dots shown to represent electrons are not intended to denote positions; they only indicate the number of electrons in a given orbital. Here the K shell mentioned above contains two electrons in what is designated the 1s orbital. This orbital (as with all s orbitals) is spherically symmetrical about the nucleus. The M shell is shown containing four orbitals, the 2s, 2p_x, 2p_y, and 2p_z orbitals, each capable of containing two electrons. The 2s orbital is spherically symmetrical but the p orbitals are directed along the coordinates x, y, and z. The energy level of the 2s orbital is appreciably less than that of the (equal-energy) p orbitals. The 2s level is accordingly filled with two electrons, leaving four more to be distributed among the 2p orbitals. These four electrons are distributed two in one p orbital and one each in the two remaining p orbitals. This then is a simplified description of the detailed electronic structure of the neutral oxygen atom in its ground or lowest energy state. The possibility of adding an electron to the two incompletely filled 2p orbitals, as by sharing an electron or overlapping an orbital of another atom, provides the means of chemical combination. The neutral hydrogen atom is simply described as a nucleus surrounded by a 1s orbital containing one electron.

For the restricted case of the combination of oxygen atoms with themselves or with hydrogen atoms an adequate understanding of the structure of the molecules formed can be had by consideration of the 2p orbitals of oxygen. The 1s orbital of oxygen can be completely neglected, and the contribution of the 2s orbital to chemical binding is, to a first approximation, negligible. In particular, the phenomenon of hybridization, in which 2s electrons are elevated in energy level to participate with 2p electrons in directed orbitals, plays only a small part in the valence characteristics of oxygen. Hybridization may not be neglected for other elements, e.g., nitrogen and carbon.

The structure of hydrogen peroxide may now be discussed in relation to two series of oxygen compounds: the first based on



(a) OXYGEN



(b) HYDROGEN PEROXIDE

FIG. 2 - A REPRESENTATION OF THE ELECTRONIC STRUCTURE OF ATOMIC OXYGEN AND HYDROGEN PEROXIDE

atomic oxygen and comprised of the species O, OH, and H₂O and the second based on molecular oxygen and comprised of the species O₂, O₂H, and H₂O₂. Further series based on higher molecular weight oxygen molecules such as O₃ or O₄ may be imagined, but will not be considered here. The electronic structure of ozone is more complicated and is still debated. Simple ozonide compounds analogous to HO₃ (27) and H₂O₃ (28) have been reported, but they are very reactive and little is known of them. The species O₄ has led a shadowy existence and is at any rate believed (25, 29) not to be bound entirely by the primary valence forces such as hold together the molecules O₂ and O₃.

The distinction between a stable molecule and a reactive one should be noticed. The stable molecule is one for which the formation from the atoms is accompanied by a decrease in energy. While undergoing translational motion two atoms or an atom and a molecule may approach each other and come into relative positions separated by distances comparable to that of a chemical bond. If conditions are not favorable for combination the atoms continue their separate ways, receding immediately from this closest approach or "collision." Under certain specific circumstances the two approaching particles may hold together at the distance of a chemical bond for a period of time longer than that occupied in this relative position during the grazing encounter just described. Such a combination is stable, even though the combining energy may be so small that the molecule formed can be easily disrupted and therefore has a very short life expectancy. A molecule so defined as stable may also be reactive in that reorganization or reaction with another molecule is energetically favorable under the imposed conditions. All the molecules mentioned above are stable then, but some have only a fleeting existence under the usual conditions of observation because they are reactive. As an example of molecules which would not be stable according to the above definition there may be cited the species H₃O and H₃O₂. These molecules might be expected to continue the two series of molecules taken for discussion, O, OH, and H₂O and O₂, O₂H, and H₂O₂, but H₃O and H₃O₂ cannot be formed from oxygen in its ground state; with

the formation of H_2O and H_2O_2 the bonding orbitals have become filled.

These two series of oxygen compounds may now be built up with reference to the oxygen atom which is depicted in Figure 2a. By allowing the 1s orbital of a hydrogen atom with its lone electron to overlap and share one of the 2p orbitals of an oxygen atom which contains only one electron, say $2p_y$ in the figure, the stable molecule hydroxyl, or OH, is formed. A lone or "odd" electron now remains in the other incomplete 2p orbital of oxygen, e.g., $2p_z$. The presence of the odd electron may be expected to confer paramagnetism on hydroxyl and to offer further opportunity for chemical combination. The average distribution of the electrons in the binding $2p_y$ -1s orbitals (or molecular sigma orbital as it is termed) may be such that the electron density is greater about the oxygen atom. The molecule may then be expected to have an electric moment. Now by similar addition of another hydrogen atom to share the $2p_z$ orbital there is formed water. Because the $2p_y$ and $2p_z$ orbitals which the hydrogen atoms share are oriented at a right angle the water molecule may be expected to have a V shape. This is found experimentally to be so. The actual angle between the OH bonds is found to be $104^\circ 31'$. The difference between 104° and 90° is ascribed to electrostatic repulsion between the hydrogen atoms and to other effects which the simple model under discussion here does not take into account, such as some contribution of hybridization. The unsymmetrical structure may also be expected to produce an electric moment for the molecule; this is found to amount to 1.85×10^{-18} esu.

The second series of compounds may now be built by first joining two oxygen atoms to form molecular oxygen, O_2 . As a first step two of the orbitals containing lone electrons may be overlapped to form a bond along the p_y axes of each oxygen atom. Now each of the joined atoms will have two p orbitals at right angles to the bonding orbital, one which contains a pair of electrons and one which contains only one electron. It is energetically more

favorable for the orbitals containing pairs of electrons not to be parallel. The final orientation is then one in which the orbitals containing pairs of electrons are parallel to the orbitals containing lone electrons. It is now possible for further bonding between the oxygen atoms to occur. The three electrons in each of the two parallel orbitals may be shared between the oxygen atoms to form what Pauling (25) terms a three-electron bond. This is simply conceived of as a situation where the pair of electrons and the odd electron continually exchange from one oxygen to the other. Each such three-electron bond has about half the strength of the two-electron, sigma bond first formed. It still remains possible to break one or both of the three-electron bonds of the oxygen molecule and for one or both of the odd electrons to be shared with other atoms. If one odd electron is shared with a hydrogen atom, perhydroxyl (or hydrogen superoxide), O_2H , is formed. This stable molecule then contains a sigma bond and a three-electron bond between the oxygen atoms and a sigma bond between an oxygen and the hydrogen atom. The OH axis should be oriented at right angles to the OO axis, giving a V shape as with water. There should be an appreciable electric moment and the presence of the remaining odd electron should cause perhydroxyl to be paramagnetic. A second hydrogen atom may now be brought up to the perhydroxyl molecule, the three-electron bond broken and the remaining odd electron shared with the hydrogen atom to produce H_2O_2 . Since in the oxygen molecule, O_2 , the orbitals containing the odd electrons were oriented at a right angle, it may be expected, now that the electrons of the hydrogen atoms are shared in these orbitals, that the planes containing the OH axes in hydrogen peroxide will also be oriented at a right angle. The molecule may possess an electric moment, but will be diamagnetic since no odd electron is present. A rational basis has now been presented for preferring the skew chain structure (Model D or Figure 1) which is given an electronic representation in Figure 2b.

It was mentioned above that in certain of the molecules the electron distribution might be altered from that which obtained in the atoms so that the electron density might be greater about

one of the atoms in the molecule. But it was to be implied that the electron distribution remained reasonably uniform. A more extreme situation is of course possible. For example, if the nucleus of one of the hydrogen atoms in the water molecule is drawn away, leaving its electron to participate in the oxygen orbitals, the familiar hydroxyl ion, OH^- , is formed. The ions O^- , O^{2-} , O_2^- , O_2H^- , and O_2^{2-} may also be formed in similar fashion from the molecules discussed above, the latter three being termed superoxide, perhydroxyl, and peroxide ions, respectively. In the neutral hydrogen peroxide molecule the perhydroxyl and peroxide ions do not exist as such. That is, the hydrogen atoms are not held to the O_2 group by electrostatic attraction to any great extent; the bonding electrons are shared fairly equally. In peroxides formed with elements of substantially lower electronegativity than hydrogen, e.g., barium, this is not the case. Barium peroxide may be said to be an electrovalent compound with the binding forces between barium and oxygen predominantly ionic in nature. Ionic bonding has been suggested as a means whereby the trigonal structure for hydrogen peroxide might be achieved. Hellmann (30) referred to the example of the carbon monoxide molecule where a part of the binding is ionic due to transfer of an electron from an oxygen p orbital to a carbon sp hybrid orbital. It may be imagined that, in a similar fashion, one of the non-bonding electrons of the oxygen atom in a water molecule might be transferred to a free oxygen atom to form the ions H_2O^+ and O^- . Electrostatic forces would then exist to hold together these ions, and, in addition, the electronic rearrangement leaves an odd electron on each oxygen which may be shared to form a sigma bond between the oxygen atoms. The planar trigonal structure of Figure 1 could thus be achieved, or, more likely, as Walsh (31) has pointed out, the pyramidal trigonal structure, model F of Figure 1, would occur because of the directional characteristics of the oxygen orbitals. This structure is a stable one, according to the definition given above, but so much less so than the skew chain form that the pyramidal structure involving ionic forces of importance cannot have a long existence at ordinary

temperatures. It is conceivable that extreme low temperature may allow relatively long lifetime to such a form, but this remains a matter for experimental verification.

The foregoing qualitative description of the electronic structure of hydrogen peroxide was given quantitative expression by Penney and Sutherland (32) in 1934. Because an unequivocal choice of structure could not be made before quantum mechanical calculations were undertaken, Penney and Sutherland chose to use the valence bond or electron pair method of calculation. This method is less precise than the alternative molecular orbital method, but since knowledge of the relative magnitudes of the energy of the various configurations was sufficient for making a choice between the two general forms, the much less tedious electron pair method was deemed more suitable to the problem. Only the four 2p electrons of each of the oxygen atoms were considered, the remaining ones playing a negligible part in the determination of the binding energy. Penney and Sutherland found that the planar trigonal structure would possess only weak ionic, Coulomb, and van der Waals attractive forces and was therefore improbable. This conclusion agreed with that of Kazarnovskii (33), who calculated that the bonding of an oxygen atom to the oxygen of a water molecule through polarization forces would result in a bond of only 0.58 kcal/mole energy--far less than the facts require.

With the trigonal form eliminated (the pyramidal trigonal form was not specifically considered), Penney and Sutherland investigated in detail the most stable relative arrangement to be chosen from the remaining obvious configurations, i.e., models A - D of Figure 1. As a beginning, the skew chain structure, model D, was adopted as the most logical choice on the basis of qualitative knowledge such as was outlined above. The effect then of varying the HOO angle, θ , and the dihedral or azimuth angle, ϕ , between the planes containing the OH groups on the relative stability of the molecule was studied. The effects which had been ignored in reaching the first conclusion that the azimuth, ϕ , was 90° were interaction between atoms not coupled by bonds, and

van der Waals and ionic forces. The following assumptions were made by Penney and Sutherland in order to investigate these effects: a) the effect of one OH group on the other hydrogen atom was the same as the effect occurring in the water molecule of the hydrogen atoms on each other; b) the HOO angle, θ , = 110° , i.e., the same as the HOH angle in water, c) the O-O bond distance = $1.4 \overset{\circ}{\text{A}}$, d) the O-H bond distance = $1.0 \overset{\circ}{\text{A}}$. Using these assumptions, the energy was calculated for values of ϕ varying between 0° and 180° . The result of this calculation is shown in the curve in Figure 3, which confirms that the choice $\phi = 90^\circ$ was nearly correct, requiring only adjustment to about 100° . Although it might have been expected that interaction of the hydrogen atoms or of the OH bonds would favor the trans planar chain structure, these calculations show that the dominant factor governing the dihedral angle, ϕ , is the repulsive interaction of the unpaired electrons on each oxygen atom, which is greatest when the orbitals containing the lone pairs are parallel.

With a choice determined for the dihedral angle, Penney and Sutherland then made calculations to confirm that the assumed HOO angle, θ , of 110° was consistent with the value of 100° determined for the dihedral angle. It was pointed out that if perfect electron pairing existed the HOO angle would be 90° . However, repulsive interactions of the atoms of one OH group force the other hydrogen atom off of its bonding orbital axis by an angle ψ_1 . Since the OO bond is not infinitely strong there results an additional angular reorientation, ψ_2 , of the OH bonding orbital to maintain the orbital overlapping of the hydrogen and oxygen at a maximum. It is required that the oxygen orbitals remain perpendicular, causing the OO bonding orbitals also to be shifted by an angle ψ_2 from the line of OO centers. The dependence of the energy upon the angles ψ_1 and ψ_2 concerns the OH and OO bond energies, the hydrogen-hydrogen and OH group steric repulsions, and the OH dipole interactions. Penney and Sutherland calculated the minimum energy to occur for the values $\psi_1 = \psi_2 = 5^\circ$. Thus $\theta = 90^\circ + \psi_1 + \psi_2 = 100^\circ$.

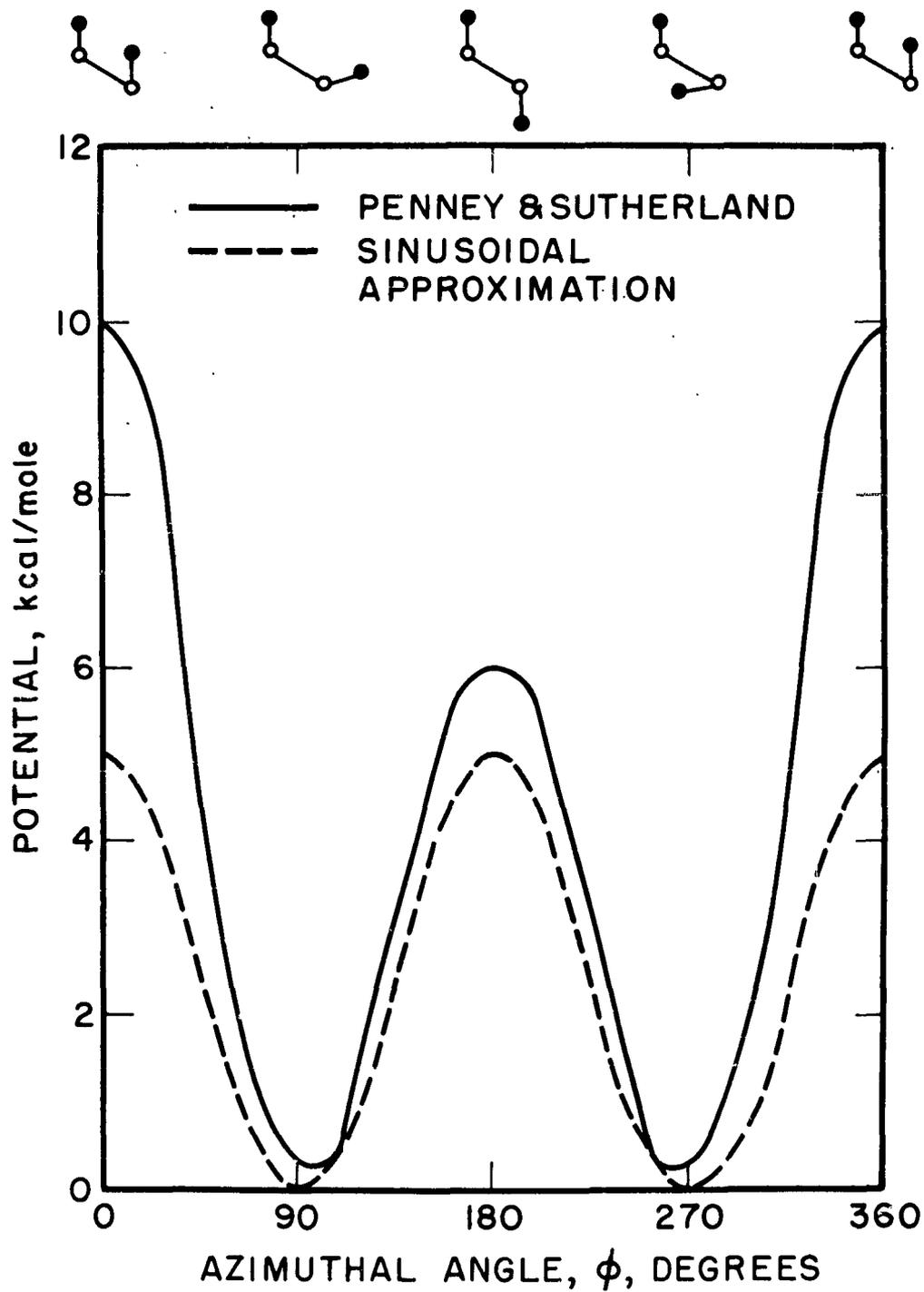


FIGURE 3—POTENTIAL ENERGY AS A FUNCTION OF ANGLE OF TORSION IN HYDROGEN PEROXIDE

This brief outline has given the basis upon which the conclusion is reached that the skew chain molecule, model D, with the angles $\theta \cong \phi \cong 100^\circ$ represents the true structure of hydrogen peroxide. Penney and Sutherland calculated a dipole moment for this model of 2×10^{-18} esu, in good agreement with experiment. Similar agreement was given by the calculations of dipole moment by Randall (34) and Jaktar (35).

The energy barriers indicated by Figure 3 imply that free rotation of the OH groups with respect to each other is improbable; this motion must be limited to a torsional oscillation. This restriction permits two mirror image or enantiomorphous forms of hydrogen peroxide to exist. However, in the vapor phase the restriction on rotation holds only for periods of time long relative to the period of oscillation. The barrier to rotation is not so high that suitable molecular collisions may not impart enough energy to overcome it. In addition, it may be calculated that an OH group may pass from one potential minimum to the other about once in every 40 oscillations through the "tunnel effect." The presence of these isomers would not be expected to impart optical activity to hydrogen peroxide since the opposed groups are identical (36). In condensed phases where intermolecular association imposes additional restriction on the rotation the presence of the isomers may be evident in the two different stereochemical forms possible (37).

It also must be pointed out that the curves shown in Figure 3 suggest more accuracy than is actually warranted. The curve of Penney and Sutherland probably gives good qualitative representation of the shape, i.e., shows the two minima separated by maxima of unequal height with reasonable relative energies, but the absolute magnitudes shown may require revision. The approximation of the potential barrier by the sinusoidal relation

$$V = \frac{1}{2} V_0 (1 + \cos 2\phi) \quad (1)$$

(shown in Figure 3 for $V_0 = 5$ kcal/mole) is used only as a mathe-

matical expedient. When used with a properly chosen single value for the potential, V_0 , useful calculations, as of the thermodynamic functions, are made practical.

Lassettre and Dean (38) examined hydrogen peroxide as an example in the development of a theory of the potential barriers hindering rotation around single bonds, and found additional confirmation of the structure chosen by Penney and Sutherland. All of the intramolecular interactions considered by Penney and Sutherland were included by Lassettre and Dean in their treatment. These interactions were expressed by Lassettre and Dean in terms of the electrostatic forces between the various electron distributions in the molecule; for hydrogen peroxide these are: a) between the two OH bonds, b) between the OH bonds and the unshared pair on opposite oxygens, and c) between the unshared pair on each oxygen. It was hypothesized that the unshared pairs have no dipole moment and that their important interaction therefore involves only their quadrupole moments.* After estimation of the quadrupole moments, Lassettre and Dean calculated the dihedral or azimuthal angle corresponding to minimum energy for the molecule. These calculations were made for a reasonable range of quadrupole moments to allow for the uncertainty in their estimation, and values of ϕ between 94° and 113° were obtained, although the heights obtained for the barrier to internal rotation were rather high on the basis of certain of the assumptions.

Mulliken (39) wrote the following shorthand expression for the orbitals of hydrogen peroxide, noting the approximate location of the orbitals with respect to the atoms concerned in them as well as an estimate of the ionization potential of an electron in each orbital.

* The potential at a distance from a charge distribution is expressed as the sum of a series of terms in powers of the distance. The potential due to the dipole moment is inversely proportional to the square of the distance, that due to the quadrupole moment is inversely proportional to the cube of the distance.

| | | | | | | | |
|----------------------|----------|----------|-----------|-----------|-----------|----------|---------------------|
| Electron designation | $(2s)^2$ | $(2s)^2$ | $[y^1]^2$ | $[z^1]^2$ | $[z^1]^2$ | $(2x)^2$ | $(2x)^2$ |
| Location | 0 | 0 | OO | OH | OH | 0 | 0 |
| Ionization potential | | 32 | 18 | 17.5 | | | 13 (electron volts) |

The work of Robertson (40) now offers the opportunity to check these ionization potentials against experiment and provides a very convincing argument against any lingering preference for the trigonal form of hydrogen peroxide at ordinary temperatures. Robertson subjected hydrogen peroxide vapor to the impact of a beam of electrons of known and controlled energy. The potential at which the resulting positive ions appeared and their relative intensities at various potentials were determined with a mass spectrograph. These results are given in Table 1.

Robertson found that the ions H_2O^+ , O_2^+ , and O^+ observed were derived from water vapor present in the apparatus because of heterogeneous decomposition of some hydrogen peroxide. The observed appearance potential of O^+ of 18.9 ev is of particular significance. This is just the potential observed for the appearance of O^+ in water vapor alone, whereas Robertson estimates that the potential for the formation of O^+ from the trigonal form of hydrogen peroxide should not exceed 15.6 ev. Robertson believed his evidence to show that the trigonal form could not be present in a proportion of more than one part in 1400. The observed potential of 12.1 ev for the production of $H_2O_2^+$ evidently corresponds to the removal of a non-bonding electron of an oxygen atom in hydrogen peroxide. This value is lower than Mulliken's estimate of 13 ev cited above and near to that for the lowest ionization potential of molecular oxygen (12.25 ev).

Spectroscopic Investigation of Structure

Spectroscopic and diffraction observations of hydrogen peroxide provide confirmation of its structure and afford measurements of the dimensions and angles of the molecule. The results

TABLE 1

RELATIVE INTENSITIES AND APPEARANCE
POTENTIALS OF IONS PRODUCED IN
HYDROGEN PEROXIDE VAPOR,
FROM ROBERTSON (40)

| Ion | Relative Intensity* at | | | Appearance Potential, ev |
|--|------------------------|-------|-------|-----------------------------|
| | 20 ev | 30 ev | 40 ev | |
| H ₂ O ₂ ⁺ | 100 | 100 | 100 | 12.1 ± 0.3 |
| HO ₂ ⁺ | 3.5 | 6 | 10 | 16.1 ± 0.4 |
| OH ⁺ | 200 | 200 | 200 | 16.0 ± 0.3 |
| O ⁺ | 2 | 2 | 2 | 18.9 ± 0.4 |

*reduced to arbitrary standard, H₂O₂⁺ = 100

of electron and X-ray diffraction studies give such values rather directly and may be cited first.

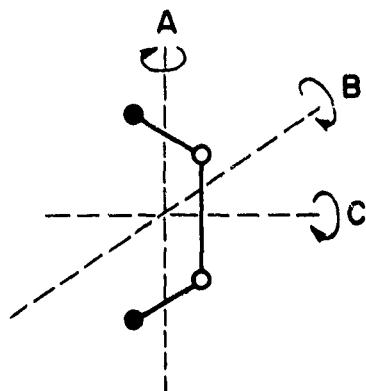
Giguere and Schomaker (41) found the O-O bond length to be 1.47 ± 0.02 Å as a result of their electron diffraction study of the vapor. The position of the hydrogen atoms cannot be located by this method. The X-ray diffraction study of urea hydroperoxidate by Lu, Hughes, and Giguere (37) provided the value 1.46 ± 0.03 Å for the O-O bond length, the value 106° for the dihedral angle, ϕ , and the value 101.5° for the OOH angle, θ . Although it is reasonable to suppose that these angles as determined in urea hydroperoxidate apply also to free hydrogen peroxide, they may be distorted somewhat in the solid urea compound.

Abrahams, Collin, and Lipscomb (42) measured the O-O bond length to be 1.49 Å, the dihedral angle, ϕ , to be $93^\circ 51'$, and the OOH angle, θ , to be $96^\circ 52'$ through X-ray diffraction study of crystalline, anhydrous hydrogen peroxide. Measurements (see Chapter 12 for discussion) have been made of the O-O bond length in other peroxy compounds, both organic and inorganic, by diffraction methods, and the best evidence indicates that little difference from the value found for hydrogen peroxide occurs.

The infrared and Raman spectra of hydrogen peroxide provide the major source of data for the dimensions of the hydrogen peroxide molecule. Because of the experimental difficulties involved, the complexity of the spectrum, and the faintness of absorption in some regions there remain a number of uncertainties, but a conclusive interpretation may be given to the main features of the spectrum.

The preferred structure of hydrogen peroxide, model D of Figure 1, has 12 possible modes of motion which may occur in the vapor state and, with various restrictions, in the condensed phases. Three of these motions are simply the translational motions in the coordinates of space and do not come into consideration in spectroscopy. The remaining motions, three of which are the rotations of the molecule as a whole about its axes and six of which are intramolecular vibrations, are depicted and identified in Figure 4. This model has one axis of symmetry, axis C of Figure 4a, which is the line bisecting the line of oxygen centers and lying in the plane which bisects the dihedral angle β . Rotation by 180° about this axis produces a configuration which cannot be distinguished from the original one. No other operation of rotation or reflection will reproduce the original configuration. This configuration is classified as a member of the point group C_2 and spoken of as having a two-fold axis of symmetry.

With the establishment of the symmetry of a molecule much can be predicted about its interaction with radiation, or, conversely and more important, the structure may be determined from the spectrum. The complex details of this theory are given by Herzberg (43), but a few elementary predictions about the spectrum of hydrogen peroxide may be given here: a) since hydrogen peroxide possesses a permanent dipole moment it must have an absorption spectrum due to rotational motion, b) because each of the vibrational motions shown in Figure 4 involves a change of dipole moment, each will manifest an infrared absorption band, c) similarly, since each vibrational motion involves



a. ROTATION

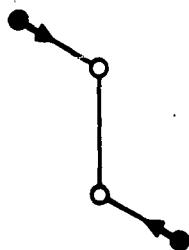
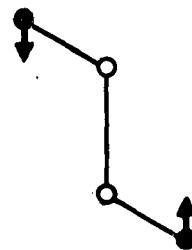
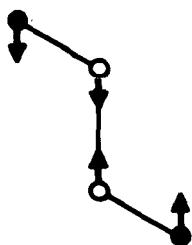
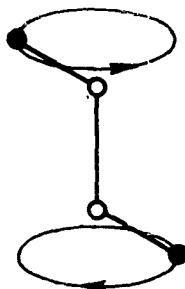
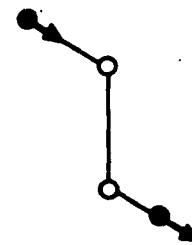
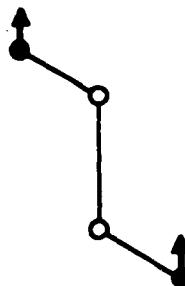
b. OH STRETCHING VIBRATION, ν_1 c. SYMMETRIC BENDING, ν_2 d. OH STRETCHING VIBRATION, ν_3 e. TORSIONAL OSCILLATION, ν_4 f. OH STRETCHING VIBRATION, ν_5 g. UNSYMMETRICAL BENDING, ν_6

FIGURE 4 - MODES OF ROTATIONAL AND VIBRATIONAL MOTION FOR THE HYDROGEN PEROXIDE MOLECULE

a change in the molecular refractivity, each will exhibit a band in the Raman spectrum. In addition to the fundamental frequencies observed for the vibrational motions there may be observed various overtone and combination frequencies. The overtones are due to the raising of the energy of a vibration by more than one quantum level at a time, and the combinations are due to the raising of the energy of two vibrations simultaneously.

The use of these predictions about the spectrum, or selection rules, permits a tentative choice of the configuration of hydrogen peroxide from several possibilities such as shown in Figure 1. For example, it has just been stated that model D of Figure 1 will show six Raman lines; application of the selection rules to the linear chain model A and the trans planar chain model B predicts only three Raman lines for these forms, none of which should also be active in the infrared spectrum. Now a total of five fundamental Raman lines have actually been observed, each with an infrared counterpart, and these models can therefore apparently be eliminated from consideration. However, these models were eliminated earlier on the basis of the observed dipole moment. On the other hand the cis planar chain model C should also have six frequencies active in the Raman spectrum. It is distinguished from model D by possessing only five possible infrared fundamentals, whereas model D should have six. Five infrared fundamentals have been observed with certainty, a sixth being less certain. Model D thus seems to be favored, but a more detailed consideration is necessary to make a decision.

The rotational spectrum of hydrogen peroxide has so far only received a limited amount of study. The spectrum due to pure rotation alone which occurs in the microwave region has been observed, and two studies have been made of the rotational fine structure of two vibrational overtone or combination bands. Overtone or combination bands are in general weaker than fundamentals and present a more complicated appearance, but it is useful to study them since they occur in a region of the spectrum accessible to photographic recording. Formerly this was the only method for making high dispersion studies.

All of the fundamental vibrational frequencies have now been observed under the restriction of these complications: a) the absorption in infrared spectrum is in general weak, limiting the precision of location of the band centers, b) two fundamental frequencies, ν_2 and ν_4 , and the Raman spectrum have only been observed in the condensed phases and an uncertain effect of molecular association upon the observed frequencies must be allowed for, c) two fundamentals, namely ν_1 and ν_5 , have very nearly the same frequency*; separation has been observed in the condensed phases, but a unique characterization for them has not been completely established. With this background the identification or assignment of the frequencies may be made, and these conclusions applied to the calculation of the bond lengths, angles, moments of inertia, and force constants of hydrogen peroxide.

Identification of the observed absorption bands with the vibrational motions or assignment of the frequencies of hydrogen peroxide has been carried out by Bailey and Gordon (44), Simon and Feher (45), and Giguère (46). The earlier assignments by Bailey and Gordon and Simon and Feher were made under the handicap of limited observation of the spectrum (only three certain Raman lines) and, apparently, limited precision in the determination of the absorption intensity and location of band centers in the infrared spectrum. For example, Bailey and Gordon found little difference between the infrared spectra of the vapor and the liquid, whereas experience indicates that an appreciable difference is to be expected for a hydroxylic compound, which possesses a tendency for association in the liquid phase.

The vibrational spectra observed for hydrogen peroxide have been summarized in Table 2 according to the frequency assignments given by Giguère (46). The order of numbering, ν_1 , ν_2 , etc., is in accordance with the amplitude and symmetry of the

* This occurrence is sometimes spoken of as "accidental degeneracy" although strictly speaking, two bands should be of the same symmetry to be degenerate. Here it is better spoken of as overlapping or coincidence.

TABLE 2

SUMMARY OF THE VIBRATIONAL SPECTRUM OF HYDROGEN
AND DEUTERIUM PEROXIDES*

| Assignment | Hydrogen Peroxide | | | Raman, $\Delta\sigma$, cm^{-1} | |
|---------------------------------|----------------------------|-----------------------------------|----------------------------------|--|-------------------------|
| | Infrared, cm^{-1} | | | Liquid | Solid |
| | Vapor | Liquid (-30°C) | Solid (-78°C) | (-40°C) | (-20°C) |
| ν_4 | 465 575 | 635 m | 660 s | 525 | -- |
| ν_3 | 877 vw | 878 vw | 878 vw | 882 | 878 |
| $2\nu_4$ | -- | -- | 1300 | -- | -- |
| ν_6 | 1266 vs | 1353 ms | 1378 s | -- | -- |
| ν_2 | -- | -- | 1430 w | 1402 | 1408 |
| $\nu_2 + \nu_6$ | 2630 w | 2796 mw | 2733 m | 2815 | 2790 |
| ν_1 | 3590 s | 3360 vs | 3218 vs | 3364 | 3203 |
| ν_5 | 3590 s | 3360 vs | 3218 vs | 3364 | 3331 |
| $\nu_5 + \nu_6$ | -- | 4715 vw | 4595 vw | -- | -- |
| $\nu_1 + \nu_5$ | 7036.6 vw 7041.8 vw | -- | -- | -- | -- |
| $3\nu_5$ or $2\nu_1 + \nu_5$ | 10283.7 vw 10291.1 vw | 9900 **vw | -- | -- | -- |

| Assignment | Deuterium Peroxide | | | Raman, $\Delta\sigma$, cm^{-1} Liquid** |
|---------------------------------|----------------------------|-----------------------------------|----------------------------------|--|
| | Infrared, cm^{-1} | | | |
| | Vapor | Liquid (-30°C) | Solid (-70°C) | |
| ν_4 | -- | 538 m | 480 m | -- |
| ν_3 | -- | 878 vw | -- | 877 |
| $2\nu_4$ | -- | -- | -- | -- |
| ν_6 | 947 vs | 1004 s | -- | -- |
| ν_2 | -- | -- | -- | 1009 |
| $\nu_2 + \nu_6$ | 1944 w | 2087 mw | -- | 1990 |
| ν_1 | 2680 s | -- | -- | 2510 |
| ν_5 | 2680 s | 2482 vs | -- | -- |
| $\nu_5 + \nu_6$ | -- | -- | -- | -- |
| $\nu_1 + \nu_5$ | 5236 vw | -- | -- | -- |
| $3\nu_5$ or $2\nu_1 + \nu_5$ | -- | -- | -- | -- |

* For explanation of symbols (43) see p. 129 of Chapter 5

** room temperature

vibration (43). Aside from some differences in location, the chief difference between the assignments given in Table 2 and those of Bailey and Gordon and Simon and Feher lies in the interpretation of the 1400 cm^{-1} Raman shift. Simon and Feher observed this to consist of two peaks separated by about 27 cm^{-1} . This was interpreted to be an accidental degeneracy, and Bailey and Gordon assigned these peaks to ν_2 and ν_4 . A value of the magnitude of 1400 cm^{-1} for ν_4 , the torsional oscillation, was held to be unreasonably high and Simon and Feher assigned the two peaks at 1400 cm^{-1} to ν_2 and ν_6 . More recent work has not substantiated the splitting of the 1400 cm^{-1} band observed by Simon and Feher, and it is believed that only the single frequency ν_2 can be attributed to it.

A short summary somewhat like that given by Giguère (46) of the reasoning underlying the frequency assignments of Table 2 may now be presented.

ν_3 , the OO stretching vibration: The fact that the absorption at 877 cm^{-1} remains unchanged in both hydrogen and deuterium peroxides makes it clear that this is due to the OO stretching vibration, which is not affected by the mass of the hydrogen atoms. Further evidence of the correctness of this choice is given by the small effect of phase change on this frequency and its weakness in the infrared relative to that in the Raman spectrum which is to be expected for the small change in dipole moment associated with this vibration. Giguère (47) has concluded that this band has never been observed with certainty in hydrogen peroxide vapor. The low depolarization ratio observed for the Raman line of this frequency also indicates that it arises from a symmetric vibration, that is, a vibration during which the symmetry of the molecule is maintained. This frequency has also been observed in other peroxides (48). Application of Badger's rule (49), an empirical relation between bond length and the force constant associated with a given frequency, to this frequency yields the value 1.48 \AA for the OO distance, in good agreement with the electron diffraction value.

ν_1 and ν_5 , the symmetrical and unsymmetrical OH stretching vibrations: These vibrations are identified with the absorption near 3600 cm^{-1} in the vapor, 3400 cm^{-1} in the liquid, and 3200 cm^{-1} in the solid. A similar frequency due to OH stretching occurs for water. The frequency of this band is altered by a factor of about $1/\sqrt{2}$ on going from hydrogen peroxide to deuterium peroxide, confirming that it arises from a hydrogen motion. With the water molecule in the vapor phase the frequencies of the symmetric and antisymmetric OH vibrations are separated by about a hundred wave numbers due to the rigid coupling of the OH groups. The near coincidence, or degeneracy, of these vibrations in hydrogen peroxide has been ascribed to loose coupling between the OH groups. The demonstration by Taylor that the Raman shift of 3200 cm^{-1} in the solid can be resolved into two peaks separated by about 130 cm^{-1} , and that a separation of about the same magnitude can be observed in the solutions offers good evidence that this is correct. It is true that a single OH frequency might be expected to be split into several components on going to a condensed phase because of molecular association effects, but such a large separation seems unlikely to follow. Because the separation has not been observed in the vapor there is some uncertainty involved in choosing the proper value for the unperturbed molecule. It would not be expected to be as large as in the condensed phases and the failure to observe it in the vapor limits it to the precision of the infrared spectroscopy. The vibrations ν_1 and ν_5 are best placed at 3610 cm^{-1} (50). Application of Badger's rule with this frequency yields the value 0.98 \AA for the OH bond distance.

ν_6 , the unsymmetrical bending vibration: The infrared absorption band observed at 1266 cm^{-1} in the vapor, 1353 cm^{-1} in the liquid, and 1378 cm^{-1} in the solid has been ascribed to the unsymmetrical bending of the OH groups. This is suggested by the frequency magnitude of the similar vibration in water. The frequency change for the deuterium-substituted peroxide confirms that this motion involves a hydrogen atom. This frequency in hydrogen peroxide is differentiated from that at 1400 cm^{-1}

(observed only in the condensed phases) by its greater intensity, as expected for an unsymmetrical vibration in the infrared, and by the occurrence of the Q branch to be expected for a predominantly parallel dipole oscillation.

ν_2 , the symmetrical bending vibration: Of the two remaining fundamental vibrations, that observed at about 1400 cm^{-1} in the Raman spectrum and the infrared spectrum of the solid at -78°C has the proper isotopic frequency change to permit its identification with the symmetrical bending vibration. Since this band, expected to be of low intensity in the infrared, had not been observed at first in the spectrum of the vapor a somewhat arbitrary correction for the effect of association had to be made. This was taken to be about 100 cm^{-1} , and Giguère and Bain (50) gave ν_2 as 1315 cm^{-1} . More recently Bain (51) has identified the symmetrical bending vibration superimposed on the ν_6 band in the vapor spectrum and gave 1280 cm^{-1} as the band center for ν_2 .

ν_4 , the torsional oscillation: Experimental evidence for the absorption due to the torsional oscillation of the OH groups was the last to be observed, accounting for earlier uncertainty in the frequency assignments. The band observed near 600 cm^{-1} by Taylor (52) and Giguère (46) is of the proper magnitude for the energy expected to be associated with this motion. Just as with the other OH vibrations there is an uncertain correction to be made for association in the condensed phases. Giguère (46) placed ν_4 at 500 cm^{-1} in the vapor, and Giguère and Bain (50) changed this to 660 cm^{-1} . Bain (51) has recently observed a broad, strong band in the vapor extending from 660 cm^{-1} to beyond the limit of potassium bromide optics near 440 cm^{-1} . This appears to be composed of overlapping bands with centers near 465 and 575 cm^{-1} . The difference between the observed values of this frequency in the infrared and Raman spectrum of the liquid indicated in Table 2 remains unexplained. Further complication was introduced by the results of a study of the microwave absorption spectrum of hydrogen peroxide. Massey and Bianco (16) deduced that the most probable value for the torsional oscillation was 113 cm^{-1} . On the basis of the

sinusoidal potential barrier (equation 1) this was the value they found consistent with the rotational constants derived from their measurements. Further work will be necessary before the energy of this vibration can be established with certainty.

Overtone and Combination Bands: Several infrared bands and one Raman band have been identified as overtone or combination frequencies. These assignments are fairly certain, but it is not impossible that another interpretation might be given them. Taylor (52) suggested that a shoulder at 1300 cm^{-1} on the low frequency side of the 1400 cm^{-1} band in the infrared spectrum of crystalline hydrogen peroxide was due to the first overtone, $2\nu_4$, of the torsional oscillation frequency. The band observed at about 2800 cm^{-1} in the condensed phases and near 2600 cm^{-1} in the vapor was first considered to be a triple combination, $\nu_2 + \nu_3 + \nu_4$ (46). The magnitude of the change on going to deuterium peroxide shows this band to originate in a hydrogen motion, and it now seems best represented as a combination of $\nu_2 + \nu_6$ (50), although it may represent unresolved overtones of ν_2 or ν_6 alone (52). The infrared band at 4715 cm^{-1} in the liquid appears to allow the unambiguous assignment $\nu_5 + \nu_6$. The band at 7040 cm^{-1} was identified (46) definitely as the combination of $\nu_1 + \nu_5$ from a study of its fine structure. Two assignments appear to be possible for the band at 10290 cm^{-1} : either $3\nu_5$ or $2\nu_1 + \nu_5$ (46). The observation that this band is of the hybrid type rules out the cis planar structure for hydrogen peroxide (53). Additional overtones and combinations undoubtedly exist, possibly even in regions of the spectrum already subjected to search. The weakness of the absorption by hydrogen peroxide in general may make the discovery and resolution of such bands difficult.

Moments of Inertia

The moments of inertia of hydrogen peroxide about the three axes shown in Figure 4a have been determined by calculations (46, 50) based on the dimensions and angles measured for the molecule, by study of the fine structure of the spectrum due to molecular rotation (46, 53) and by study of the pure rotational spec-

trum (16). Zumwalt and Giguère (53) evaluated the rotational constants of hydrogen peroxide from the rotational fine structure of the 10290 cm^{-1} infrared band. The assumption was made that the rotational energy of hydrogen peroxide could be represented by that of a symmetric rotator. This is reasonable in view of the relatively large mass of the oxygen atoms. Thus the moment about axis A of Figure 4a is the unique one and the moments perpendicular to it, the moments I_B and I_C , are nearly equal. In fact, Zumwalt and Giguère concluded that the form of the molecule with azimuthal angle, ϕ , of 90° was insignificantly asymmetric and that certain features of the spectrum due to asymmetry could not be accounted for if ϕ lay between 85° and 95° . Zumwalt and Giguère obtained the values $2.78_6 \times 10^{-40} \text{ g cm}^2$ for the small moment of inertia, I_A , and $33.9 \times 10^{-40} \text{ g cm}^2$ for the harmonic mean of the two larger moments of inertia, $2I_B I_C / (I_B + I_C)$, for hydrogen peroxide in the ground state.

The evaluation by Giguère (46) of the rotational constants from a study of the fine structure of the 7040 cm^{-1} band gave agreement with the earlier high dispersion study. Giguère (46) calculated the moments of inertia corresponding to values of the azimuthal angle between 0° and 180° , using the dimensions 1.48 \AA for the OO distance, 0.98 \AA for the OH distance, and 102° for the OOH angle (the equations relating the moments of inertia to the atomic masses and molecular dimensions were given by Wilson and Badger (54)). The extremes of the values obtained for the moments of inertia ($\text{g cm}^2 \times 10^{40}$) in these calculations as the azimuthal angle was varied from 0° to 180° were: I_A , 2.89 to 2.76; I_B , 32.0 to 35.1; and I_C , 35.0 to 32.4. These moments are compatible with values of the rotational constants such as were determined from the study of the 10290 and 7040 cm^{-1} bands. It can be seen that the harmonic mean of the larger moments is quite insensitive to the value of the azimuthal angle. The smaller moment of inertia varies about 5% in going from the cis to the trans configuration. The more important dependence of the magnitude of this moment upon the value of the uncertain OH distance makes it of little value in establishing the azimuthal angle. Giguère calcu-

lated that the best agreement of the smaller moment of inertia with the observed rotational constant would follow if the OH distance in hydrogen peroxide were somewhat greater than that in water, where it has the value 0.957 \AA .

The problem of selecting molecular dimensions compatible with the moments of inertia was examined further by Giguère and Bain (50), who made use of their spectroscopic study of deuterium peroxide. By applying the Teller-Redlich product rule (43), a dimensionless relation between the ratio of the fundamental frequencies of two isotopic molecules and the product of their ratios of mass and moments of inertia and a symmetry factor, Giguère and Bain determined that the ratio $I_C^D/I_C = 1.12$ and the ratio $I_A^D I_B^D / I_A I_B = 2.11_3 \pm 0.02$, where the superscript D denotes the moment of inertia of deuterium peroxide. The former ratio, I_C^D/I_C , cannot be considered precise since it was calculated from the ratio of the symmetric vibration frequencies, some of which have only been observed in the liquid and to which an uncertain correction must be applied. The value of the latter ratio, $I_A^D I_B^D / I_A I_B$, is more certain, having been calculated from vapor-phase observed frequencies to which a small factor was applied to correct for the use of observed rather than zero-order values. The range of values of the azimuthal angle, ϕ , consistent with the latter ratio was then determined for various values of the molecular dimensions. The OO bond length was taken as 1.49 \AA , the OH bond length was varied between 0.957 and 1.01 \AA , and the OOH angle varied between 96° and 105.5° . Giguère and Bain (47) now believe the OH bond distance in hydrogen peroxides can be given as $0.965 \pm 0.01 \text{ \AA}$. The results of these calculations were given (50) in the form of curves showing the loci of consistent values of the various parameters, and it was concluded that the azimuthal angle must lie within the range $82 \pm 20^\circ$.

The value of the smaller moment of inertia, I_A , was calculated to be $2.959 \times 10^{-40} \text{ g cm}^2$ by Massey and Bianco (16) as a result of their study of the microwave absorption spectrum. With the OO distance of 1.49 \AA and the OH distance 0.98 \AA this

moment of inertia was calculated to be most consistent with an OOH angle, θ , of close to 90° .

Force Constants

The identification of the vibrational frequencies allows the calculation of the force constants, i.e., the restoring force per unit displacement of two atoms along their bonding axis, associated with the vibrations. Bailey and Gordon (44) calculated the force constants for hydrogen peroxide, but since their frequency assignments have been rejected as incorrect these values need not be cited. Giguère and Bain (50) determined the force constants for hydrogen and deuterium peroxides after their investigation of the molecular dimensions and frequency assignments. The results of these calculations, made with a suitable quadratic potential function, are given in Table 3. Some uncertainties remain regarding these force constants since further amendment of the fundamental frequency values and the molecular dimensions may be warranted.

Final Selection of Structure

The molecular dimensions given in Table 3 may be chosen as the most reliable for the structure of hydrogen or deuterium peroxide in the vapor state. It should be remembered that these parameters are interdependent to various degrees.

The value for the OO bond length is certainly well established.

The limits set by Giguère and Bain (50) (between 0.957 and 1.01 Å) vary likely comprise the possible range of values for the OH distance in hydrogen peroxide. The value of 0.97 Å chosen here is somewhat greater than known for water (0.957 Å) and only slightly less than that measured for hydroxyl radical (0.971 Å).

The choice of 100° for the OOH angle, θ , is something of a compromise. It appears unlikely that this angle is as large as the apical angle in water, yet some departure from the unperturbed orbital angle of 90° certainly occurs. The measured rotational constants appear to place a lower limit of 96° , while the microwave absorption study suggested 90° . The value of 96° is near that in-

TABLE 3

PROBABLE VALUES OF MOLECULAR PARAMETERS
FOR HYDROGEN PEROXIDE

(See Discussion for Sources)

| | H ₂ O ₂ | D ₂ O ₂ |
|--|-------------------------------|-------------------------------|
| Fundamental Frequencies, cm ⁻¹ : | | |
| 1 | 3610 | 2670 |
| 2 | 1315 | 1000 |
| 3 | 877 | 877 |
| 4 | 660 | 480 |
| 5 | 3610 | 2680 |
| 6 | 1266 | 947 |
| Force Constants, dynes/cm x 10 ⁻⁵ : | | |
| k _{O-H} | 7.28 | 7.53 |
| k' _{O-H} | <0.01 | 0.03 |
| k _{O-O} | 3.84 | 4.04 |
| δ _{OOH} | 0.89 | 0.95 |
| δ' _{OOH} | -0.04 | -0.09 |
| γ _{HO-OH} | 0.11 | 0.11 |
| k* * | 0.30 | 0.58 |
| Bond Lengths, Å: | | |
| OH | 0.97 ± 0.005 | 0.97 ± 0.005 |
| OO | 1.49 ± 0.01 | 1.49 ± 0.01 |
| Bond Angles, degrees: | | |
| ∅ | 95 ± 10 | 95 ± 10 |
| θ | 100 | 100 |
| Moments of Inertia, g cm ² x 10 ⁴⁰ : | | |
| I _A | 2.83 | 5.14 |
| I _B | 33.6 | 38.3 |
| I _C | 33.7 | 37.9 |

* a constant added to the potential function (50)

licated by the X-ray diffraction study of the crystal, whereas the study of urea hydroperoxidate suggested a value near 102° . Both of these values of course refer to the molecule in a condensed phase where a certain contribution of intermolecular attraction must affect this angle.

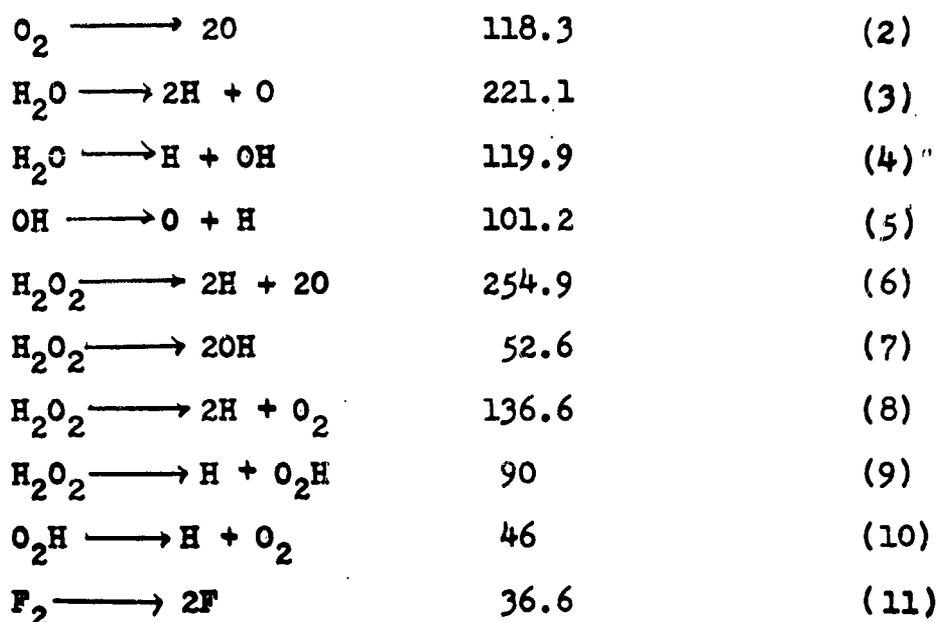
The selection of the equilibrium value for the azimuthal angle, θ , is likewise uncertain. The value of 82° given by the study of the moments of inertia must be taken along with the limits of precision of $\pm 20^\circ$. A distinction cannot be made between this acute value for the azimuth of the molecule in the vapor which is set by the study of the rotational spectrum and the obtuse angle with values between 90° and 113° suggested by the quantum mechanical calculations and measured by X-ray diffraction of hydrogen peroxide in condensed phases. The evidence would seem to favor a slightly obtuse angle, but all the methods for evaluation are insensitive to small variations.

Bond Energies in Hydrogen Peroxide

The energy associated with the bond between two atoms in a molecule is a quantity useful for comparison and prediction of structure. It is realized that to regard a certain portion of the energy of a molecule as localized in one bond is a somewhat formal procedure, but the concept is useful and justified within certain limits of precision. The definition of the bond energy must accordingly be made carefully. The discussions by Walsh (55) and Szwarc (56) of the definition of bond energy will be found particularly enlightening; the review by Glockler (57) and the comments by Baughan (58) will also be found useful. The bond energy refers to the particular portion of the total energy possessed by a molecule which is concerned with the binding of two or its atoms in the exact electronic states in which they exist in the molecule. The sum of all the bond energies in the molecule is equal to the heat of atomization of the molecule into atoms retaining the same valence states possessed in the molecule. The bond energy is not equivalent to the energy of dissociation of a molecule into two parts separated at the bond under consideration, although if relatively small energy

quantities due to rotation, vibration, and zero-point vibration are neglected, the dissociation energy of a diatomic molecule may be considered the same as the bond energy. With a polyatomic molecule there may occur relatively large energy-liberating reorganizations of the parts dissociated at a particular bond, and the dissociation energy is thus in general not equivalent to the bond energy. At the same time, however, it is difficult or as yet impossible to make a measurement which convincingly represents the localization of a certain portion of the molecular energy in one bond. Because of this, certain expedients have been found necessary, and the values of the various heats of dissociation find frequent use in the estimation of bond energies. For example, in a molecule XY_n the XY bond energy is taken as $1/n$ of the heat of atomization of XY_n , a reasonable procedure. With unsymmetrical molecules or in cases where question arises regarding the equivalence of a given bond in the different environments of two disparate molecules the procedure becomes more subtle. The problems which arise in establishing the bond energies in hydrogen peroxide are outlined below.

In order to arrive at the bond energies of the OH and OO bonds in hydrogen peroxide the energies of a number of reactions may be considered. The following values in kcal/mole are for reaction at 25°C and bond energies calculated from them therefore contain a small contribution due to the pressure-volume change of the reaction under consideration. This may be neglected within the precision with which the bond energies can be established. All the values given below are well established (59) except the two next to last; the basis for the choice of these latter two uncertain values was given in Chapter 5 in the discussion of thermodynamic properties. The reason for the inclusion of the last reaction, involving fluorine, will become apparent in the discussion.



It is presumed that the two OH bonds in hydrogen peroxide are equivalent, therefore if the OH bond energy is known, the OO bond energy follows through use of equation (6), and vice versa. If the value for one of these bond energies is known in another compound, it may be assumed as a first approximation that the same value for the bond energy obtains in hydrogen peroxide. It was in this way that Pauling (25) first determined the bond energies in hydrogen peroxide. The value of 118 kcal/mole from equation (2) cannot be taken as the value for the OO bond energy in hydrogen peroxide since the above approximation cannot be expected to hold; in the O_2 molecule there exist two three-electron bonds in addition to the single bond occurring between the oxygen atoms in hydrogen peroxide. On the other hand the OH bonds in water must be quite similar to those in hydrogen peroxide. If half of the value for reaction (3), 110.5 kcal/mole, is taken as the value of the OH bond energy in hydrogen peroxide, then by use of reaction (6) the OO bond energy in hydrogen peroxide must be 33.8 kcal/mole. Using slightly different thermochemical data, Pauling arrived in this way at the value 34.9 kcal/mole.

The method of choosing the value of the OH bond energy for the above calculation shows up the difference between bond

energy and dissociation energy. For example, the chosen bond energy of 110 kcal from equation 3 may be compared with the dissociation energies of 120 kcal necessary to remove the first hydrogen from water and 101 kcal to remove the second. Although the sum of these reactions equals the sum of the OH bond energies, it is more difficult to remove the first hydrogen. The situation is a little different with hydrogen peroxide. The thermochemical data for the hydrogen-removing dissociations (reactions (9) and (10)) are not known with certainty, but it appears that the energy required for removal of the first hydrogen from hydrogen peroxide is about twice, more or less, that required to remove the second. However, in both cases the bond energy chosen above is greater than the dissociation energy. Evidently the reorganization after dissociation of the remaining fragments, first O_2H , then O_2 , yields some energy which is applied to reducing the dissociation energy below that of the bond energy.

It is, of course, possible that the OH bonds in hydrogen peroxide differ significantly from those in water, invalidating the assumption made above. Such a criticism has been given by Skinner (60) and Walsh (55). Skinner argued that hydrogen peroxide, like the hydroxyl radical, does not possess certain resonance energy of ionic forms which water does. He therefore believed the OH bond energy observed in hydroxyl to be more appropriate to hydrogen peroxide. Using the value 102 kcal/mole, Skinner calculated the OO bond energy to be about 52 kcal/mole. The basis of this conclusion was challenged by Glockler and Matlack (61), who found reason to believe that hydrogen peroxide possesses much the same ionic resonance energy that water does and that this energy is denied to hydroxyl. As additional proof that the 35 kcal estimate for OO bond energy is correct, Glockler and Matlack showed the coincidence of this value with a curve relating the dissociation energies of ozone and molecular oxygen, O_2 , in several electronic states with interatomic distance. Without further justification, it seems likely that this coincidence is only fortuitous.

The problem of selecting the basis upon which the OH bond energy ought to be chosen was discussed from several viewpoints by Walsh (55). Walsh gave reasons for assuming the OH bond in hydrogen peroxide to be more polar than that in hydroxyl and concluded that it should therefore be weaker. Confirmation of this was found in the estimate of 1.01 \AA for the OH bond length in hydrogen peroxide given by Giguère (62) in a prepublication note versus the length of 0.97 \AA in hydroxyl and in the value of the force constant for OH stretching in hydrogen peroxide given by Bailey and Gordon (44). Thus Walsh assumed the OH bond energy in hydrogen peroxide to be less than 100 kcal, setting a lower limit of 56 kcal for the OO bond energy. The values chosen were 96 kcal for the OH bond and 64 kcal for the OO bond. This higher value of the OO bond energy appeared to Walsh to be much more satisfactory on several counts: it gave a higher value for OO bonding than for SS (51 kcal/mole) or Se-Se (41 kcal/mole) bonding in accord with the idea that the smaller atoms should be more strongly bound, it compared well with the cited value of 64 kcal/mole for the FF bond, and it aided in explaining the character of the electronic structure of oxygen bonds.

Unfortunately, as Giguère (63) pointed out, the data upon which Walsh based his reasoning was not sound. As reference to the previous discussion of the structure of hydrogen peroxide will show, the values for the OH bond length and force constant used were erroneous. The corrected value for the heat of dissociation of fluorine, reaction (10), shows it to be of comparable magnitude with the 34 kcal/mole OO bond energy. The lower energy of the OO bond (and the FF and NN bonds) in relation to the bond energies of heavier atoms is believed to be well accounted for. Briefly, in the heavier atoms inner-shell repulsion reduces the orbital overlapping and bond energy; in the lighter atoms closer approach and stronger bonds are possible with the exception that with nitrogen, oxygen and fluorine the repulsion of close-approaching filled orbitals limits the strength of the bond.

The best estimate of the bond energies in hydrogen peroxide thus remains that of Pauling, slightly corrected values of which were

given above. It ought not be overlooked, however, that this remains an estimate because a sufficiently precise value cannot be obtained from other considerations. Although Walsh was led to extreme values not accepted here, his lengthy discussion of the relationship between bond energy, other bond properties, and electron structure remains worthy of study for the many suggestive points raised for consideration. When such relationships become more quantitative and more precise measurements are available it is not impossible that a small upward revision of the values of the OO bond energy in hydrogen peroxide may be warranted.

Comparative Structure

It is of interest to compare the structure of hydrogen peroxide with other compounds. A simple subdivision of such comparisons is: a) with substituted hydrogen peroxide, b) with "per" compounds of the oxygen homolog elements, and c) with compounds of the elements neighboring oxygen--carbon, nitrogen and fluorine. A few comments on each of these may be given.

a) A rational basis for classifying elements according to whether or not peroxides are formed was proposed by Haissinsky (64), who concluded that elements of electronegativity equal to or less than that of hydrogen-formed peroxides. When such peroxides are formed the element appears always to enter the peroxide in its highest valence state. The success of this classification was explained by Walsh (65) in terms of the improved atomic orbital overlapping between element and peroxide-oxygen possible with elements of lower electronegativity. Thus the largely ionic nature of sodium peroxide and the failure to observe halogen peroxides finds common explanation in the fact that, to be stable, the peroxide group requires considerable charge transfer to it. This subject receives further discussion in Chapter 12.

Such a consideration apparently has not been extended to the large field of organic peroxides. It has been suggested (66) that the enhanced reactivity of acyl-substituted peroxides

over that of aryl may be due to the greater electronegativity of the acyl groups. So few studies of the pertinent physical properties of organic peroxides have been made that little generalization can be given. In the discussion of spectroscopy it was mentioned that the OO vibration appears the same in many organic peroxides. The energies of dissociation at the OO bond commonly observed are generally lower than that in hydrogen peroxide (56). Little is known about the orientation of organic groups substituted in hydrogen peroxide. For example, the reasonable suggestion (55) that di tert butyl peroxide might have the trans configuration comes into question as a result of recent dipole moment measurements (20). As far as stability or reactivity of the peroxide group is concerned it appears that inorganic peroxides are in general more stable than hydrogen peroxide. With organic peroxides no such generalization can be made; by reputation they are perhaps justly considered more unstable than hydrogen peroxide, but the occurrence of such stable ones as benzoyl peroxide and di tert butyl peroxide and the possibility of even preparing for identification such compounds as acetylene peroxides (67) underscores the impossibility of prediction at present.

b) The structure of hydrogen persulfide, H_2S_2 , has received considerable study (54, 68). The molecule is much like hydrogen peroxide with an SS bond length of 2.05 Å and an azimuthal angle very close to 90° . The similarity extends to chemical properties as well (69). Some differences in behavior related to differences in associative properties have been discussed (70), but the effect of the changed electronic structure upon reactivity has not received detailed consideration. The possibility of halogen substitution of hydrogen persulfide, e.g., to form S_2Cl_2 , and the occurrence of hydrogen trisulfide, H_2S_3 , illustrate the effect of the reduced electronegativity of sulfur.

This comparison unfortunately cannot be extended to the selenium and tellurium compounds. The existence of hydrogen perselenide has been suggested, but no further evidence is available.

c) In the carbon compounds which might be compared with hydro-

gen peroxide the importance of hybrid orbitals in the structure introduces a considerable difference in binding energy; the partial s character of the carbon bonds makes them much stronger. This is appreciable in ethane, and in acetylene, the carbon formula analog of hydrogen peroxide, the comparison becomes remote because of the π bond structure here, i.e., the comparison is not being made with a single bond. A much closer comparison occurs with nitrogen in the form of hydrazine, N_2H_4 . This has been given considerable discussion (71, 72), bringing out the fact that hydrazine bears much the same relationship to ammonia that hydrogen peroxide does to water. The structure (32) of hydrazine is like that of hydrogen peroxide. In hydrazine a plane may be imagined which bisects an HNH angle and contains the two nitrogen atoms; there are two such planes, one for each HNH group, and these planes are perpendicular. The calculations show that this structure is somewhat more stable than the trans structure because of a slight hybrid character of the nitrogen orbitals. Properties of both hydrogen peroxide and hydrazine are combined in hydroxylamine, NH_2OH , and an intercomparison of these substances has been made by Angeli (73). This molecule appears to have the cis structure (74), although the trans structure or a mixture is not ruled out completely. Luft (75) compared hydrogen peroxide, hydrazine and hydroxylamine in terms of the internal rotation possible in each.

If the series of compounds, N_2H_4 , NH_2OH , H_2O_2 , FOH , and F_2 , is considered, there is present on each central atom a pair of unbonded s electrons; in addition there is present successively zero up to four sets of unbonded p electron pairs on the central atoms. It should be informative to correlate the properties of this series of molecules with their structures. In connection with this series it is of interest to consider the little-known fluoramine molecule, FNH_2 (76), which may be considered (31) to be the isoelectronic, valence bonded analog of the pyramidal trigonal hydrogen peroxide molecule discussed earlier. The fluorine atom may be regarded as the "compound atom" of the OH group, that is, it is isoelectronic with hydroxyl. As such, experience indicates that the compound atom should be similar

in properties to the group it represents. This appears to hold reasonably well for the fluorine-hydroxyl case. Hydrogen peroxide has sometimes been spoken of as a "pseudo halogen," particularly with regard to its photolytic dissociation (77).

Other comparisons of hydrogen peroxide might be made. For example, it might be viewed as a member of a series of hydrides (71). Or the comparison of oxygen compounds begun in the discussion of electronic structure might be extended. Such comparisons should become more useful and informative as the quantitative theory of chemical bonding is improved.

MOLECULAR ASSOCIATION OF HYDROGEN PEROXIDE

The intermolecular forces between hydrogen peroxide molecules or between hydrogen peroxide and other molecules in mixture with it, are responsible for determining the character of many of the commonly observed physical properties. Although the emphasis in the study of the hydrogen peroxide molecule itself has been aimed at explaining its chemical properties, the structure is nonetheless important in establishing the forces external to the molecule. The kinds of relationships with neighboring molecules which these forces permit set the conditions under which chemical reaction must occur, as well as determining physical properties.

The possession of a structure adapted to strong hydrogen bonding is the consideration of greatest importance in determining the associative properties of hydrogen peroxide. Coincident with this structure is a large permanent dipole moment, which contributes appreciably to association. The obvious similarity of hydrogen peroxide and water in respect to these characteristics underlies the close correspondence of the magnitudes of such of their properties as boiling point, surface tension and dielectric constant. The hydrogen bond may be simply regarded as an attraction which exists between the residual positive and negative charges which occur, respectively, on the hydrogen and oxygen atoms of different molecules. The electronic arrangement responsible for this attraction, involving the presence of asymmetric (and therefore partially hybrid)

non-bonding electron pairs on the relatively small sized oxygen atoms (78), cannot, of course, be stated in such simple terms as this. The hydrogen bond is definitely oriented in direction; its axis is an extension of that of the molecular OH bond which furnishes the hydrogen participating in the hydrogen bond. Each oxygen may attract two hydrogens, but size limits the participation of the hydrogen to but one bond. Thus water donates two hydrogens to form hydrogen bonds and its oxygen may participate in two. Hydrogen peroxide also may donate two hydrogens, but its two oxygens may coordinate four hydrogen bonds. A discussion may now be given of the association of hydrogen peroxide in the various phases.

Association in the Solid Phase

The crystal structure of hydrogen peroxide was determined by X-ray diffraction by Abrahams, Collin, and Lipscomb (42), who gave the following data: tetragonal crystal with dimensions $a = b = 4.06 \pm 0.02 \text{ \AA}$, $c = 8.00 \pm 0.02 \text{ \AA}$, space group $D_4^4 - P4_12_1$ (enantiomorphous with $D_4^8 - P4_32_1$), four molecules per unit cell, volume of unit cell 131.9 \AA^3 . These results substantiate the earlier work of Feher and Klötzer (79), and Natta and Rigamonti (80). This crystal is quite dense, with hydrogen bonds forming the principal binding between molecules. The OO distance in the hydrogen bond, O-H-O, was found to be 2.78 \AA , about the same as that occurring in water ice. Each molecule is linked to every other molecule through the network of hydrogen bonds. An infinite helix may be followed along the four-fold screw axes of the crystal. It was concluded that the crystal should have no residual entropy at absolute zero.

Abrahams, Collin, and Lipscomb suggested a means whereby the crystal might be modified by the participation of water molecules, thus accounting for solid solution formation. However, true solid solutions have been shown not to exist, removing the necessity of such consideration. The only stable association of hydrogen peroxide with water in the solid phase appears to be the hydrate, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. Evidence was cited in the discussion of the

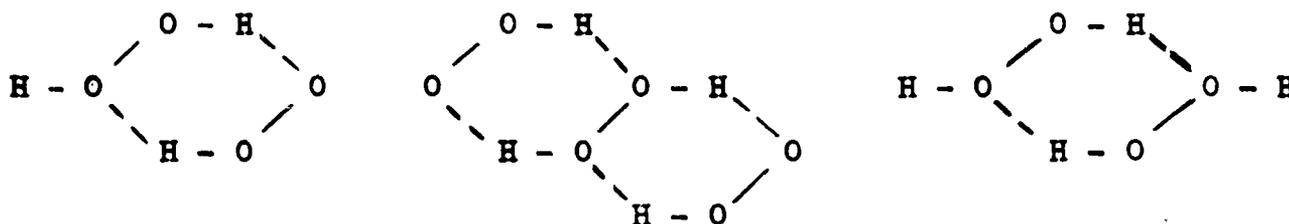
phase diagram in Chapter 5 to indicate that some distortion of the hydrogen peroxide molecule is involved in forming this hydrogen-bonded compound. The only other addition compound of hydrogen peroxide which has received careful structural study is that with urea, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$ (37).

Association in Anhydrous Liquid Hydrogen Peroxide

It was concluded in the discussion of molecular structure that the failure of some constitutive properties, e.g., the parachor, to give an insight to the structure gave evidence that hydrogen peroxide is associated. Ample additional evidence that this is so is available. Maass and Hatcher (81) cited the low value of the Ramsay-Eötvös-Shields constant, which depends upon the surface tension and density, to show that hydrogen peroxide is associated to much the same degree as water. Trouton's rule leads to somewhat more quantitative evidence in this respect. According to Trouton's rule, the entropy of vaporization at the normal boiling point has a value of 21 cal/mole $^\circ\text{K}$ for most substances. The high values for hydrogen peroxide (26.6) and water (26.1) show that these substances must possess some additional attraction between molecules in the liquid state which other substances in general do not. Both hydrogen peroxide and water have been shown not to be associated in the vapor, therefore their states in the vapor are the same, except for volume differences, as those of the substances which determine the "normal" value of the Trouton constant. This additional orderliness or restriction on completely random motion in liquid water and hydrogen peroxide is due to the linking together of groups of molecules through hydrogen bonding. Thus the forces holding the molecules together in the liquid state are on the average greater, increasing the density, surface tension, and energy required for vaporization. The high dielectric constant of hydrogen peroxide illustrates this further. The dielectric constant is proportional to the square of the dipole moment, thus if the molecules link together in such a fashion that the dipole moments of the aggregates are enhanced, then even though the total number of dipoles is reduced the net effect is to increase the dielectric con-

stant. The presentation of Pauling (25) suggests that the dielectric constant of hydrogen peroxide at room temperature would lie in the range of 10 to 20 in the absence of association, whereas its actual value is near 80.

Few proposals have been made regarding the exact orientation of associated hydrogen peroxide molecules. Randall (34) came to the conclusion after an X-ray diffraction study that the anhydrous liquid could be represented as an assemblage of hydroxyl groups with a close packed structure of the face centered cubic type in which each hydrogen peroxide molecule has between 6 and 12 closest neighbors. It was suggested by Hart and Matheson (82) that the occurrence of a hydrogen bonded complex of hydrogen peroxide with one or two perhydroxyl radicals, as shown below, might explain certain decomposition processes. Luft (83) amplified this to suggest that cyclic dimers of hydrogen peroxide might exist and pointed out spectroscopic evidence in support of this.



Whatever their orientation, it should be remembered that thermal agitation of the molecules in the liquid is sufficient to cause both the disruption and formation of hydrogen bonds; a hydrogen bonded aggregation does not maintain its identity long.

Comparison With Water

The comparable values for the Trouton constant for water and hydrogen peroxide indicate a similar degree of association in the two liquids at their boiling points. A more appreciable difference apparently exists in the two liquids at their nearly coincident freezing points. The heat of fusion of hydrogen peroxide (2.9 kcal/mole) is about twice that of water (1.4 kcal/mole). Therefore if the intermolecular forces are about the same it ap-

pears that more of the association is lost on melting in hydrogen peroxide than in water. Pauling (25) estimates that 15% of the hydrogen bonds in ice are broken on melting; Giguere (71) suggests that 20% are broken in hydrogen peroxide.

The changes in the infrared absorption spectrum on going from the vapor to the liquid are much the same with hydrogen peroxide and water. As discussed by Rodebush (84), the fundamental stretching frequencies decrease, while the fundamental bending frequencies increase; both increase in intensity and breadth. Giguere (71) concluded that the larger shift of frequency observed with hydrogen peroxide was an indication that the hydrogen bonds in hydrogen peroxide are slightly stronger than those in water. Additional evidence that fewer hydrogen bonds are broken on melting water than hydrogen peroxide was found by Taylor (85) in the fact that the appearance of the 3400 cm^{-1} OH band in supercooled hydrogen peroxide was observed to have little of the detail found for this band with the crystal. With water, on the other hand, this band shows much the same character in both liquid and solid.

The relative values of the dielectric constant also show evidence of a lower degree of association in hydrogen peroxide. Although hydrogen peroxide has a larger dipole moment than that of water, the dielectric constant of water is greater than that of hydrogen peroxide. Since the dielectric constant is a function of both the number of dipoles per unit volume and the magnitude of the dipoles, it is difficult to predict the net effect of both changing the moment of the monomer and the degree and specific orientation of aggregation. Gross and Taylor (86) suggest that it is not unlikely that the larger moment of hydrogen peroxide is compensated by a decreased degree of association and refer to theoretical reasoning (87) regarding hydrogen peroxide which underlies such a conclusion.

One signal difference between hydrogen peroxide and water is found in the direction of change of volume on melting. The molar densities of the solid are about the same for both substances, yet water becomes more dense on melting and hydrogen peroxide becomes

less dense. The portions of the crystals which pass unbroken into the liquid on melting presumably continue to contribute the same effect to the density. The remaining molecules, freed from the crystalline association, are bound less strongly to each other, but there is an increased number of near neighbors at greater distances. The net effect for water seems to be one of greater attraction; with hydrogen peroxide the increased number of contacts seems not to outweigh the decreased strength of each. Taylor (85) has suggested that the ready supercooling of hydrogen peroxide indicates that the molecule must be distorted in order to fit into the crystal. This may be correct if nucleation is not the determining factor. The associative properties of other hydrides have been compared with those of hydrogen peroxide by Giguere (71).

Association in Solution

Solutions of hydrogen peroxide in water are shown to be non-ideal by each of the three tests usually applied: the volume of a solution is less than the sum of the volumes of the components, there is an appreciable heat effect upon mixing, and the vapor pressures of the solutions do not follow Raoult's law. Further evidence is found in the irregular relationships between solution concentration and such properties as viscosity, surface tension, and dielectric constant. The direction of the departure from ideality in each case seems to point to an enhancement of either the number or the force of the attractions between molecules upon forming the solutions, e.g., the reduction of total volume and vapor pressure and the evolution of heat which occur on mixing. Because of the similarity in magnitude and nature of the intermolecular forces of these two substances it seems most reasonable to conclude that this behavior is due to the formation of additional hydrogen bonds, or, to put it another way, it may be assumed that hydrogen bonds between water and hydrogen peroxide molecules are more stable than those between the molecules of these substances themselves.

These general conclusions have not yet been much amplified in detail. Morissette and Giguere (88) have explained the endothermic effect (discussed in Chapter 5) occurring on dilution of certain concentrations of hydrogen peroxide at temperatures below 21°C as follows: Suppose the addition of some hydrogen peroxide to water at 0°C breaks more hydrogen bonds between water molecules than are formed between water and hydrogen peroxide; the net reduction in number of hydrogen bonds yields an endothermic heat effect. At higher temperatures, i.e., above 21° , there exist fewer hydrogen bonds between water molecules, then fewer are broken on the addition of hydrogen peroxide and relatively more are formed between water and hydrogen peroxide. Thus the heating of a solution from 0° to a temperature above 21°C breaks more water-water hydrogen bonds than water-hydrogen peroxide bonds.

The existence of the addition compound, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, has often been invoked to explain the non-ideal characteristics of hydrogen peroxide-water solutions. Thus Voznesenskaya and Zaslavskii (89) found the maximum in the departure from additivity on a volume concentration basis of the "atomic concentration" to occur for the composition $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. Gross and Taylor (86) speak of the possible effect of $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ in producing the maxima in the dielectric constant-composition isotherms. It is true that the maximum irregularity of many of the solution properties lies near enough the composition of $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ to suggest a special role for it, but the relationship is vague and inconsistent. The very flatness of the maximum in the freezing point diagram which reveals the existence of the addition compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ indicates that it must be almost completely dissociated in the liquid. It seems more reasonable to conclude that, of all the possible aggregates of hydrogen peroxide and water together, only that of composition $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ can maintain its identity on going to the solid phase.

Wynne-Jones (90) has compared hydrogen peroxide-water solutions with ethanol-water solutions, pointing out in terms of

their excess thermodynamic properties how hydrogen peroxide can fit into the water structure whereas ethanol cannot be accommodated into the water structure.

Little study has been made of other types of intermolecular forces in hydrogen peroxide solutions, such as ion-dipole, or dipole-induced dipole attractions. Gorin (91) found hydrogen peroxide to be "salted in" to a number of electrolyte solutions. It was concluded that hydrogen peroxide molecules tend to replace water molecules about the ions with the exception of hydrogen ion. This action was explained in terms of the higher dipole moment of hydrogen peroxide.

The Energy of the Hydrogen Bond

Pauling (25) attributed about a quarter of the heat of sublimation of ice (12.2 kcal/mole) to van der Waals forces and the remainder to hydrogen bonds. Since there are two hydrogen bonds per molecule this leads to a value of 4.5 kcal/mole for the energy of a hydrogen bond in water. The heat of sublimation of hydrogen peroxide was taken as 14.1 kcal/mole by Pauling, and after subtraction of an estimated 5 kcal/mole for van der Waals forces this led to the same value for the energy of a hydrogen bond in hydrogen peroxide. If the estimate of the energy of the van der Waals forces remains valid, the improved value for the heat of sublimation of hydrogen peroxide of 15.5 kcal/mole would indicate a slightly stronger hydrogen bond in hydrogen peroxide than in water in agreement with the conclusion reached on the basis of other evidence. Scatchard, Kavanagh, and Ticknor (92) calculated the energy of formation of a hydrogen bond upon the mixing of equal parts of hydrogen peroxide and water to be 4.5 kcal/mole. This seems to constitute acceptable agreement with Pauling's estimate.

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