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Vapor-Liquid Equilibrium. VIII. Hydrogen Peroxide-Water Mixtures[1]

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Equilibrium vapor pressures and compositions of hydrogen peroxide-water mixtures have been measured over the whole range of composition at 60, 75 and 90° and for approximately equimolal mixtures at 45 and 105° in an improved still designed to meet the special difficulties of this system. The pressure measurements were used to determine improved values of the compositions and the thermodynamic properties of the mixtures by means of a four parameter expression for the free energy of mixing as a function of the temperature and the liquid composition. The vapor pressures of pure hydrogen peroxide are computed from those of mixtures in this temperature range and are extrapolated by applying the Ramsay-Young relation with water as standard. The thermodynamic properties of mixtures are calculated on the assumptions that the variation with composition of the cohesive energy of hydrogen peroxide-water mixtures is due entirely to hydrogen bonds and that the energy of a hydrogen bond is independent of the nature of the molecules involved or of other reactions of either molecule involved. This simple theory provides a fair approximation to the dependence on composition and leads to reasonable values for the extent of association and for the strength of the hydrogen bond.

The prevalence of hydrogen bonding which accounts in large part for the physical similarities between liquid water and hydrogen peroxide leads also, particularly enough, to a considerable deviation from ideality in mixtures of these components. Vapor-liquid equilibrium measurements reflect substantial negative deviations and negative heats of mixing for this system, which may be represented approximately in terms of the changing amount of hydrogen bonding which results from mass-action influences in the various solutions.

The Equilibrium Still.—The still used in this investigation is similar to the one previously in use in this Laboratory,[2] with modifications to improve the former still and to provide for the special characteristics of hydrogen peroxide solutions. A diagram is shown as Fig. 1.

The liquid in the still is heated in one arm of a U shaped tube projecting below the main body of the still; heat is supplied from a fluid circulating through a heating jacket on the tube, an arrangement facilitating rapid convective circulation with attendant smooth boiling. Vapor from the boiler passes through a jacket around the inner chamber as in the older still; extension of this jacket over the top of the inner space has eliminated the possibility of condensation at the top of the inner chamber.

Perhaps the major difficulty in using the older still had been a tendency of the liquid level in the inner boiler to change during a run whenever steady heat transfer inward through the walls of the inner chamber from the region of slightly higher temperature in the outer jacket was not properly compensated by the heat loss up the thermocouple well. In the new still the possibility of such compensation has been removed by the elimination of heat transfer up the thermocouple well; to establish a heat balance, a cooling finger was installed in the stream entering the inner chamber. The design of the cooling finger necessitated a change in the inner boiler construction to provide a workable Cottrell pump in an arrangement which would drain back completely for sampling and cleaning.

The condenser is identical in operation to the earlier model, but the trap has been made in the shape of a long U to facilitate the rapid exchange of liquid and to eliminate stagnant spots. The trap and its overflow to the boiler meet at the bottom of a 20-mm. tube provided with a ground glass cap which permits the trap to be sampled and the outer boiler to be drained.

Pressure Measurement and Control.—The system for controlling pressure has been extensively rebuilt but is still the same in principle as the original equipment. It consists mainly of a large volume (90 liters) kept at constant temperature, and with provision for introduction or withdrawal of confining gas in small measured amounts. The original glass system for adjusting the amount of confining gas has been replaced by a metal system with solenoid operated valves, and a differential manometer has been added. These modifications allow facile adjustment from a convenient position.

In order to permit pressure measurements below the previous limit of about 100 mm., two extra arms have been added to the manometer, one on each side of the main tubes, and provision has been made for varying the amount of mercury in the system. Readings of low pressures are made by comparing the average level in the two side tubes with the level in the evacuated center tube. The manometer lighting system has been modified to provide the vertically parallel, horizontally diffuse light recommended by Beattie and co-workers.[3]

(1) This paper is based on the Ph.D. Thesis of G. M. Kavanagh, 1949. This work received support from Navy Bureau of Ordnance Contract N5ori - 07819, NR-223-008. Paper VII in this series appeared in THIS JOURNAL, **68**, 1960 (1946).

(2) G. Scatchard, C. L. Raymond and H. H. Gilman, *ibid.*, **60**, 1275 (1938).

(3) J. A. Beattie, D. D. Jacobus, J. M. Gaines, Jr., M. Benedict and B. B. Blaisdell, *Proc. Am. Acad.*, **74**, 327 (1941).

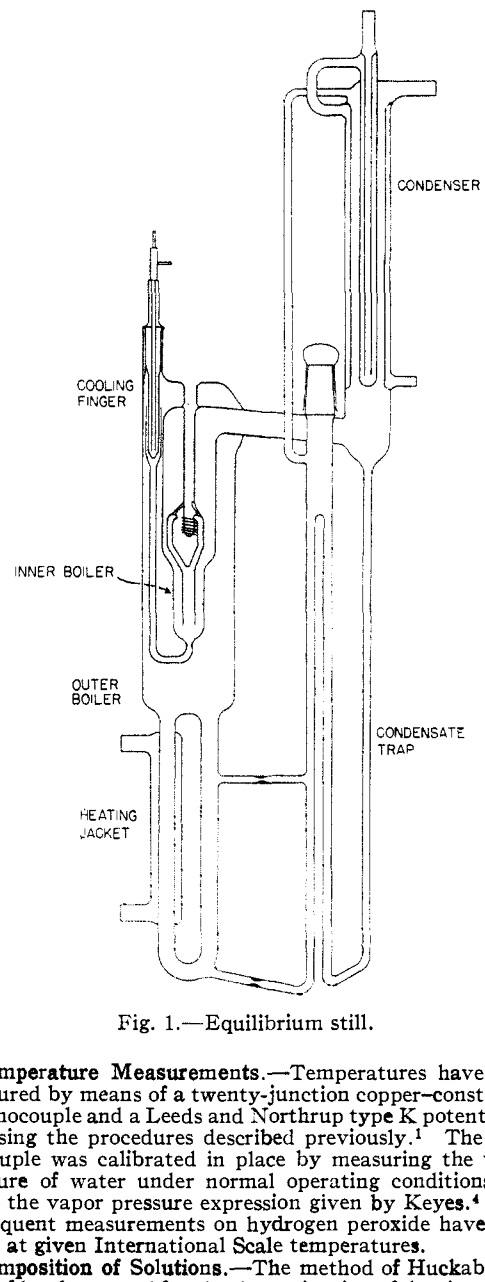

Fig. 1.—Equilibrium still.

Temperature Measurements.—Temperatures have been measured by means of a twenty-junction copper–constantan thermocouple and a Leeds and Northrup type K potentiometer using the procedures described previously.[1] The thermocouple was calibrated in place by measuring the vapor pressure of water under normal operating conditions and using the vapor pressure expression given by Keyes.[4] The subsequent measurements on hydrogen peroxide have been made at given International Scale temperatures.

Composition of Solutions.—The method of Huckaba and Keyes[5] has been used for the determination of density of the solutions, and their values for the density–composition relation have provided the composition. The accuracy of the determination is estimated to be one part in 5000 or 0.02% of the total range of composition.

Operation.—The modifications in the still were not entirely satisfactory and operation has not been without difficulty. In the system hydrogen peroxide–water, the relative volatility of water is so great that substantial fractionation occurs in the outer jacket, with a consequent difficult approach to the proper steady-state relation between the compositions in the inner and outer boilers. Regulation of the heat balance around the inner boiler during this process has been unsatisfactory, not because of difficulty in controlling the transfer through the finger, a fairly simple operation, but because of the delay in determining the change in liquid level in the inner boiler while boiling is going on. This delay in obtaining information necessary to keep the heat transfer in its proper relation to the changing conditions in the still has been sufficiently serious that a complete attainment of steady state has been prevented, and the measured vapor concentrations are relatively inaccurate.

In spite of the difficulty with concentrations, it has been possible to operate the still in such a way that good measurements have been obtained of the vapor pressures corresponding to the liquid in the inner boiler. With the closed system at constant pressure and the temperature read continuously, the heat transfer has been adjusted to give a constant temperature; the inner boiler thus maintains a constant composition, though its volume may be changing, and the resulting vapor pressure measurements are reliable.

When the system has run smoothly under these conditions for from 15 minutes to a half-hour within a few hundredths of a degree of the desired temperature, and for about five minutes within a hundredth of a degree, the manometer and surge tank are shut off from the still, and boiling is abruptly terminated by increasing the pressure to atmospheric. Samples are then taken as quickly as possible from the inner boiler and from the condensate trap, using jacketed pipets through whose jackets ice-water is circulated; and the solutions are transferred with reasonable dispatch to the pycnometers for analysis. The pressure in the large tank is then read carefully with the accurate manometer more or less at a leisure, but usually within 15 minutes of shutting down.

Measurements on Solutions.—The results of the measurements on hydrogen peroxide–water solutions are presented in Table I as smoothed or calculated values plus deviations, and the vapor pressures are shown in Fig. 2. In the table, x represents the liquid composition in mole fraction of water; P is the total vapor pressure; and y, the composition of the liquid removed from the trap, represents the vapor composition.

TABLE I

SMOOTHED PRESSURES AND CALCULATED COMPOSITIONS

Temp., °C.	Liquid comp. mole fract. water	Smoothed vapor pressure mm.	Deviation measured minus smoothed	Calculated vapor comp.	Deviation measured minus calculated
44.50	0.4860	27.417	+0.06	0.8904	−0.0177
60.00	.0381	19.30	+ .13	.1245	− .0217
	.1577	26.10	+ .11	.4419	− .0118
	.3169	39.46	+ .33	.7188	− .0139
	.4221	51.64	+ .37	.8312	− .0069
	.5925	77.26	−1.05	.9339	− .0188
	.7190	99.97	−0.72	.9710	− .0107
	.7964	114.50	+ .32	.9841	+ .0055
	.9095	134.99	+ .36	.9953	− .0007
75.00	.0404	42.72	− .44	....	.....[a]
	.1428	53.86	− .51	.3852	− .0233
	.2540	70.01	− .15	.6013	+ .0080
	.4249	105.20	+ .10	.8149	+ .0017
	.5037	126.06	+1.03	.8757	+ .0129
	.5101	127.88	+1.00	.8799	+ .0125
	.6759	180.53	−0.09	.9540	− .0008
	.7223	196.67	− .24	.9665	+ .0068
	.8028	225.10	+ .19	.9820	+ .0013
	.9255	266.77	+ .47	.9955	+ .0009
90.00	.0403	84.62	+ .30	.1174	− .0032
	.1582	108.88	+ .75	.4061	− .0043
	.3454	165.69	− .32	.7166	+ .0118
	.4882	227.55	− .31	.8543	− .0059
	.5020	234.46	+ .08	.8642	+ .0016
	.6743	331.13	+ .86	.9484	+ .0057
	.8046	412.37	− .64	.9798	− .0043
	.9006	471.11	− .04	.9925	− .0014
105.00	.5015	413.33	−2.35	.8489	+ .0017

[a] Insufficient condensate for analysis.

Calculation of Thermodynamic Properties.—Calculation of the thermodynamic properties has been made from the vapor pressure alone because, as discussed above, the vapor compositions have

(4) F. G. Keyes, *J. Chem. Phys.*, **15**, 602 (1947).

(5) C. E. Huckaba and F. G. Keyes, This Journal, **70**, 2578 (1948).

not been determined to the same degree of accuracy as the vapor pressures. Knowledge of the free energy or chemical potentials as a function of concentration at various temperatures allows calculation of the other properties of interest; the potentials are therefore expressed in terms of the total vapor pressure by changing the expressions

$$\mu_1^{\mathrm{E}} = RT \ln \frac{Py}{P_1 x} + (\beta_1 - V_1)(P - P_1) \quad (1)$$

$$\mu_2^{\mathrm{E}} = RT \ln \frac{P(1-y)}{P_2(1-x)} + (\beta_2 - V_2)(P - P_2) \quad (2)$$

into the exponential form and adding

$$P = P_1 x e^{\mu_1^{\mathrm{E}}/RT - \frac{(\beta_1 - V_1)(P - P_1)}{RT}} + P_2(1-x)e^{\mu_2^{\mathrm{E}}/RT - \frac{(\beta_2 - V_2)(P-P_2)}{RT}} \quad (3)$$

With the subscripts 1 and 2 referring to water and hydrogen peroxide, respectively, P_1 and P_2 denote the pure component vapor pressures and μ_1 and μ_2 the excess chemical potentials in the solution being considered. The terms in β and V represent the contribution from gas law deviations and liquid volume differences, respectively; the treatment and notation conform to previous practice.[6]

The potentials cannot of course be determined directly from this equation because they both appear in it as unknowns, and the Gibbs–Duhem relation between them is an expression for differentials of otherwise unknown form and values which thus cannot be integrated directly for substitution into equation (3); but use of an assumed free energy relationship which satisfies the Gibbs–Duhem equation for any values of arbitrary constants makes it possible to avoid this difficulty and provides a means of calculating the constants by fitting the total pressure curve over the range of compositions at each temperature.

The assumed excess free energy equation

$$F_x^{\mathrm{E}} = x(1-x)[B^0 + B'(1-2x) + B''(1-2x)^2] \quad (4)$$

involves the chemical potentials

$$\mu_1^{\mathrm{E}} = (1-x)^2[B^0 + B'(1-4x) + B''(1-2x)(1-6x)] \quad (5)$$

$$\mu_2^{\mathrm{E}} = x^2[B^0 + B'(3-4x) + B''(1-2x)(1-6x)] \quad (6)$$

and leads to the vapor pressure equation

$$P = P_1 x e^{\left\{\frac{(1-x)^2}{RT}[B^0 + B'(1-4x) + B''(1-2x)(1-6x)] - \frac{(\beta_1 - V_1)(P-P_1)}{RT}\right\}} + P_2(1-x)e^{\left\{\frac{x^2}{RT}[B^0 + B'(3-4x) + B''(1-2x)(5-6x)] - \frac{(\beta_2 - V_2)(P-P_2)}{RT}\right\}} \quad (7)$$

This may be fitted to the experimental points if values for the vapor pressures and liquid volumes of the pure components and for the gas correction terms are available.

The values of β were calculated for hydrogen peroxide as previously in this Laboratory,[6] using the theory of corresponding states and the equation of Keyes, Smith and Gerry,[7] and for water were found directly from the equation. The critical constants of hydrogen peroxide were guessed by assuming the critical temperatures to be proportional to the atmospheric boiling temperatures and by taking the ratio p_c/T_c to be the same for both substances: the small size of the correction justifies this crude approximation. The liquid molar volumes are well known for water; for hydrogen peroxide the density measurements of Huckaba and Keyes[5] have been used.

(6) G. Scatchard and C. L. Raymond, THIS JOURNAL, **60**, 1278 (1938).

(7) F. G. Keyes, L. G. Smith and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **70**, 319 (1936).

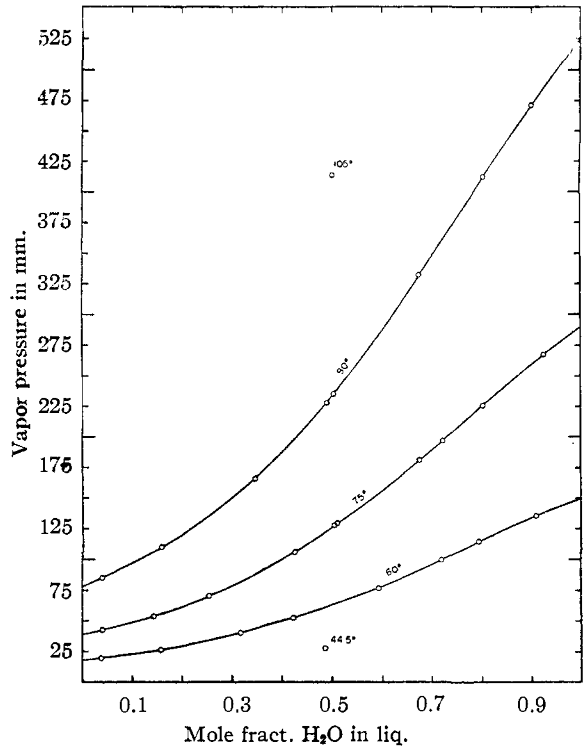

Fig. 2.—Vapor pressures of solutions of hydrogen peroxide–water, temp. in °C.

The vapor pressures of the components must be known to a higher degree of accuracy than the above correcting terms. The vapor pressures of water have been obtained from the equation of Keyes.[4] Data are available on the vapor pressure of pure hydrogen peroxide,[8] but the values may also be determined from the present measurements by extrapolation of the vapor pressures of mixtures. It is believed that this gives an estimate more accurate than the published values, and it serves also for a comparison. The extrapolation has been carried out first graphically and then analytically as described below.

The constants in the pressure equation were first calculated independently at 60, 75 and 90°, using a successive approximation form of the method of least squares, and were then smoothed with respect to temperature, taking into some account the single measurements at 44.5 and 105°. The smoothed constants are

$$B^0 = -752 + 0.97t, \quad B' = +85, \quad B'' = +13$$

Here t represents centigrade temperature.

A comparison at the experimental points of the measured and smoothed pressures and compositions is shown in Table I; the smoothed function

(8) O. Maass and P. G. Hiebert, THIS JOURNAL, **46**, 2693 (1924).

has been drawn in Fig. 2. There are seen to be noticeable deviations between the measured compositions and those calculated from the pressures: the latter values are to be preferred.

Vapor Pressures of Hydrogen Peroxide.—Between steps in the successive approximation for the constants, new values for the hydrogen peroxide vapor pressure were calculated by use of the improving constants and experimental pressures. Substitution of the constants and an experimental pressure into equation (7) allows calculation of P_2 for each experimental point. This was done for the two measurements most concentrated in hydrogen peroxide. The two values of P_2 were then averaged, double weight being given to the determination more concentrated in hydrogen peroxide, and the resulting value was used in the next step of the calculation.

The final extrapolation for the vapor pressures was made with the least squared constants before they had been temperature smoothed. The values of the vapor pressure finally found and their weighted averages are given in Table II.

TABLE II

HYDROGEN PEROXIDE VAPOR PRESSURES

Temp., °C.	Comp. of solution measured mole fract. water	P_2, mm.	Weighted average	Eq. (8)
60	0.0381	17.63		
	.1577	17.49	17.6	17.6
75	.0404	39.02		
	.1428	39.26	39.1	38.5
90	.0403	77.74		
	.1582	78.11	77.9	78.3

Vapor Pressure Extrapolation.—Measurements of hydrogen peroxide vapor pressure are traditionally pushed considerably beyond the range of experimentation because of the need for estimates under conditions where decomposition makes direct measurement very difficult. It appears that the present measurements may add significantly to the knowledge of vapor pressures at higher temperatures; an extrapolation will thus be made of the measurements and the results will be compared with the previous knowledge.

The extrapolation has been made by the Ramsey–Young method, assuming that the ratio between the temperatures at which hydrogen peroxide and water have the same vapor pressure is constant. Since this application of the Ramsey–Young method is not particularly convenient for routine use, a vapor pressure equation having four constants was made to pass through the Ramsey–Young points at 75, 150, 300 and 450° leading to

$$\log_{10} P_2 = 44.576 - 4025/T - 12.996 \log_{10} T + 0.004605T \quad (8)$$

This equation leads to a normal boiling point of 150.2°. The values of p calculated at the experimental temperatures are included in Table II.

A comparison of the equation with the vapor pressure results of Maass and Hiebert[8] may be made in order to judge the consistency of the available measurements. Excepting the two points at the highest temperatures, the equation represents their measurements substantially as well as their own smooth function; from 4.65 to 76.1°, the standard deviation from equation (8) is 0.46 mm. while it is 0.33 mm. for the same points from the function given by Maass and Hiebert.

The deviations of −2.15 mm. at 81.05° and of −7.19 at 90.35° must be considered because these measurements, being the farthest in the direction of desired extrapolation, have been of importance in the extrapolation of the early measurements. Even when compared with the Maass and Hiebert smooth function the 90.35° value appeared low by 3.6 mm. When compared with our equation, which satisfactorily represents the earlier measurements at the lower temperatures and our measurements at the higher temperatures, it appears that the two higher values of Maass and Hiebert are definitely out of line. There is some further reason for accepting this judgment implicit in the discussion in the Maass and Hiebert paper. They used the static method, which is much more susceptible to errors from permanent gas production than the dynamic method. They stated that difficulty was encountered at the higher temperatures, and they attempted to compensate for the error. It is true that the evidence indicates that the error is in the wrong direction, but this perhaps indicates that it was overcorrected. There is unfortunately no indication in the paper as to how much correction was applied. The comparison with Maass and Hiebert's measurements supports the conclusion that equation (8) is the best available representation in the range of measurement and for purposes of extrapolation.

Free Energy, Entropy and Enthalpy.—The constants found may be substituted directly into equation (4) to give the excess free energy of mixing.

$$F_x^E = x(1 - x)[- 752 + 0.97t + 85(1 - 2x) + 13(1 - 2x)^2] \quad (9)$$

The excess entropy and the enthalpy of mixing are therefore

$$S_x^E = - x(1 - x)[0.97] \quad (10)$$

$$H_x^M = x(1 - x)[- 1017 + 85(1 - 2x) + 13(1 - 2x)^2] \quad (11)$$

The values of F_x^E at 75°, of TS_x^E and H_x^M are shown in Fig. 3. The uncertainty of TS_x^E or H_x^M is much greater than that of F_x^E. Since they are determined from differences at absolute temperatures which differ by only 10%, the uncertainty is about ten times as great. Our equations make them independent of the temperature because the precision of our measurements is not sufficient to determine the variation with temperature. This makes the uncertainty even greater at any temperature other than about 75°.

In Fig. 4 are shown curves for F_x^E at 30, 45 and 60° from equation (9), and points representing the measurements of Giguère and Maass.[9] Their results agree with ours within their scatter.

The only measurements relating to heats of mixing to be found in the open literature are the measurements on dilution heats of Roth, Grau and Meichsner.[10] Agreement between these measurements and dilution heats for the measured concentrations calculated from the present work is very poor. It is suggested that, pending further direct measurements, the heat of mixing relation presented here provides the most reliable estimate of heats of dilution.

Association in Hydrogen Peroxide–Water Mixtures.—In both water and hydrogen peroxide and in mixtures of the two, the most important interaction is that of hydrogen bonding, which is so limited to specific sites on the molecule that it is convenient to treat it as a chemical association. Each water molecule has two bonding protons and two acceptor sites. Each peroxide molecule has two bonding protons and four acceptor sites. So either component or mixtures of the two should be expected to form three dimensional polymers and

(9) P. Giguère and O. Maass, *Can. J. Research*, **18B**, 181 (1940).

(10) W. A. Roth, R. Grau and A. Meichsner, *Z. anorg. Chem.*, **193**, 165 (1930).

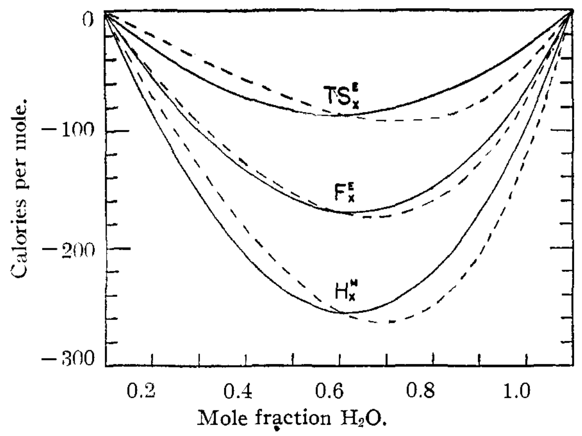

Fig. 3.—Thermodynamic functions for hydrogen peroxide–water at 75°. Broken lines calculated by Equation 26.

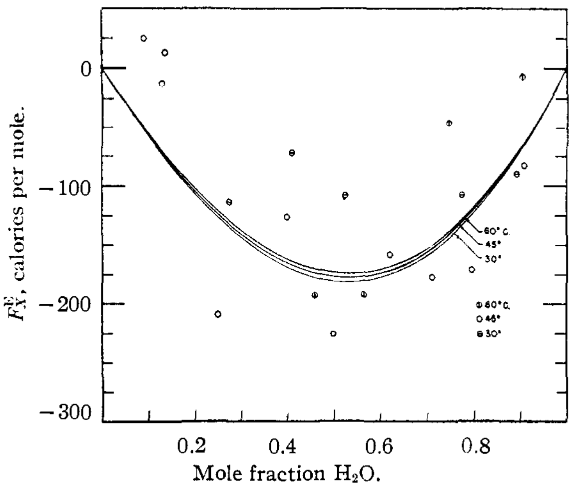

Fig. 4.—Excess free energy, hydrogen peroxide–water. Comparison of smoothed values with measurements of Giguère and Maas.

copolymers which differ from those studied by Stockmayer[11] and by Flory[12] only in the fact that here the half-life of a bond is extremely short.

To study this association we will make the simplest possible assumptions. We will assume that the heat of mixing is proportional to the change in the number of hydrogen bonds and that the resulting polymers and copolymers mix without change in enthalpy. We will further assume that the enthalpy and entropy changes in the formation of a hydrogen bond are independent of the source of the proton or of the acceptor, whether either be part of a water molecule or of a peroxide molecule, and whether or not that molecule has reacted at any of its other sites.

According to the theory of Flory[13] and Huggins[14] the free energy of mixing of any athermal mixture from separate solutions of each polymer and copolymer species is

$$F_x^M = RT \sum_j x_j \ln z_j \tag{12}$$

in which the x_j and z_j are, respectively, the mole and volume fractions and the summation is over all polymer and copolymer species. The corresponding chemical potential of species k is given by

$$\mu_k^M = RT\left[\ln z_k + 1 - \frac{\sum_j N_j V_k}{\sum_j N_j V_j}\right] \tag{13}$$

For monomer the potentials of mixing from hypothetical solutions of water or hydrogen peroxide monomer are

$$\mu_{w_1}^M = RT\left[\ln z_{w_1} + 1 - \frac{V_w \sum_j N_j}{\sum_j N_j V_j}\right] \tag{14}$$

$$\mu_{p_1}^M = RT\left[\ln z_{p_1} + 1 - \frac{V_p \sum_j N_j}{\sum_j N_j V_j}\right] \tag{15}$$

where V_w and V_p are the molal volumes of water and of hydrogen peroxide.

(11) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).
(12) P. J. Flory, *Chem. Revs.*, **39**, 137 (1946).
(13) P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941).
(14) M. L. Huggins, *ibid.*, **9**, 440 (1941).

The chemical potential of mixing of the complex pure component in the solution is the difference of the mixing potentials of monomer in pure component and in solution

$$\mu_w^M = \mu_{w_1}^M - \mu_{w_{10}}^M = RT\left[\ln\frac{z_{w_1}}{z_{w_{10}}} + \left(\frac{\sum_j N_j}{n}\right)_{w_0} - \frac{V_w \sum_j N_j}{V_w n_w + V_p n_p}\right] \tag{16}$$

$$\mu_p^M = \mu_{p_1}^M - \mu_{p_{10}}^M = RT\left[\ln\frac{z_{p_1}}{z_{p_{10}}} + \left(\frac{\sum_j N_j}{n}\right)_{p_0} - \frac{V_p \sum_j N_j}{V_w n_w + V_p n_p}\right] \tag{17}$$

Here subscripts 0 refer to the pure component water or hydrogen peroxide. The n's are stoichiometric numbers of monomer units. The excess potentials are

$$\mu_w^E = RT\left[\ln\left(\frac{N_{w_1}}{n_w}\right)\left(\frac{n_{w_0}}{N_{w_{10}}}\right)\left(\frac{V_w}{V_x}\right) + \left(\frac{\sum_j N_j}{n}\right)_{w_0} - \frac{V_w \sum_j N_j}{V_x(n_w + n_p)}\right] \tag{18}$$

$$\mu_p^E = RT\left[\ln\left(\frac{N_{p_1}}{n_p}\right)\left(\frac{n_{p_0}}{N_{p_{10}}}\right)\left(\frac{V_p}{V_x}\right) + \left(\frac{\sum_j N_j}{n}\right)_{p_0} - \frac{V_p \sum_j N_j}{V_x(n_w + n_p)}\right] \tag{19}$$

where

$$V_x = x_w V_w + x_p V_p$$

Ratio of Monomer to Total Units.—The monomer to unit ratio which appears in the logarithmic term is estimated on the basis of the simple assumptions of random bonding. For any solution

$$\left(\frac{N_{w_1}}{n_w}\right) = (1 - \alpha)^2(1 - \beta)^2 \tag{20}$$

and

$$\left(\frac{N_{p1}}{n_p}\right) = (1 - \alpha)^2(1 - \beta)^4 \qquad (21)$$

where α is the fraction of hydrogens bonded and β the function of acceptors bonded. The α's and β's in a particular solution are stoichiometrically related so that

$$\beta = \left[\frac{n_w + n_p}{n_w + 2n_p}\right]\alpha = \frac{\alpha}{2 - x_w} \qquad (22)$$

For a relation covering the variations in bonding with solution concentration we may take the odds that a hydrogen is bonded to be proportional to the concentration of unbonded acceptors

$$\frac{\alpha}{1 - \alpha} = k\left[\frac{(1 - \beta)(2n_w + 4n_p)}{n_w V_w + n_p V_p}\right] \qquad (23)$$

This implies also that the odds that an acceptor is bonded are proportional to the concentration of unbonded hydrogens, and that the two proportionality constants are the same. This relation, together with the α–β dependence, permits the calculation of α and β in any mixture if k is known, or the calculation of k if α is known for any one mixture, including either of the components.

In terms of the fractions of bonds the excess potentials are

$$\mu_w^E = RT\left[\ln\frac{(1 - \alpha)^2(1 - \beta)^2}{(1 - \alpha_w)^4}\left(\frac{V_w}{V_x}\right) + \left(\frac{\sum_j N_j}{n}\right)_{w0} - \frac{V_w \sum_j N_j}{V_x(n_w + n_p)}\right] \qquad (24)$$

$$\mu_p^E = RT\left[\ln\frac{(1 - \alpha)^2(1 - \beta)^4}{(1 - \alpha_p)^2\left(1 - \frac{\alpha_p}{2}\right)^4}\left(\frac{V_p}{V_x}\right) + \left(\frac{\sum_j N_j}{n}\right)_{p0} - \frac{V_p \sum_j N_j}{V_x(n_w + n_p)}\right] \qquad (25)$$

and the excess free energy

$$F_x^E = RT\left\{x_w \ln\frac{(1 - \alpha)^2(1 - \beta)^2}{(1 - \alpha_w)^4}\left(\frac{V_w}{V_x}\right) + x_p \ln\frac{(1 - \alpha)^2(1 - \beta)^4}{(1 - \alpha_p)^2\left(1 - \frac{\alpha_p}{2}\right)^4}\left(\frac{V_p}{V_x}\right) + \left[x_w\left(\frac{\sum_j N_j}{n}\right)_w + x_p\left(\frac{\sum_j N_j}{n}\right)_p - \frac{\sum_j N_j}{n_w + n_p}\right]\right\} \qquad (26)$$

Degree of Polymerization.—The first two terms of equation (26) are independent of the degree of polymerization. The term in square brackets is the deviation from linearity of the reciprocal of the average degree of polymerization. It is negligibly small relative to the logarithmic terms, but the proof that this is so is rather complicated.

Application of the method of Flory[12] to water gives

$$\left(\sum_j N_j/n_j\right)_{w0} = (1 - 2\alpha')\left(\frac{\alpha'}{\alpha}\right)^2 \qquad (27)$$

in which $\alpha' = \alpha$ if α is less than $^1/_3$, the critical value for network formation. For $\alpha > {}^1/_3$, α' and α are the complementary real roots of the equation

$$\alpha(1 - \alpha)^2 = \alpha'(1 - \alpha')^2 \qquad (28)$$

with α' the smaller root. Equation (22) without this term with $V_p/V_w = 1.361$ and $F_x^E = -0.17$ kcal./mole for an equimolal mixture at 75° gives $\alpha_w = 0.720$ which gives α_w' about 0.06 and $(\sum_j N_j/n_j)_{w_0}$ about 0.006. The corresponding quantities in hydrogen peroxide and in the mixtures are smaller.

Values of F_x^E calculated for $V_p/V_w = 1.325$ and $\alpha_w = 0.720$ at 75° are compared with the measured values as the broken lines in Fig. 3. The asymmetry is in the proper direction but greater than the measured asymmetry. The maximum discrepancy is 14 cal./mole in F_x^E at 75°, and 1.5 cal./mole is the difference between F_x^E at 90° and at 60°.

The Energy of the Hydrogen Bond.—The values of α at 75° are 0.886 for hydrogen peroxide and 0.840 for the equimolal mixture. The mixing of equal parts of water and hydrogen peroxide results in the formation of $2\left(0.840 - \frac{0.720 + 0.886}{2}\right) = 0.072$ mole of bonds per mole of solution. With the enthalpy decrease of 0.254 kcal./mole, this gives an enthalpy decrease of $-0.254/0.072 = -3.4$ kcal./mole for the enthalpy of formation of the hydrogen bond in liquid water. The value of α_w is sensitive to the ratio of the association constants for the various types of binding. The energy of the bonds may be also. If either component is both a stronger acid and a weaker base than the other, which is highly probable, the value of α_w will be smaller. If the products of the two constants are different for peroxide than for water, the asymmetry will be altered. The assymmetry will also be changed if a constant for any group depends upon what has happened at the other sites in the molecule. The constants could doubtless be adjusted in several ways to fit the measurements more precisely. The value of 0.720 for α_w at 75° may be compared with Pauling's value[15] of 0.85 at 0°. Pauling obtains 4.5 kcal./bond mole for the difference in enthalpy between hydrogen bonded and unbonded liquid water molecules, where we obtain 3.4. Our simple assumptions lead to an α_w somewhat larger and a ΔH per bond somewhat smaller than Pauling's, but the agreement is surprisingly good considering the restrictions of our assumptions.

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(15) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 304.