FULL PAPER

On the Analyses of Mixture Vapor Pressure Data: The Hydrogen Peroxide/Water System and Its Excess Thermodynamic Functions

Stanley L. Manatt* and Margaret R. R. Manatt*[a]

Abstract: Reported here are some aspects of the analysis of mixture vapor pressure data using the model-free Redlich–Kister approach that have heretofore not been recognized. These are that the pure vapor pressure of one or more components and the average temperature of the complex apparatuses used in such studies can be obtained from the mixture vapor pressures. The findings reported here raise questions regarding current and past approaches for analyses of mixture vapor pressure data. As a test case for this analysis approach the H_2O_2–H_2O mixture vapor pressure measurements reported by Scatchard, Kavanagh, and Tickner (G. Scatchard, G. M. Kavanagh, L. B. Ticknor, *J. Am. Chem. Soc.* **1952**, *74*, 3715–3720; G. M. Kavanagh, PhD. Thesis, Massachusetts Institute of Technology

(USA), **1949**) have been used; there is significant recent interest in this system. It was found that the original data is fit far better with a four-parameter Redlich–Kister excess energy expansion with inclusion of the pure hydrogen peroxide vapor pressure and the temperature as parameters. Comparisons of the present results with the previous analyses of this suite of data exhibit significant deviations. A precedent for consideration of iteration of temperature exists from the little-known work of Uchida, Ogawa, and Yamaguchi (S. Uchida, S. Ogawa, M.

Yamaguchi, *Japan Sci. Eng. Sci.* **1950**, *1*, 41–49) who observed significant variations of temperature from place to place within a carefully insulated apparatus of the type traditionally used in mixture vapor pressure measurements. For hydrogen peroxide, new critical constants and vapor pressure–temperature equations needed in the analysis approach described above have been derived. Also temperature functions for the four Redlich–Kister parameters were derived, that allowed calculations of the excess Gibbs energy, excess entropy, and excess enthalpy whose values at various temperatures indicate the complexity of H_2O_2–H_2O mixtures not evident in the original analyses of this suite of experimental results.

Keywords: hydrogen peroxide · liquid mixture vapor pressures · phase equilibria · thermodynamics · water chemistry

Introduction

Studies of multicomponent liquid–vapor equilibria give insights regarding the molecular forces and effects existing in such systems and allow determination of the excess thermodynamic functions. The latter represent the differences between the actual values of these functions and the values given by the ideal solution laws at the same pressure and temperature. Knowledge of multicomponent liquid–vapor equilibria also plays a vital role in the development of distillation and other separation procedures and apparatus in industry and chemical research.

The usual analyses of multicomponent liquid–vapor data start with a set of vapor pressure (VP) measurements for mixtures of various mole fractions of the liquids of interest, knowledge of the vapor pressure–temperature (VP–T) equations of the pure components and the temperatures for each suite of mixtures mole fractions studied. Many times the knowledge of the pure component VP–T function for one or more mixture components is marginal or not available over the temperature range of interest. Here it is demonstrated that mixture vapor pressure data of good quality at a particular temperature will allow the pure component vapor pressure of at least one component to be determined to high accuracy. In addition, it was found that fitting of the experimental data can be improved significantly if the absolute temperature is also made a parameter. We were led to consider this latter factor by the work reported some 54 years

[a] Dr. S. L. Manatt,[+] Prof. M. R. R. Manatt
    Department of Chemistry and Biochemistry
    California State University, Los Angeles
    CA 900032 (USA)
    E-mail: manatt@ktb.net

[+] Present address: K-2 Technical Services, 5447 La Forest Dr.
    La Cañada, CA 91011 (USA)

⌨ Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Hydrogen peroxide and water 2nd virial coefficients calculated from the Tsonopoulos equations[12] and the Keyes, Smith and Gerry equations[21] and hydrogen peroxide and water activities in mixtures at selected temperatures between 0 and 105 °C.

ago by Uchida, Ogawa, and Yamaguchi[1] who observed temperature variations within an apparatus used for mixture vapor pressure measurements; the significance of these authors' work has gone unrecognized by workers in the mixture vapor pressure field.

Although we have investigated several systems, here, to demonstrate the use of the above mentioned observations, we show as an example the results for the H_2O_2–H_2O system. Knowledge of hydrogen peroxide (HP) vapor composition above H_2O_2–H_2O mixtures has assumed some degree of importance recently. The vapor composition above such mixtures is important to know in schemes for generating ·OH radicals[2] and in spectroscopic studies.[3, 4] The recent detection of hydrogen peroxide on the surface of Europa[5] has caused renewed interest in the vapor pressures above liquid and solid H_2O_2–H_2O mixtures.

The group of George Scatchard from the 1930s to the 1960s has provided a legacy of careful experimental vapor–liquid equilibria measurements on a number of systems.[6] The measurements on the H_2O_2–H_2O system[6h, 8] made over 50 years ago by Scatchard, Kavanagh, and Ticknor stand as the definitive results on this system. No other as extensive experimental measurements on this system have been reported since their work. Based on the approach outlined above, detailed analyses of their original data have been carried out which yield results that fit the measurements significantly better than the original analyses. These results were needed[2–5] as the basis for deriving vapor pressure–composition data for the H_2O_2–H_2O system for compositions and temperatures other than those exhibited in tables in the literature,[7] in the original work[6k, 8] and in currently available manufacturer's literature.[9]

Hydrogen peroxide (HP) is unique because a number of its physical properties such as boiling point (BP) at atmospheric pressure and critical constants can not be measured directly because of its instability. In the course of working with the Scatchard, Kavanagh, and Ticknor data,[6h, 8] values of certain hydrogen peroxide physical properties were reevaluated, newer liquid density functions for both hydrogen peroxide[10] and water (W)[11] were used, newer vapor pressure data for water[11] were used, second virial coefficients, required for nonideal gas corrections, were calculated by using current, well-tested empirical equations of Tsonopoulos,[12] and data were discovered in the Kavanagh thesis[8] supporting a small correction for hydrogen peroxide decomposition. Combining the pure hydrogen peroxide vapor pressure data of Maass and Hiebert[13] with the pure hydrogen peroxide vapor pressure data from the present work, new hydrogen peroxide VP–T equations have been derived, one of which appears to be valid even close to the hydrogen peroxide critical region. From the fitting of the Scatchard group's data to four parameter Redlich–Kister analyses (a model-free approach),[14] equations for the temperature functions of these latter parameters were derived. From these functions values for the excess Gibbs energy, excess entropy and excess enthalpy of mixing were calculated; the values of the latter two parameters show the complexity of H_2O_2–H_2O mixtures that was not revealed by the excess functions reported in the original work.[6h, 8]

Theoretical Considerations

Many approaches to the analysis of isothermal, total vapor pressure data of multicomponent liquid–vapor mixtures have been reported.[15, 16] The Redlich–Kister expansion for the excess energy,[14] which was used in the original analyses,[6h, 8] is still held to be valid and convenient.[15, 16] Thus, a four-parameter expansion for a binary mixture is given in Equation (1), where X_1 is the liquid mole fraction of water, X_2 the liquid mole fraction of hydrogen peroxide, and the B_i values are parameters (calories mol^{-1} in equations used here and in original analyses[6h, 8]) to be determined from experimental data at various temperatures.

$$g_X^E = X_1 X_2 [B_0 + B_1(X_1 - X_2) + B_2(X_1 - X_2)^2 \\ + B_3(X_1 - X_2)^3 + \ldots] \tag{1a}$$

or

$$g_X^E = X_1(1 - X_1)[B_0 + B_1(1 - 2X_1) + B_2(1 - 2X_1)^2 \\ + B_3(1 - 2X_1)^3 + \ldots] \tag{1b}$$

From the relations given in Equation (2a) and (2b),[17, 18] where the μ_i^E values are excess chemical potentials, the Redlich–Kister expansion Equation (1b) leads to Equation (3) and Equation (4), where μ_1^E and μ_2^E are the excess chemical potentials for water and hydrogen peroxide, respectively.

$$\mu_1^E = g_X^E + (1 - X_1)\partial g_X^E / \partial X_1 \tag{2a}$$

$$\mu_2^E = g_X^E - X_1 \partial g_X^E / \partial X_1 \tag{2b}$$

$$\mu_1^E = (1 - X_1)^2 [B_0 + B_1(1 - 4X_1) + B_2(1 - 2X_1)(1 - 6X_1) \\ + B_3(1 - 2X_1)^2(1 - 8X_1) + \ldots] \tag{3}$$

$$\mu_2^E = X_1^2 [B_0 + B_1(3 - 4X_1) + B_2(1 - 2X_1)(5 - 6X_1) \\ + B_3(1 - 2X_1)^2(7 - 8X_1) + \ldots] \tag{4}$$

Equations (3) and (4) lead to the total vapor pressure Equation (5), as detailed in standard texts,[15, 16] that is the heart of the original analyses[6h, 8] (pressures in mm Hg), where P is the total vapor pressure above a binary mixture, P_1 the water vapor pressure, P_2 the hydrogen peroxide vapor pressure (P_{HP}), T the absolute temperature, R the gas constant in appropriate units, IGC_1 the imperfect gas correction for water, and IGC_2 the imperfect gas correction for hydrogen peroxide.[19] The Scatchard group's initial analyses of the H_2O_2–H_2O experimental mixtures' vapor pressures only considered three parameters B_0, B_1, and B_2 with a fourth linear temperature dependence folded into B_0, that is, $B_0 = B_0' + kt$ where k was a constant and t the temperature in Celsius. The gas law deviations terms used in the present analysis have the forms given in Equations (6) and (7), where β_1 and β_2 are second virial coefficients for water and hydrogen peroxide, respectively, V_1 and V_2 are the corresponding liquid molar volumes at temperature T, $\delta_{12} = 2\beta_{12} - \beta_1 - \beta_2$ where β_{12} is the second virial cross coefficient and Y_1 is the vapor mole fraction of water.[15, 16]

$$P = P_1 X_1 \exp[((1-X_1)^2/RT)(\mu_1^E + IGC_1)] \\ + P_2(1-X_1)\exp[(X_1^2/RT)(\mu_2^E + IGC_2)] \tag{5}$$

$$IGC_1 = (\beta_1 - V_1)(P-P_1)/RT - P(1-Y_1)^2 \delta_{12}/RT \tag{6}$$

$$IGC_2 = (\beta_2 - V_2)(P-P_2)/RT - PY_1^2\delta_{12})/RT \tag{7}$$

The calculation of the virial coefficients will be discussed below. The initial analyses by Scatchard's group[6h,8] only included the first terms on the right of Equations (6) and (7) and, as pointed out above, really only three Redlich–Kister parameters in their fits. Also, subsequent calculations of tables of H_2O_2–H_2O mixtures' vapor pressures by them,[6h,8] reviewers of their work,[7] and commercial tables[9] were all formulated without consideration of any gas law deviation term although the fit parameters used were derived with one. It was found here that if the data is fit initially without these corrections, significantly different fit parameters result. Later work from the Scatchard group always included the full Equations (6) and (7) correction terms[6j,k] in fitting mixture vapor pressure data. Here Equations (6) and (7) were included both in the fits and all subsequent calculations on the mixture vapor pressures. As detailed below, with four Redlich–Kister parameters, iteration of P_{HP} and T and all the gas imperfection terms, significantly better fits to the data resulted along with three values for the pure hydrogen peroxide vapor pressure that are significantly different from those obtained in the initial analyses. The imperfect gas corrections in the pressure range considered are in general small but not insignificant. The second terms on the right of Equations (6) and (7) always appear to be substantially less than the first terms.

The Fitting to the Experimental Measurements

Table 1 exhibits the original data and the data corrected for decomposition as discussed below. To allow more ready comparison with the original work,[6h,8] extensive tables in the literature[7] and currently distributed manufacture's literature on H_2O_2–H_2O mixture vapor pressures,[9] the pressure

units used here are atmospheres and mm Hg (where 1 atmosphere = 1.01325 bar and 1 mm Hg = 1.33322 millibars = 1.3332237×10^2 Pascals).

In our initial consideration of the three sets of mixture vapor pressure data from Scatchard et al.[6h,8] we obtained fits in reasonable agreement with their results using their dated water VP–T equation from Keyes,[20] their temperatures of 333.16, 348.16, and 363.16 K, their pure hydrogen peroxide vapor pressure estimates, their dated virial coefficient equations[21] for water and hydrogen peroxide, their use of only one gas imperfection term (two terms seems to be the norm now[15,16]), their use of three Redlich-Kister parameters, their use of a linear temperature term folded into the Redlich–Kister B_0 term and no consideration of a decomposition correction to the mixtures' vapor pressures.[22] Because of the number of experimental mixture vapor pressure measurements at a particular temperature, it also seemed valid to carry out a second set of fits including the pure vapor pressure for hydrogen peroxide as a parameter. This led to Redlich–Kister parameters substantially different

Table 1. Total vapor pressure for H_2O_2–H_2O mixtures; all pressures in mm Hg and temperatures in °C.

temp.[a] (real temp.)[b]	mole fraction water	vapor mole fraction water	measured vapor pressures	calcd[c] minus measured	iterated temp.	decomposition corrected pressures[d]	calcd minus measured[g]
		Thesis measurements				Present work	
44.51 (44.486)	0.4860	0.8727	27.47	−0.06	–	27.397	–
60.01 (59.991)	0.0381	0.1028	19.43	−0.13	59.996	19.357	0.032
	0.1577	0.4301	26.21	−0.11		26.137	−0.111
	0.3169	0.7049	39.79	−0.33		39.717	0.282
	0.4221	0.8243	52.01	0.37		51.937	−0.288
	0.5925	0.9151	76.21	1.05		76.137	0.065
	0.7190	0.9603	99.25	0.72		99.177	0.187
	0.7964	0.9896	114.82	0.32		114.747	−0.233
	0.9095	0.9946	135.35	0.36		135.277	0.067
75.01 (74.999)	0.0404	_[e]	42.28	0.44	75.072	42.207	−0.008
	0.1428	0.3619	53.35	0.51		53.277	0.005
	0.2540	0.6093	69.86	0.15		69.787	−0.092
	0.4249	0.8166	105.30	−0.10		105.227	0.465
	0.5037	0.8886	127.09	−1.03		127.017	−0.308
	0.5101	0.8924	128.88	−1.00		128.807	−0.279
	0.6759	0.9532	180.44	0.09		180.307	0.266
	0.7223	0.9733	196.43	0.24		196.357	0.197
	0.8028	0.9833	225.29	−0.19		225.217	−0.354
	0.9255	0.9964	267.24	−0.47		267.167	0.090
90.01 (90.011)	0.0403	0.1142	84.92	−0.30	90.019	84.847	0.029
	0.1582	0.4018	109.63	−0.75		109.557	0.108
	0.3454	0.7284	165.37	0.32		165.297	−0.274
	0.4882	0.8484	227.24	0.31		227.167	0.358
	0.5020	0.8658	234.54	−0.08		234.467	0.016
	0.6743	0.9541	331.99	−0.86		331.917	−0.394
	0.8046	0.9765	411.73	0.64		411.657	0.350
	0.9006	0.9911	471.07	0.04		470.997	−0.134
105.01 (105.026)	0.5015	0.8506	413.33	2.35	–	413.257	–
	sum of squares of pressure errors		7.0051[f]			1.4277	
	absolute mean of pressure errors		0.4757[f]			0.1919	

[a] Thesis temperatures are 0.01° lower, because $t = T−273.16$ was used instead of $t = T−273.15$. [b] Corrected thesis temperatures. [c] From "temperature-smoothed" parameters. [d] 0.073 mm Hg decomposition correction subtracted from each thesis pressure measurement. [e] Insufficient sample for analysis in original work; value used in the present work, 0.1085, has negligible effect on fit. [f] These are 12.532 and 0.524, respectively, when measurements at 44.5 and 105 °C included. [g] Fits made with four Redlich–Kister parameters.

from the former fits but essentially the same pure hydrogen peroxide vapor pressures as previously reported.[6h,8]

It is clearly evident from Tables 1 and 2 that the "temperature-smoothed" parameters (to be explained below) do not reproduce the experimental mixture vapor pressures well at the three temperatures in view of the vapor pressure experimental error estimates in the thesis[8] of ±0.01 to ±0.05 mm Hg (and better than ±0.01 °C). The fit errors in the original work (shown in Table 1 and Table 2) with the unsmoothed parameters derived from the individual sets of data are much smaller (sum of squares of vapor pressure errors 3.806, absolute mean error 0.327 and standard deviation 0.390) than what is calculated from the "temperature-smoothed" parameters (7.006, 0.420, and 0.524, respectively). Also, the linear temperature term of the original work for B_0 does not compensate for the temperature dependencies clearly evident in the parameters shown in Table 2.

On comparison of the fits of the present work and those of the original work,[6h,8] the one shortcoming that stands out in the latter then is the fact that results were "smoothed with respect to temperature." What this phrase means is that the averages of each of the three parameters at the three temperatures were taken as constants with a linear temperature correction for B_0. The results in the previous work for B_0' and k in the expression $B_0 = B_0' + kt$ for each data set were not given, but the "temperature-smoothed" result $B_0 = -752 + 0.97t$ was given. Thus, the extent of the temperature variation of B_0' and k is not clear in the original work.[6h,8]

An aspect of the fitting of mixture vapor pressure data that appears not to have been recognized heretofore is that the temperatures in the complex glass systems used in such studies, even though carefully insulated from ambient temperatures, are not constant at every location. This observa-

tion was first reported some 54 years ago by Uchida, Ogawa, and Yamaguchi[1] in their studies of benzene–toluene mixtures and several other mixtures. They found that individual thermocouples gave rather different temperatures depending on their location in the apparatus and on the rate of heating, rate of condenser cooling liquid flow and the surface area of the condensing vapor. These authors could find no experimental settings that completely eliminated the small temperature differences within the volume of their well-insulated apparatus. They did not consider iteration of the temperature in the analysis of their data.

It should be noted that usually mixture vapor pressure apparatuses are calibrated using water and multijunction thermocouple systems. The heating system is usually set to achieve a desired temperature based on the relation of EMF to a VP–T equation for water.

In unpublished mixture vapor pressure work by one of the present authors an array of eight precision-matched thermocouples was employed in the usual, complicated boiler-condensation system used in mixture vapor pressure measurements.[23] Water was used for the temperature calibrations. The system was used for determination of mixture vapor mole fractions of binary systems where one component was very flammable. However, the electronics in this apparatus allowed individual thermocouples to be sampled. This latter provision was made in light of the observations by the former Japanese workers.[1] Differences from ±0.01 to as large as ±1.00 K from location to location in the volume of the well insulated apparatus (also fitted with a circulation fan) were found to exist in studies of various solvent mixtures and even in the water calibrations. These differences again depended strongly on the rate of heat input and condenser coolant flow rate and could not be eliminated completely. In the original Scatchard, Kavanagh, and

Table 2. Redlich–Kister parameters, P_{HP} values, T values, and goodness of fit parameters.

Source and T[a]	B_0[b]	B_1[b]	B_2[b]	B_3[b]	P_{HP}[c]	AME[d]	SDE[e]	SSQPE[f]
thesis (three parameters with $B_0 = B_0' + kT$)								
333.16	−690.5	109.4	12.6	–	17.56	0.4625	0.5385	2.0374
348.16	−686.3	56.4	−16.5	–	39.14	0.2960	0.3505	1.1234
363.16	−661.4	92.5	42.0	–	77.93	0.2288	0.2981	0.6451
group errors totals						0.3265	0.3901	3.8059
thesis (temperature-smoothed parameters)								
333.16	−694.0	85.0	13.0	–	17.6	0.4238	0.5510	2.1277
348.16	−679.0	85.0	13.0	–	39.1	0.4220	0.5462	2.8698
363.16	−665.0	85.0	13.0	–	77.9	0.4125	0.5279	2.0082
group error totals						0.4196	0.5241	7.0057
group error totals with 317.66 and 378.16 K points						0.4757	0.6811	12.5318
present work (three parameters)								
333.290	−689.5965	128.6024	−14.3819	–	17.457	0.2586	0.3370	0.7949
348.208	−689.5556	60.8988	−29.0154	–	39.056	0.2116	0.2799	0.7049
363.095	−659.4681	88.7518	31.8563	–	77.900	0.3368	0.4243	1.2601
group error totals						0.2646	0.3323	2.7598
present work (four parameters)								
333.146	−732.1492	86.7641	−86.6240	−139.8383	18.304	0.1579	0.1976	0.2733
348.222	−680.0356	70.3986	−10.7520	27.9217	38.652	0.2064	0.2667	0.6403
363.169	−641.6787	108.6281	63.0625	59.4221	76.340	0.2079	0.2703	0.5115
group error totals						0.1919	0.2388	1.4251

[a] In K. [b] Units of B_i values are cal mol^{-1} here as in the original work (references[6h] and [8]). [c] Pressure in mm Hg. [d] Absolute mean error of experimental vapor pressure measurements minus calculated in mm Hg. [e] Standard deviation of latter differences. [f] Sum of squares of experimental vapor pressure measurements minus the calculated.

Ticknor work[6h,8] a 20-junction thermocouple system was employed, but no details regarding the placement of the individual thermocouples was given or how matched in precision the individual thermocouples were. It has been found here that the goodness of the fits of their data for H_2O_2–H_2O mixtures are extremely sensitive to very small variations of temperature (i.e. ±0.002 K).

Thus, it is argued here that various mole fraction mixtures give rise to mixture vapor pressures reflecting an average temperature in the apparatus with the temperature slightly different at different points in the apparatus volume for the same EMF setting, no matter how carefully the system is insulated from ambient temperature and how carefully the input energy and condensation parameters are held constant or regulated. For mixtures these small temperature differences possibly might be due to each mole fraction mixture exhibiting slightly different heat transfer properties stemming from the heat of vaporization differences of the components.[24] Thus, it is felt that it is totally reasonable to expect the goodness of fit for mixtures vapor pressure data at a nominal temperature to exhibit a dependence on very small changes of temperature. Other sets of mixture vapor pressure data from the Scatchard group[6g,j,k] have been tested and in every case the fits were very sensitive to very small temperature variations of the order of ±0.002 K. Always significant improvements in the fits to the observed mixture vapor pressures were found upon iteration of the temperature but always the best fit temperature was close (i.e. within ±0.3 K) to the temperature stated in the original works. It is suggested here that the effect first observed by Uchida, Ogawa, and Yamaguchi[1] represents an unrecognized source of error in the analysis of vapor pressure data for multicomponent systems. The implication of this suggestion is that the iterated temperature arrived at represents an average for a suite of vapor pressure measurements of various mixture mole fractions for a particular setting of heater-condensation parameters. The temperature differences between mixture mole fractions will be small and also represent an error contribution to any pure component vapor pressure determined and to the resulting fit parameters.

The final fits carried out in the present work used the new constants and equations derived below, the pure hydrogen peroxide vapor pressure as a parameter, the iteration of the absolute temperature, the inclusion of two gas imperfection terms, the use of four Redlich–Kister parameters, and the iteration of the water and hydrogen peroxide vapor phase mole fractions.[25] These latter two parameters makes only

very insignificant contributions to the goodness of fit. Table 1 and 2 exhibit the parameter results plus fits from the original work and fits using three and four Redlich–Kister parameters with iteration of T and P_{HP}; the fits made without any corrections for gas imperfection also gave different parameters and somewhat different P_{HP} values (not exhibited here). As the temperature was iterated, the water vapor pressures going into Equation (5) were calculated from Antoine equations[26] with a small added correction which was a part of the fit equations in the fitting program. For each T the sum of squares of the pressure residuals were monitored and the T varied to give a minimum. At the same time the water and hydrogen peroxide vapor mole fractions calculated were put back in the fit equations in the imperfect gas correction terms.[25] As can be seen the final values of T are not much different from the corrected values of T of the original work. The pure hydrogen peroxide vapor pressures from the three-parameter Redlich–Kister fits made here are essentially the same as those in the original work and the fit to the experimental data somewhat better than the latter analyses.

The classic, two-parameter VP–T Equation (8) (pressure in mm Hg), which is valid over small temperature ranges, where A and B are constants, was used as a test of the pure vapor pressures obtained in the various fits.

$$\log_{10} P_{HP} = A + B/T \tag{8}$$

In Table 3 some of these results, which include those from the original work and the fits (always using two gas imperfection terms) using three parameters and four parameters, are shown. The pure hydrogen peroxide vapor pressure fits to Equation (8) from the former two fits all exhibited deviations far exceeding the estimated experimental mixture vapor pressure errors of ±0.01 mm Hg for pressures above 100 mm Hg and between ±0.02 and ±0.05 mm Hg below 100 mm Hg.[8] However, as shown in Table 3, the three pure hydrogen peroxide vapor pressures from the latter four-parameter analyses exhibit a very precise fit to the simple two-parameter Equation (8) in the 60–90 °C range. The latter fit errors to Equation (8) were somewhat less than the Equation (8) fit errors of the new water vapor pressure data[11] over the same temperature range or over the same vapor pressure range.

Table 3. Fits of P_{HP} values (mm Hg) from experimental data with the two-parameter equation $\log_{10}P_{HP} = A + B/T$, where A and B are least-square constants determined from three values of P_{HP} at the values of T indicated.

T[a]	P_{HP}[b]	$P_{HP}^{Eq (8)}$	$\Delta P^{Eq (8)}$	$P_{HP}^{Eq (9)}$	$\Delta P^{Eq (9)}$	T[b,c]	P_{HP}[c]	$P_{HP}^{Eq (8)}$	$\Delta P^{Eq (8)}$
333.15	17.56	18.01_4	0.45_4	17.53_0	-0.03_0	333.146	18.304	18.296	-0.008
348.15	39.14	38.69_8	-0.44_2	38.44_6	-0.69_4	348.222	38.652	38.558	0.008
363.15	77.93	78.04_4	0.11_4	78.23_6	0.30_6	363.169	76.340	76.330	-0.002
absolute mean error			0.33_7		0.34_3				0.006
standard deviation			0.45_2		0.50_9				0.008

[a] In K. [b] From three-parameter Redlich–Kister fits of references [6h,8]. [c] From fits with four Redlich–Kister parameters, with hydrogen peroxide vapor pressure as a fifth parameter and with temperature and hydrogen peroxide vapor mole fraction iterations.

Hydrogen Peroxide Vapor Pressure–Temperature Equations

The original workers[6h, 8] used three pure hydrogen peroxide vapor pressure values[27] and a modified Ramsey–Young treatment[28] to derive the four-parameter hydrogen peroxide VP–T equation given in Equation (9) (pressure in mm Hg), and, as discussed below, it was initially used here to estimate the hydrogen peroxide boiling point.

$$\log_{10} P_{HP} = 44.5760 - 4025.3/T - 2.9960 \log_{10} T + 0.0046055 T \tag{9}$$

Here a different and perhaps more valid approach has been taken to derive hydrogen peroxide VP–T equations. The three pure hydrogen peroxide vapor pressures from the four-parameter Redlich–Kister fits discussed above and the 21 pure hydrogen peroxide vapor pressure data points of Maass and Hiebert[13] were next combined to derive VP–T equations. We realized that Maass and Hiebert estimated errors[13] of ± 0.1 mm Hg and ± 0.1 K are significantly greater than those estimated for the Scatchard group's mixture vapor pressure measurements, but it was felt that successive least squares fitting of these data combined with three P_{HP} values from the fits of the present work would flag one or more data points in substantial error which could be thrown out in the next iteration; always the three P_{HP} values determined here were kept. Four- and seven-parameter VP–T equations were sought. Variant data points of these former workers exhibiting fit errors greater than ± 0.3 mm Hg were eliminated in successive iterations. The criteria of a minimum of 10 points and inclusion always of the three P_{HP} values from the present work were set for the determination of the four- and seven-parameter VP–T equations. The fitting and data point elimination procedure cut off at 11 remaining points when the absolute mean deviation was ± 0.080 mm Hg and the standard deviation was 0.12 mm Hg; these values are close to the corresponding errors estimated by Maass and Hiebert.[13] Attempts to derive similar VP–T equations for hydrogen peroxide using the vapor pressures from the three-parameter Redlich–Kister fits or the Wilson treatment[29] fits (not exhibited here), combined with the Maass and Hiebert[13] data, yielded no satisfactory equations. Thus, the four-parameter Redlich–Kister excess energy expansion with two gas imperfection terms leads to much improved fits, P_{HP} values at three different temperatures that exhibit extremely good fits to Equation (8) over the range 60–90 °C and, combined with selected data of Maass and Hiebert,[13] give the seven- and four-parameter pure hydrogen peroxide VP–T equations given in Equation (10) and (11) (pressures in mm Hg; temperature in K).

$$\log_{10} P_{HP} = 24.8436 - 3511.54/T - 4.61453 \log_{10} T - 3.60245 \times 10^{-3} T - 7.73423 \times 10^{-6} T^2 + 1.78355 \times 10^{-8} T^3 - 2.27008 \times 10^{-13} T^4 \tag{10}$$

$$\log_{10} P_{HP} = 38.8572 - 3627.72/T - 1.2133 \log_{10} T - 4.74132 \times 10^{-2} T \tag{11}$$

The values of mixtures' vapor pressures and hydrogen peroxide vapor mole fraction are strongly influenced by the VP–T equation(s) used in mixture vapor pressure Equation (5). The differences of mixture vapor pressures between the present results and those of the original analysis are larger (ranging from 10–23 %) at the lower temperatures (0–40 °C) and at large hydrogen peroxide mole fractions as exhibited in Table 4. Deviations of the hydrogen peroxide vapor mole fractions as high as 29 % were found in the lower temperature range (0–40 °C) (see Table 5) which is that most important temperature in ·OH radical generation work.[2] These deviations indicate the shortcomings of the previously reported four-parameter hydrogen peroxide VP–T Equation (9).[6h, 8] Deviations at higher temperatures were in general smaller. The satisfactory agreement with the results of Giguère and Maass[30] at 30 °C for H_2O_2–H_2O mixtures (average error of -0.15 mm Hg or -1.9 %) supports the validity of the above hydrogen peroxide VP–T equations and also the Redlich–Kister parameter temperature functions for the lower temperature range[31] that are derived below. The limitations of Equations (10) and (11) have been tested several ways. As discussed below, the Equation (10) is not valid either in the critical region or at a T_r ($T_r = T/T^c_{HP}$ where T^c_{HP} is the hydrogen peroxide critical temperature) of 0.7, giving an unrealistic P^c_{HP} (hydrogen peroxide critical pressure), and an ω_{HP} (hydrogen peroxide acentric factor) which is way too low. Table 6 compares the vapor pressures for Equations (9), (10), and (11) over the range 0 to 160 °C. The deviations of Equation (9) from the results of Equations (10) and (11) are very significant at most temperatures except in the 60–90 °C range. The differences between Equations (10) and (11) between 0 and 90 °C are not significant, but above 90 °C the P_{HP} from Equation (10) significantly exceeds that from Equation (11). As discussed below, the P^c_{HP} calculated from Equation (11) is very close to the corresponding state theory[32–35] estimate of 249.4 atm, so Equation (11) seems valid for vapor pressure estimates in the higher temperature range even up to the critical region.

A more telling test of the range of validity of Equations (10) and (11) comes from calculations of the hydrogen peroxide heat of vaporization, H_v, in regions where the higher order virial coefficients (i.e. third and higher ones) are not important, from Equation 12[36, 37] where V_L and V_{sat} are the molar volumes of the liquid and saturated vapor, respectively, P_{sat} is the corresponding vapor pressure and β_{HP} is the hydrogen peroxide virial coefficient.

$$\Delta H_v = RT^2(1 - V_L/V_{sat})(\partial \ln P_{sat}/\partial T)(1 + \beta_{HP}/V_{sat}) \tag{12}$$

It was found that the ΔH_v values from the vapor pressure Equation (10) above 90 °C did not diminish at the rate one would expect and by 115 °C actually were increasing significantly, as shown in Table 7. This behavior is counter to the expected behavior for a ΔH_v. Careful scrutiny of the first and second derivatives of Equation (10) indicated significant deviations from those of Equation (11) (and Equation (9) too) above 90 °C. Thus, although Equation (10) is valid from 0 to 90 °C, above the latter temperature Equation (11) was used in the present work.

Table 4. Total vapor pressure (mm Hg) of hydrogen peroxide-water mixtures; % error with original work indicated in parenthesis.

Temp. [°C]	Mole fraction hydrogen peroxide in liquid phase										
	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
0.0	0.352	0.486	0.714	0.996	1.326	1.727	2.225	2.822	3.470	4.082	4.585
	(−22.7)	(−16.8)	(−16.9)	(−14.0)	(−8.9)	(−4.0)	(−1.2)	(−0.5)	(−0.6)	(−0.5)	(−0.1)
10.0	0.777	1.045	1.510	2.077	2.738	3.540	4.531	5.713	6.995	8.207	9.212
	(−19.2)	(−14.0)	(−14.6)	(−12.3)	(−7.7)	(−3.4)	(−0.9)	(−0.3)	(−0.5)	(−0.5)	(−0.1)
20.0	1.612	2.137	3.014	4.094	5.351	6.868	8.736	10.958	13.364	15.642	17.542
	(−15.8)	(−11.3)	(−12.3)	(−10.6)	(−6.6)	(−2.7)	(−0.5)	(−0.1)	(−0.4)	(−0.4)	(−0.1)
25.0	2.274	2.986	4.175	5.636	7.338	9.388	11.907	14.898	18.136	21.204	23.770
	(−14.1)	(−9.9)	(−11.1)	(−9.7)	(−5.9)	(−2.3)	(−0.3)	(0.1)	(−0.3)	(−0.4)	(−0.1)
30.0	3.166	4.119	5.709	7.664	9.940	12.679	16.040	20.022	24.331	28.417	31.844
	(−12.5)	(−8.4)	(−9.9)	(−8.7)	(−5.3)	(−1.9)	(−0.0)	(0.2)	(−0.3)	(−0.4)	(−0.1)
40.0	5.919	7.542	10.268	13.643	17.586	22.328	28.132	34.991	42.401	49.438	55.365
	(−9.4)	(−5.3)	(−6.9)	(−6.3)	(−3.6)	(−0.8)	(0.6)	(0.6)	(−0.1)	(−0.3)	(−0.1)
50.0	10.590	15.382	21.860	28.652	35.615	43.266	52.118	62.245	73.041	83.399	92.588
	(−6.5)	(−15.9)	(−22.2)	(−21.8)	(−17.6)	(−12.3)	(−7.8)	(−4.7)	(−2.6)	(−1.0)	(−0.0)
60.0	18.218	25.743	36.141	47.209	58.602	71.049	85.301	101.439	118.518	134.876	149.502
	(−3.8)	(−12.5)	(−19.4)	(−19.8)	(−16.4)	(−11.8)	(−7.7)	(−4.7)	(−2.7)	(−1.0)	(−0.0)
70.0	30.262	42.098	58.303	75.796	93.986	113.747	135.997	160.735	186.601	211.373	233.839
	(−1.4)	(−10.3)	(−17.3)	(−18.5)	(−15.9)	(−11.9)	(−8.2)	(−5.2)	(−2.9)	(−1.1)	(−0.0)
75.0	38.540	54.919	72.945	93.363	116.345	141.730	169.228	198.510	229.112	260.069	289.246
	(−0.2)	(−12.0)	(−16.0)	(−16.4)	(−14.7)	(−11.7)	(−8.1)	(−4.7)	(−2.0)	(−0.5)	(−0.0)
80.0	48.719	61.703	76.878	96.843	122.895	155.072	192.337	233.065	275.451	317.359	355.327
	(0.8)	(−0.6)	(0.5)	(1.0)	(0.7)	(0.1)	(0.0)	(0.2)	(0.3)	(0.2)	(−0.0)
90.0	78.236	96.906	119.670	148.859	186.631	233.284	287.480	346.897	408.847	470.163	525.921
	(2.6)	(−0.4)	(0.4)	(1.1)	(1.1)	(0.7)	(0.4)	(0.4)	(0.4)	(0.3)	(−0.0)
100.0	116.181	147.075	180.413	222.488	276.409	342.676	419.550	503.934	592.176	679.865	760.000
	(4.24)	(0.6)	(1.0)	(1.5)	(1.4)	(1.0)	(0.7)	(0.6)	(0.6)	(0.3)	(0.0)
110.0	172.781	213.359	256.643	310.878	380.173	465.315	564.238	673.126	787.415	901.504	1006.40
	(5.7)	(3.5)	(5.0)	(6.4)	(7.0)	(7.2)	(7.2)	(7.3)	(7.3)	(7.1)	(6.8)
120.0	251.34	313.00	378.46	459.85	563.08	689.25	835.38	996.03	1164.67	1333.25	1488.72
	(6.9)	(3.0)	(2.9)	(3.1)	(2.7)	(2.1)	(1.6)	(1.2)	(0.9)	(0.5)	(0.0)
130.0	358.29	441.84	530.33	639.93	778.63	947.95	1144.08	1359.94	1586.97	1814.54	2025.32
	(8.0)	(4.2)	(4.1)	(4.1)	(3.6)	(2.8)	(2.1)	(1.6)	(1.1)	(0.5)	(0.0)
140.0	501.34	612.44	729.90	874.93	1058.05	1281.42	1540.23	1825.42	2125.96	2428.09	2709.15
	(8.9)	(5.3)	(5.1)	(5.1)	(4.5)	(3.5)	(2.6)	(1.9)	(1.3)	(0.6)	(0.0)
150.0	689.57	834.81	988.12	1176.90	1414.83	1704.88	2041.12	2412.11	2803.93	3199.00	3568.19
	(9.6)	(6.3)	(6.1)	(6.0)	(5.3)	(4.2)	(3.1)	(2.3)	(1.5)	(0.7)	(0.0)
160.0	933.62	1120.49	1317.47	1559.47	1864.01	2235.14	2665.65	3141.42	3645.06	4154.50	4632.83
	(10.2)	(7.1)	(7.0)	(6.9)	(6.0)	(4.9)	(3.7)	(2.7)	(1.8)	(0.8)	(0.0)

Concerning the Temperature Dependence of the Redlich–Kister Parameters

As exhibited in Table 2 for the various fits to the experimental data with either a three- or four-parameter Redlich–Kister approach, all the parameters are significantly temperature dependent in the range of 60–90 °C. The linear T function for B_0 and the "temperature smoothing" offered by the Scatchard group insufficiently represent what is really happening. The percentage contributions of each term in the Redlich–Kister chemical potential expansion and the imperfect gas correction terms as a function of T were evaluated for various liquid mole fractions at the three nominal temperatures 60, 75, and 75 °C. Results from these calculations revealed that the predominant term by far is B_0. Thus, it would seem that its temperature dependence would be the most important to characterize in some detail. To do this, first it was assumed that none of the Redlich–Kister parameters are discontinuous; there is no evidence otherwise. Second, the two mixture vapor pressures at the corrected t values[38] of 44.486 °C (317.636 K) and 105.026 °C

(378.176 K), respectively, were assumed to have errors of the same magnitude as the other mixture vapor pressure measurements. Third, the following assumptions were made regarding the temperature dependence of the B_1, B_2, and B_3: B_1 can be fitted to a Lorentzian curve from the three values obtained in the fits by Equation (13), where the C_i values are constants and the three values the B_2 and B_3 parameters can be fitted to sigmoid curves of the general form given in Equation (14), where the C_{ij} values are constants.[39]

$$B_1 = C_0 + C_1 C_2 / \pi (C_2{}^2 + (T - C_3)^2) \tag{13}$$

$$B_i = C_{0j} + C_{1j} / [1 + \exp\{C_{2j}(T - C_{3j})\}] \tag{14}$$

The parameters for Equations (13) and (14) are shown in Table 8. For the two temperatures of 317.636 and 378.176 K the values for B_i were then calculated from the above equations. These values, along with the two corresponding liquid mole fractions, the temperature-dependent liquid molar volumes, the appropriate virial coefficients, and the water and hydrogen peroxide vapor pressures (calculated from vapor

Table 5. Mole fraction of hydrogen peroxide above H_2O_2–H_2O mixtures; % error with original work indicated in parenthesis.

Temp. [°C]	Mole fraction hydrogen peroxide in vapor								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.0	0.0028	0.0087	0.0208	0.0430	0.0793	0.1350	0.2217	0.3698	0.6371
	(−27.5)	(−27.3)	(−28.6)	(−27.9)	(−23.9)	(−16.8)	(−9.0)	(−4.7)	(−5.9)
10.0	0.0032	0.0099	0.0232	0.0472	0.0861	0.1451	0.2356	0.3870	0.6518
	(−22.9)	(−23.0)	(−24.5)	(−24.1)	(−20.4)	(−13.8)	(−6.5)	(−3.0)	(−4.7)
20.0	0.0036	0.0110	0.0256	0.0514	0.0928	0.1548	0.2489	0.4031	0.6651
	(−18.3)	(−18.7)	(−20.6)	(−20.5)	(−17.1)	(−10.9)	(−4.3)	(−1.6)	(−3.8)
25.0	0.0038	0.0116	0.0267	0.0535	0.0960	0.1595	0.2553	0.4109	0.6715
	(−16.0)	(−16.6)	(−18.6)	(−18.7)	(−15.5)	(−9.5)	(−3.6)	(−1.0)	(−3.5)
30.0	0.0040	0.0121	0.0279	0.0555	0.0992	0.1642	0.2616	0.4186	0.6779
	(−13.7)	(−14.4)	(−16.6)	(−18.8)	(−13.9)	(−8.3)	(−2.5)	(−0.5)	(−3.2)
40.0	0.0044	0.0134	0.0300	0.0593	0.1054	0.1736	0.2749	0.4354	0.6924
	(−8.2)	(−9.4)	(−12.2)	(−13.1)	(−10.8)	(−6.0)	(−1.2)	(−0.1)	(−3.1)
50.0	0.0046	0.0138	0.0315	0.0623	0.1111	0.1835	0.2909	0.4578	0.7137
	(0.28)	(−2.1)	(−6.2)	(−8.5)	(−7.7)	(−4.4)	(−1.3)	(−1.3)	(−4.1)
60.0	0.0052	0.0151	0.0337	0.0657	0.1157	0.1899	0.2997	0.4693	0.7240
	(2.2)	(0.9)	(−2.5)	(−4.6)	(−4.0)	(−1.4)	(0.8)	(−0.4)	(−3.8)
70.0	0.0060	0.0170	0.0366	0.0693	0.1200	0.1949	0.3057	0.4750	0.7255
	(−0.8)	(0.5)	(−0.8)	(−1.4)	(−0.3)	(2.0)	(3.4)	(1.5)	(−2.6)
75.0	0.0064	0.0185	0.0389	0.0719	0.1239	0.1040	0.3233	0.4924	0.7172
	(−1.2)	(−2.7)	(−2.2)	(−1.0)	(−0.0)	(0.2)	(−0.1)	(−0.7)	(−0.8)
80.0	0.0069	0.0193	0.0401	0.0741	0.1284	0.2125	0.3352	0.5006	0.7108
	(−2.0)	(−2.0)	(−0.9)	(−0.2)	(−0.3)	(−1.2)	(−1.7)	(−1.0)	(0.8)
90.0	0.0076	0.0211	0.0435	0.0797	0.1367	0.2229	0.3455	0.5067	0.7098
	(−1.1)	(−1.4)	(−0.6)	(−0.1)	(−0.3)	(−0.9)	(−1.0)	(0.3)	(2.2)
100.0	0.0083	0.0229	0.0469	0.0849	0.1439	0.2316	0.3542	0.5133	0.7131
	(−0.1)	(−0.6)	(0.0)	(0.5)	(0.3)	(−0.1)	(−0.0)	(1.2)	(2.8)
110.0	0.0090	0.0246	0.5000	0.0899	0.1508	0.2401	0.3633	0.5215	0.7185
	(1.1)	(0.4)	(0.9)	(1.2)	(1.0)	(0.5)	(0.6)	(1.7)	(3.1)
120.0	0.0096	0.0263	0.0531	0.0947	0.1576	0.2488	0.3730	0.5308	0.7255
	(2.7)	(1.7)	(1.9)	(2.0)	(1.6)	(0.9)	(0.8)	(1.8)	(3.0)
130.0	0.0103	0.0280	0.0562	0.0995	0.1644	0.2575	0.3829	0.5405	0.7328
	(4.2)	(3.0)	(2.9)	(2.7)	(2.0)	(1.2)	(0.9)	(1.7)	(2.8)
140.0	0.0110	0.0297	0.0593	0.1044	0.1712	0.2661	0.3926	0.5500	0.7400
	(5.4)	(3.9)	(3.5)	(3.1)	(2.2)	(1.2)	(0.8)	(1.5)	(2.5)
150.0	0.0118	0.0315	0.0625	0.1093	0.1781	0.2748	0.4023	0.5593	0.7470
	(6.34)	(4.6)	(4.0)	(3.4)	(2.3)	(1.1)	(0.6)	(1.2)	(2.2)
160.0	0.0125	0.0334	0.0658	0.1144	0.1851	0.2834	0.4119	0.5685	0.7538
	(7.0)	(5.1)	(4.2)	(3.4)	(2.2)	(0.9)	(0.31)	(0.9)	(1.9)

Table 6. P_{HP} in mm Hg calculated from various equations.

Temp. [°C]	2-parm.[a]	4-parm.[b]	7-parm.[c]	Thesis 4-parm.[d]	Y-parm.−X-parm.[e]	Thesis 4-parm.−X-parm.[e]
0.0	0.411	0.356	0.352	0.272	0.004 (1.1)	−0.080 (−22.7)
10.0	0.865	0.781	0.777	0.627	0.004 (0.5)	−0.150 (−19.3)
20.0	1.731	1.614	1.612	1.357	0.002 (0.1)	−0.255 (−15.8)
25.0	2.407	2.274	2.274	1.952	0.000 (0.0)	−0.322 (−14.2)
30.0	3.309	3.163	3.166	2.769	−0.003 (−0.1)	−0.397 (−12.5)
40.0	6.069	5.910	5.918	5.360	−0.008 (−0.1)	−0.558 (−9.4)
45.0	8.102	7.948	7.958	7.325	−0.010 (−0.1)	−0.633 (−8.0)
50.0	10.720	10.579	10.590	9.899	−0.011 (−0.1)	−0.691 (−6.5)
60.0	18.299	18.214	18.218	17.521	−0.004 (−0.0)	−0.697 (−3.8)
70.0	30.279	30.277	30.262	29.839	−0.015 (−0.0)	−0.423 (−1.4)
75.0	38.529	38.566	38.540	38.427	0.026 (0.1)	−0.112 (−0.3)
80.0	48.693	48.753	48.719	49.077	0.033 (0.1)	0.358 (0.7)
90.0	76.283	76.261	76.269	78.200	−0.008 (−0.0)	1.931 (2.5)
100.0	116.666	116.181	116.452	121.058	0.271 (0.2)	4.877 (4.20)
105.0	143.068	142.091	142.675	149.118	0.584 (0.4)	7.027 (4.9)
110.0	174.512	172.781	173.886	182.528	1.105 (0.6)	9.747 (5.6)
120.0	255.748	251.342	254.546	268.650	3.205 (1.3)	17.308 (6.9)
130.0	367.759	358.294	366.117	386.760	7.824 (2.2)	28.466 (7.9)
140.0	519.610	501.338	518.448	545.601	17.110 (3.4)	44.263 (8.8)
150.0	722.267	689.575	724.145	755.430	34.569 (5.0)	65.855 (9.6)
160.0	988.812	933.624	999.372	1028.100	65.748 (7.0)	94.475 (10.1)

[a] Calculated from Equation (8). [b] Calculated from Equation (11). [c] Calculated from Equation (10). [d] Calculated from Equation (9). [e] Percent deviation indicated in parenthesis; up to 90 °C X is 7 and Y is 4; above 90 °C X is 4 and Y is 7.

Table 7. Calculations of H_v (in cal mol^{-1}) from Equation (24) for hydrogen peroxide which was used as a test for Equations (9), (10), and (11).

Temp. [°C]	Equation (9) col.I	Equation (11) col.II	Equation (10) col.III	%diff. I and II	Diff. II and III (%diff. II and III)	Experimental
0.0	12932	12126	12246	6.6	120 (1.0)	12620[a]
25.0	12587	11878	11913	6.0	35 (0.3)	12340[b]
45.0	12331	11695	11688	6.0	−7 (−0.1)	
60.0	12149	11567	11550	5.0	−17 (−0.1)	
75.0	11977	11446	11442	4.6	4 (−0.0)	
90.0	11815	11330	11368	4.3	38 (0.3)	
100.0	11712	11255	11340[c]	4.1	85 (0.8)	
105.0	11662	11218	11332[c]	4.0	114 (1.0)	
110.0	11613	11182	11330[c]	3.9	148 (1.3)	
115.0	11565	11146	11333[c]	3.8	187 (1.7)	
150.0	11260	10903	11498[c]	3.3	595 (5.6)	

[a] W. T. Foley, P. A. Giguère, *Can. J. Chem.* **1951**, *29*, 895–903. [b] P. A. Giguère, B. G. Moréssette, A. W. Olmos, O. Knop, *Can. J. Chem.* **1955**, *33*, 804–820. [c] Note here that H_v from Equation (10) passes through a minimum and then begins to increase with temperature, which is wrong.

348.222 K to 391.463 K, a 2° polynomial (parameters P_{2i}) was fit to the B_0 values at 348.222, 363.169, and 378.176 K; above 391.463 K B_0 was taken as a constant of −612.961. The composite curve is shown in Figure 1 and the parameters for the various temperature regions are given in Table 8. The B_0 minimum at about 324 K and increase at lower temperatures are consistent, as mentioned above, with the good four-parameter Redlich–Kister fit found in the present work to
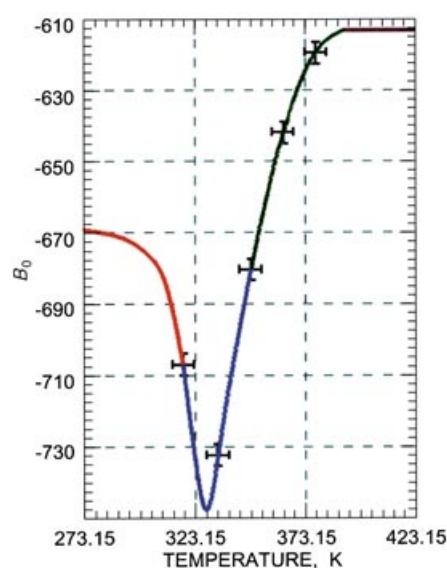
Table 8. Parameters for the Redlich–Kister temperature functions and their first derivatives for B_1, B_2, B_3 and the four regions of B_0; see Equations (13), (14), and (16)–(21).

Para-meter	Temperature range	Curve type	Constants
B_0	273.150–317.636 K	Lorentzian	$C_0 = -666.8830$
			$C_1 = -2499.584$
			$C_2 = 8.261924$
			$C_3 = 327.4487$
	317.636–348.222 K	average of above Lorentzian and 2nd order polynomial	$P_{10} = 17418.34$
			$P_{11} = -109.9125$
			$P_{12} = 0.1663847$
	348.222–391.463 K	2nd order polynomial	$P_{20} = -6110.401$
			$P_{21} = 28.08669$
			$P_{22} = -0.03587408$
	391.463–433.150 K	$B_0 = -612.9613$	
B_1	273.150–433.150 K	Lorentzian	$C_{01} = 126.7385$
			$C_{11} = -2558.776$
			$C_{21} = 12.33364$
			$C_{31} = 343.1050$
B_2	273.150–433.150 K	sigmoid	$C_{02} = 63.18354$
			$C_{12} = -149.9278$
			$C_{22} = 0.4745954$
			$C_{32} = 348.1642$
B_3	273.150–433.150 K	sigmoid	$C_{03} = 59.42228$
			$C_{13} = -199.2644$
			$C_{23} = 0.8321514$
			$C_{33} = 346.2121$

Figure 1. Composite B_0 function. Red curve is Lorentzian; blue curve is the average of a Lorentzian and a second-order polynominal; green curve is second-order polynominal; purple curve is linear region; the experimental points are crosses. The units of B_0 here are calories mol^{-1} (1 calorie = 4.184 Joules) to correspond to the other B_i results in Table 2.

the limited vapor pressure results of Giguère and Maass[30,31] for HP–W mixtures at 30°C.

For calculations of mixture total vapor pressures and vapor mole fractions, a master program was developed. The program includes sections that calculate the water vapor pressures from a seven-parameter equation and, depending on the temperature range, hydrogen peroxide vapor pressures from four- or seven-parameter equations, temperature-dependent liquid molar volumes, temperature-dependent virial coefficients, and the four temperature-dependent Redlich–Kister parameters. The outputs are mixture vapor pressures and vapor phase mole fractions calculated for the liquid mole fraction water or hydrogen peroxide at any increment desired. For comparisons the program also calculates mixtures vapor pressure data and vapor phase mole fractions using the parameters and equations from the origi-

pressure Equation (10) for the lower temperatures and Equation (11) for the higher temperatures) allowed B_0 to be varied until the observed mixture vapor pressures were obtained. Thus, two more B_0 values based on experimental mixture vapor pressures were obtained. From much experimentation it was determined that no single function could be found that would fit all five of the B_0 values. Thus, several functions were used to describe the behavior of B_0. From 273.150 to 317.636 K, a Lorentzian was used; it was fit to the B_0 values at 317.636, 333.146 and 348.222 K (parameters C_i). The average of a 2° polynomial (parameters P_{1i}) and a Lorentzian (the same from the fit over the latter temperature range) was used from 317.636 to 348.222 K. From

nal analyses.[6h,8] Optional outputs are any or all of the other quantities mentioned above and the percentage contributions for each term in the chemical potential expression. The only inputs are the absolute temperature and a small correction term to the seven-parameter water vapor pressure equation given below. These results are exhibited in Tables 4 and 5 with indications of the deviations from the original work. As discussed above deviations as high as 22% for mixtures' vapor pressures were found. Hydrogen peroxide vapor phase mole fraction deviations as high as 29% were found at the lower temperatures and around ambient temperatures which are those where much ˙OH radical generation work[2,3] and spectroscopy[3,4] are carried out.

Energy, Entropy, and Enthalpy of Mixing

The first of these quantities, g_X^E, can be found by substituting the temperature-dependent Redlich–Kister parameters into Equation (1b), where the terms $B_i(T)$ are functions of temperature.

$$g^E = X_1(1-X_1)[B_0(T) + B_1(T)(1-2X_1) + B_2(T)(1-2X_1)^2 + B_3(T)(1-2X_1)^3]$$

(1b′)

In the original work $B_0 = B_0' + kt$, where B_0' was "temperature-smoothed," and the other B_i values were taken as the "temperature-smoothed" constants. The excess entropy, s_X^E, is obtainable from Equation (15), where the constants come from Table 8.

$$s_X^E = -\partial g_X^E/\partial T = -X_1(1-X_1)[\partial B_0(T)/\partial T + \partial B_1(T)/\partial T(1-2X_1) + \partial B_2(T)/\partial T(1-2X_1)^2 + \partial B_3(T)/\partial T(1-2X_1)^3]$$

(15)

When the full temperature functions obtained here for the B_i values are inserted in Equation (15), a rather cumbersome expression results. Also, remember that $B_0(T)$ has four parts. The derivatives of the $B_0(T)$, $B_1(T)$, $B_2(T)$, and $B_3(T)$ functions are given in Equations (16)–(21).

273.15 to 317.636 K

$$\partial B_0/\partial T = -2(\alpha_0/(1 + \alpha_0^2)^2)C_1/\pi C_2^2$$
where $\alpha_0 = (T-C_3)/C_2$

(16)

317.636 to 348.222 K

$$\partial B_0/\partial T = 0.5[-2(\alpha_0/(1 + \alpha_0^2)^2)C_1/\pi C_2^2 + P_{11} + 2P_{12}T]$$

(17)

348.222 to 391.463 K (P_{2i}'s from fit to 2° polynomial)

$$\partial B_0/\partial T = P_{21} + 2P_{22}T$$

(18)

$T > 391.463$ K $\qquad \partial B_0/\partial T = 0.0$

$$\partial B_1/\partial T = -2(\alpha_1/(1 + \alpha_1^2)^2)C_{11}/\pi C_{12}^2$$

(19)

where $\alpha_1 = (T-C_{13})/C_{12}$

$$\partial B_2/\partial T = -C_{21}C_{22}\alpha_2/(1 + \alpha_2)^2$$

(20)

where $\alpha_2 = \exp(C_{22}(T-C_{23}))$

$$\partial B_3/\partial T = -C_{31}C_{32}\alpha_3/(1 + \alpha_3)^2$$

(21)

where $\alpha_3 = \exp(C_{32}(T-C_{33}))$

Using the constants in Table 8 to evaluate Equation (1b′) and, using the derivative expressions above in Equation (15), s_X^E values were calculated. The excess heat of mixing, h_X^E, is calculated from the relation $h_X^E = g_X^E + Ts_X^E$. For comparison all three quantities were also calculated using the "temperature-smoothed" constants from the original work.[6h,8] Figures 2 and 3 exhibit these results for
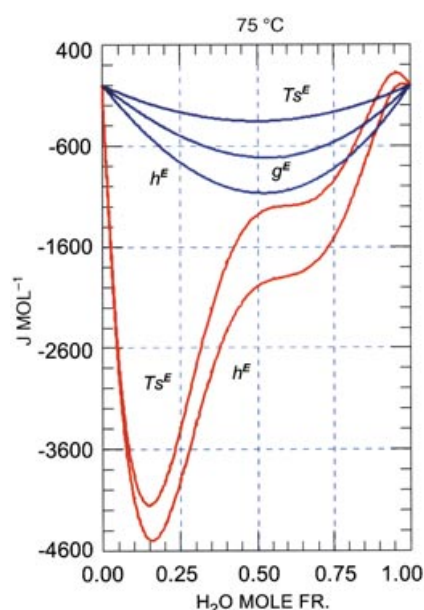

Figure 2. H_2O_2–H_2O excess functions at 75°C. The red curves are from the present work; the blue curves are from equations in references [6h,7,8]; the g^E curves from the latter workers and the present work are nearly identical.

the nominal temperatures of 60, 75, and 90°C. It can be seen that there are very significant differences between the original work and the present treatment, especially for Ts_X^E and h_X^E in the region of 75°C. These differences point up the inadequacy of the previous results.

However, the g_X^E values from both treatments are not that different at all temperatures. The equations in the original treatment yield a temperature-independent h_X^E with only very slight changes in g_X^E and Ts_X^E with temperature. The major contributions to the 75°C s_X^E in the present analysis are the slopes of the parameters near 75°C. If one were to consider approximate linear functions of temperature for B_0, B_2, and B_3 and the slope of a Lorentzian for B_1 only over the 75°C region, Ts_X^E values nearly the same as those obtained from the more complex temperature functions de-
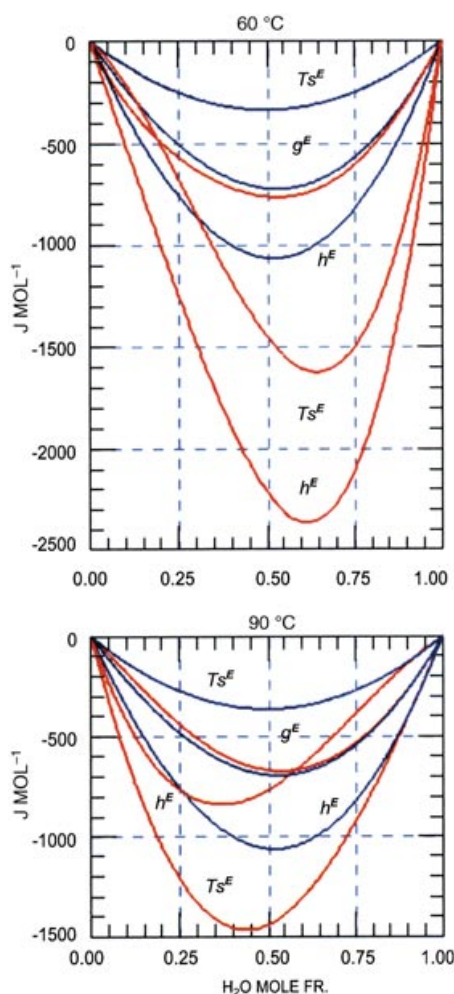
Figure 3. H_2O_2–H_2O excess functions at 60 and 90 °C. The red curves are from the present work; blue curves are from equations in references [6h, 7, 8].

Figure 4. H_2O_2–H_2O excess functions at 25 and 50 °C. The red curves are from the present work; blue curves are from equations in references [6h, 7, 8].

rived above result. Thus, from the very negative Ts_X^E values in this temperature region it appears that some rather significant changes in the H_2O_2–H_2O solution interactions are taking place at certain mole fractions. These changes are not reflected in the activity functions (given in the Supporting Information). Figure 4 and Figure 5 exhibit the excess quantities at four other temperatures. Noteworthy are the Ts_X^E maximum around 50 °C and the complexities seen at 55 °C. Further investigation of H_2O_2–H_2O mixtures in all these temperature regions by other techniques should reveal the nature of the solution interaction changes hinted at by the Ts_X^E behaviors seen here.

Discussion and Conclusions

Besides the current interest in the H_2O_2–H_2O mixtures,[2–5] the present results are of interest because the H_2O_2–H_2O system is probably the simplest binary system with extensive hydrogen bonding where the hydrogen bonding of each pure component should be very similar and because the derived thermodynamic properties might shed light on existing
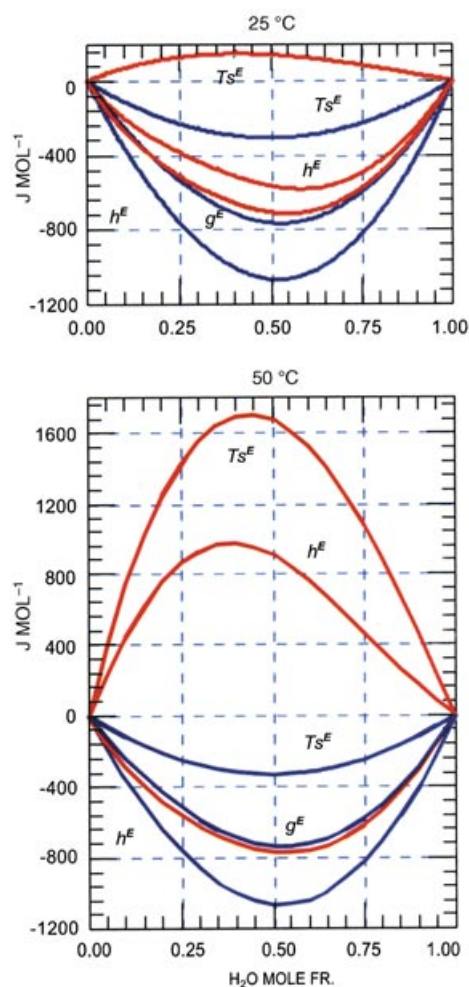
solution interactions. Although the ammonia–hydrazine system (A–HA) might be seen as a similar pair, and although there are more hydrogen bonding possibilities in that system, the types of hydrogen bonds involved are much weaker[41] so the solution interactions can be expected to be less for ammonia–hydrazine mixtures than for the case of H_2O_2–H_2O mixtures.

The vapor pressures of H_2O_2–H_2O mixtures have received little attention since the work of Scatchard, Kavanagh, and Ticknor[6h, 8] of over 50 years ago. From the detailed evaluation of these authors' work, we conclude that the experimental work was carefully done and the experimental data, outside of several minor problems, is worthy of a contemporary reanalysis using the approach outlined here and current data fitting methodology. The only significant aspect of the data with which we take issue concerns their neglect of a small correction for hydrogen peroxide decomposition; Kavanagh exhibited results[8] which he felt indicated that hydrogen peroxide decomposition was unimportant, but we feel his results warrant that a small constant decomposition correction be made to the original published data over all the temperatures.
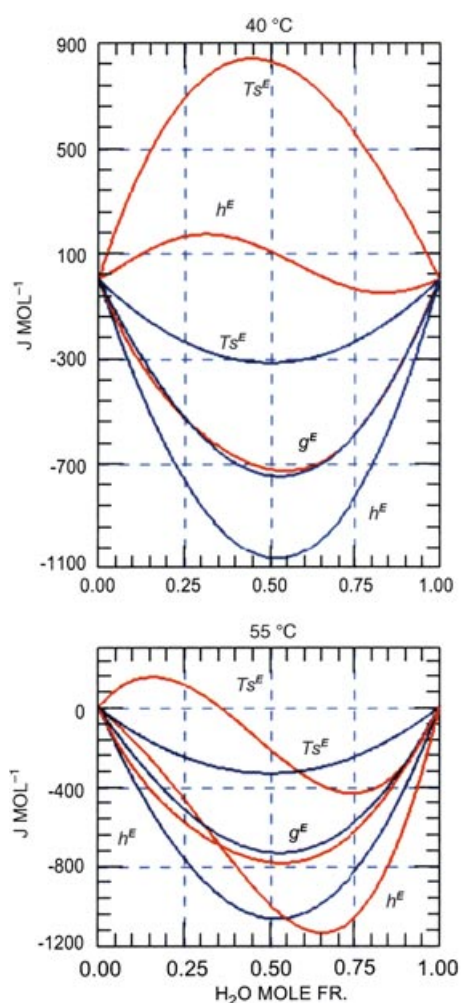
Figure 5. H_2O_2–H_2O excess functions at 40 and 55 °C. The red curves are from the present work; blue curves are from equations in references [6h, 7, 8].

In the present work various hydrogen peroxide physical constant estimates, several other constants and several equations needed in the fitting have been updated as described below. These include the following: use of new value for the gas constant; new estimates of the hydrogen peroxide critical constants based on the theory of corresponding states;[32–35] use of water vapor pressure and liquid density data taken from a recent steam table update;[11] use of newer hydrogen peroxide liquid density results;[21] use of the empirical Tsonopoulos treatment for estimation of the hydrogen peroxide second virial coefficients.[12]

A weakness in the original analyses most definitely was the "temperature smoothing" of the Redlich–Kister parameters obtained by averaging the parameters from the separate fits to the data at the three nominal temperatures 60, 75, and 90 °C. That all the parameters are substantially temperature-dependent is evident (see Table 2) even in the original work. The linear temperature dependence of B_0 previously suggested[6h, 8] is definitely insufficient. The original description of the estimations of the pure hydrogen peroxide vapor pressures from the three sets of data is somewhat confus-

ing.[27] It has been demonstrated here that these pressures can be parameters in the analyses of the data. Further it was shown above that fits with only three Redlich–Kister parameters, although leading to pure hydrogen peroxide vapor pressure values essentially the same as found in the original analyses, give pure hydrogen peroxide vapor pressure values that fit poorly to two-, four-, or seven-parameter hydrogen peroxide VP–T equations (see Table 3 and Table 4).

As shown here the goodness of the fits of mixture vapor pressure are very sensitive to small changes (of the order of ± 0.002 K) of temperature. The temperature iteration to a least-squares minimum of the vapor pressure errors suggested here leads to much improved fits. The temperature arrived at represents an average temperature seen by a suite of mixtures where the average temperature of a particular mole fraction mixture is slightly different at various locations within a well insulated apparatus, even though the input energy and condensation parameters may have been always set to give the same output of a multi junction thermocouple system. This situation was first recognized by Uchida, Ogawa, and Yamaguchi[1] some 54 years ago, but it seems not to have been noted by other workers measuring mixture vapor pressures. As mentioned above, the former workers did not consider iteration of the temperature in the analysis of their data. However, these workers' observations were incorporated by one of the present authors in the design of an apparatus for mixture vapor pressure measurements[23] and led us in the present work to consider iteration of temperature in our reanalysis of the Scatchard, Kavanagh, and Ticknor data.[6h, 8] As suggested above, possibly a major contribution to this effect arises from small differences in heat transfer for mixtures of different mole fractions due to differences in the heats of vaporization of the components.[24] This effect then represents a source of error in any parameters determined from such data and needs to be taken into account.

The findings discussed above and the demonstration that the pure hydrogen peroxide vapor pressure can be extracted from the mixture vapor pressure data should have significant practical importance in mixture vapor pressure studies. In the past for vapor pressure studies of pure hydrogen peroxide and other pure substances it was deemed necessary to carry out laborious purifications to obtain materials as close as possible to 100% purity. Previous studies of such hydrogen peroxide materials at temperatures much above 50 °C appear to have been plagued by decomposition, whereas in the case of mixtures that are 90% or so in hydrogen peroxide, the decomposition can be kept to a very low level as was done by Scatchard, Kavanagh, and Ticknor.[6h, 8] Thus, for studies of mixture vapor pressures of two components at a particular nominal temperature, if a good VP–T equation for one component is known, the pure vapor pressure of the other component should be determinable from the mixture vapor pressure data. If enough different mole fraction mixtures are studied at a nominal temperature, it also should be possible in some cases to determine the pure vapor pressures of both components.[42] Also, The approach demonstrated here can be extended to mixture vapor pressure data involving more than two components.

The use of four Redlich–Kister parameters in the fitting of the three sets of data considered herein led to much improved fits and to three pure hydrogen peroxide vapor pressure values that fit the two-parameter VP–T Equation (8) very precisely over the range 60–90°C. Combined with the pure hydrogen peroxide vapor pressure data reported by Maass and Hiebert,[13] reasonable four- and seven-parameter VP–T equations could be derived. It was found that the seven parameter equation is not valid above 90°C, but the four parameter equation appears to give reasonable pressure estimates even up to the critical region.

Attempts at fittings with five Redlich–Kister parameters and with P_{HP} and T iterations, for reasons that are not clear, did not lead to stable solutions, reasonable pure P_{HP} values, or much improved agreements with the experimental data. Perhaps, as suggested elsewhere[15,16] these sets of data may not be accurate and extensive enough to warrant use of more parameters than six.

To derive temperature functions for the four Redlich–Kister parameters, B_0, B_1, B_2, and B_3, some assumptions, described above, were adopted regarding the nature of the temperature dependencies. These led to relative simple temperature equations for these functions. The Gibbs excess energies of mixing, g_X^E, were calculated from these temperature-dependent Redlich–Kister parameters; the values found indicated negative deviations from ideal mixtures at all temperatures. The excess entropy, s_X^E, was calculated utilizing the temperature derivatives of the four Redlich–Kister parameters equations; the s_X^E behavior is driven by the nature of the derivatives of the temperature dependencies of the four Redlich–Kister parameters. It varies from a very small positive value near 0°C to a maximum positive value near 50°C to a very negative minimum near 75°C to small negative values at 120°C for large X_{HP} and small positive values at 120°C for small X_{HP}. The s_X^E behaviors in the 40, 55, and 75 degree regions (see Figure 2 to Figure 5) appear very complex and warrant further investigation by other techniques. The naive linear temperature correction to B_0 put forth in the original work[6h,8] could give no hint of the complex behavior our reanalysis of the experimental data suggest. Also, the results in the original work lead to a temperature-independent h_X^E which is certainly wrong.

It is hoped that the results presented here and the recent interest in H_2O_2–H_2O mixtures[2–5] will stimulate further studies of this system. A better characterization of H_2O_2–H_2O mixtures at temperatures below 60°C and down to ambient temperatures should be feasible; such results would test further the assumptions and analyses made in the present work regarding the parameter temperature dependencies and should provide further pure hydrogen peroxide vapor pressure values. It would appear that a vast amount of mixture vapor pressure data in the literature could be fitted substantially better in light of the results presented here.

Estimation of Constants, Derivation of Density Equations and Review of Data

Concerning the experimental data: The experimental work displayed in detail in the Kavanagh thesis[8] has been carefully scrutinized.[43] Detailed study of the rates of decomposition of hydrogen peroxide have been reported by Schumb.[44] It was not expected[8] that the decomposition rates for hydrogen peroxide would be as low as was found in this latter study due to the large and complicated surface of the vapor pressure apparatus. For various mole fraction mixtures at temperatures of 60, 75, and 90°C measurements were made by Kavanagh[8] of the pressure rise in the experimental system during the time of a usual run. The small pressure rise observed at all temperatures did indeed significantly exceed what would be expected from the work of Schumb.[44] However, it was concluded that the amount of decomposition "would not affect the results appreciably."[8] We disagree with this conclusion as it appears that the average extent of decomposition is nearly the same at all the three temperatures and all the mole fractions studied. This perhaps indicates some catalytic region of constant area at some site within the apparatus. Thus, a small correction of -0.073 mm Hg was applied to the original vapor pressure measurements in the present analysis. The original experimental data are exhibited in Table I along with the data corrected for this decomposition.[38] As mentioned above the mixture vapor pressures are given here in mm Hg $(1.0$ mm Hg$=1.3332237 \times 10^2$ Pa$)$ to facilitate comparisons with the original data and analyses,[6k,8] the results in an extensive review of the original work[7] and currently available commercial data sheets describing the vapor pressures of HP–W mixtures.[9] In other places pressure units used are atmospheres or bars $(1.0$ atm$=1.013250$ bar$)$.

Calculation of molecular volumes and water vapor pressure equation: Temperature-dependent values of water and hydrogen peroxide liquid molecular volumes are required for the gas law deviation corrections and for the empirical calculations of the virial coefficients described below. The original work[6h,8] used the hydrogen peroxide liquid density results of Huckaba and Keyes[45] extrapolated from results at 0 and 20°C to the region 60–90°C; this extrapolation seems a little unrealistic. In the present work the newer liquid density equation [Eq. (22)] of Easton, Mitchell, and Wynne-Jones,[10] based on measurements at 0, 10, 25, 50, and 96°C, was used, where a is the density of water at t [ºC], w the wt. fraction of hydrogen peroxide (here $w=1.00$) and b, c, and d are functions given elsewhere.[7,10]

$$\rho_{HP} = a + bw + cw^2 + dw^3 \qquad (22)$$

The water liquid density function developed here is based on the density data contained in the new steam table.[11] Equation (23) represents the simplest equation that gave a precise fit to the experimental data.

$$\rho_W = 1.0000 + c_1 T + c_2 T^2 + c_3/T + c_4/T^2 \qquad (23)$$

However, two sets of c_i values were required. The first set fit over the range 0 to 52.5 °C and the second set over the range 52.5 to 160 °C. The first set of parameters were derived from 14 values which included data at 1° intervals from 0 to 8 °C and at 10° intervals to 50 °C. These parameters reproduced the density maximum around 4 °C. The second set of parameters were derived from 12 values starting at 55 °C with values at 10° intervals from 60 °C to 160 °C. Possibly these two sets of parameters might be of use to others in certain cases so they are shown in Table 9. The

Table 9. Parameters for liquid water density functions based on new steam table density data[11] fitted by equation $\rho_w = 1.000 + c_1 T + c_2 T^2 + c_3 / T + c_4 / T^2$.

T range [K]	c_1	c_2	c_3	c_4
273.15–328.15	-3.171838×10^{-3}	4.279879×10^{-6}	367.0906	-59.47127
328.15–433.15	4.718129×10^{-4}	-1.709110×10^{-6}	27.28696	-7352.166

water and hydrogen peroxide liquid density equations described above then were used to calculate the liquid molecular volumes at various temperatures using the molecular weights of 18.016 for water and 34.016 for hydrogen peroxide.

The seven-parameter VP–T equation (24); pressure in mm Hg) for water derived from the new steam table data[11] was used in the simulation program described above.

$$\log_{10} P_W = 19.389127 - 2861.9133/T - 3.2418662 \log_{10} T$$
$$- 1.0799994 \times 10^{-4} T - 7.9189289 \times 10^{-6} T^2 \quad (24)$$
$$+ 1.5411774 \times 10^{-8} T^3 - 8.1926991 \times 10^{-12} T^4$$

From comparisons with the steam table data a very small correction to this equation needed to be made above 100 °C.

Hydrogen peroxide boiling point, critical constants, and Pitzer acentric factor: The conditions for the experimental determination of hydrogen peroxide critical constants probably will never be realized. For empirical calculations of virial coefficients needed for the gas law corrections terms estimates of these parameters are required. A good estimate of the hydrogen peroxide critical temperature, T^c_{HP}, can be made based on corresponding state theory.[32–35] This approach says that the ratio of the atmospheric boiling points of water, T^b_W, and its critical temperature, T^c_W, is the same for a closely related substance, in this case the ratio T^b_{HP}/T^c_{HP}. The required boiling point of pure hydrogen peroxide at atmospheric pressure (T^c_{HP}) has not been measured. However, three estimates have been reported. Maass and Hiebert[13] estimated this boiling point in two ways. From the classic, two-parameter VP–T equation (pressure in mm Hg), given in Equation (8) they calculated a value of 151.1 °C. Their other estimate was derived from the Ramsey–Young extrapolation approach,[28] which assumes that the ratio between temperatures at which a substance whose vapor pressure is to be extrapolated and a reference substance with similar solution properties or interactions has the same vapor pressure is taken as a linear function of temperature. A value of 151.4 °C was calculated; thus, both esti-

mates are very close. The other hydrogen peroxide boiling point estimate was derived by the Scatchard group[6h,8] by a somewhat modified Ramsey–Young[28] treatment that yielded the four-parameter hydrogen peroxide VP–T Equation (9) (pressure in mm Hg) exhibited above.

Equation (9) gives a boiling point of 150.2 °C. This value gives a T^c_{HP} value of 730.2 K, which was used initially in the present work to obtain the first estimated values of the second virial coefficients from the empirical equations described below. The results of the new fits with four Redlich–Kister parameters discussed above yielded significantly different values for the three pure hydrogen peroxide vapor pressures at the three nominal temperatures of "60", "75" and "90" °C. These values and selected data from Maass and Hiebert[13] were combined, as described above, to give the four- and seven-parameter hydrogen peroxide VP–T Equations (11) and (10) yielding boiling points of 153.155 °C (426.305 K) and 151.478 °C (424.628 K), respectively. These boiling points led to very slightly different critical constants, slightly different virial coefficients and different Redlich–Kister parameters, but no significant changes in the pure hydrogen peroxide vapor pressures arising from the second rounds of fitting to the experimental measurements by four Redlich–Kister parameters and iteration of T and P_{HP}.

With $T^c_W = 647.3$ K[46] and with the assumption that the ratio T^c_{HP}/T^c_W is approximately equal to the ratio T^b_{HP}/T^b_W, T^c_{HP} values of 736.6 or 739.5 K are yielded, depending on whether the boiling point is 151.478 or 153.155 °C, respectively. For comparison applying this concept to the ammonia–hydrazine pair, which are certainly also molecules having significant hydrogen bonding interactions in the liquid, the hydrazine critical temperature, T^c_{HZ}, is calculated as 653.9 K compared with a literature value of 653 K;[46] this result supports the corresponding state theory estimate[32–35] of T^c_{HP} made above.

Several suggestions have been made for estimation of the critical pressure. One is that insertion of the critical temperature into a VP–T equation will give the critical pressure. Kavanagh[8] calculated a P^c_{HP} value of 214 atm from Equation (9), which seems too low and is less than the 218.3 atm P^c_W of water.[46] For the ammonia–hydrazine pair (A–HZ) the former has a P^c_A value of 112.0 atm[46] and the latter a P^c_{HZ} value of 145 atm.[46] Another pair of molecules that suggests that the value of P^c_{HP} should be significantly greater than that of P^c_W is the methylamine–methyl hydrazine pair (MA–MH), in which the former has a P^c_{MA} value of 73.3 atm and the latter a P^c_{MH} value of 81.3 atm.[46] Using the seven-parameter hydrogen peroxide VP–T equation [Eq. (10)], P^c_{HP} is estimated as 1837 atm which is unreasonably high and higher than any known value for a critical pressure. Thus this seven-parameter VP–T equation definitely is invalid close to the critical region. However, the four-parameter VP–T equation [Eq. (11)] gives a value of 255.0 atm. In the original work P^c_{HP} was also required for calculation of the virial coefficients. Although the above Kavanagh value was exhibited as P^c_{HP}, the value used for calculation of the virial coefficients appears to have been based on the assumption that the ratio P^c_W/T^c_W is approximately equal to the ratio P^c_{HP}/T^c_{HP}. The T^c_{HP} of 730 K calculated in the origi-

nal work[8] gives a P^c_{HP} value of 247 atm. For compounds that have very similar interactions in the liquid there is support for this approximation from the law of corresponding states.[32–35] This assumption then gives P^c_{HP} as 248.4 atm for the boiling point at 151.5°C and 249.4 atm for the boiling point at 153.2°C. This assumption applied to the ammonia–hydrazine pair gives a P^c_{HZ} value of 180.4 atm, which is 24% higher than the literature value of 145 atm.[46] On consideration of the pair methylamine–methyl hydrazine, a P^c_{MH} value of 96.7 atm is calculated, which is 19% higher than the literature value of 81.3 atm.[46] Its effect in calculations below being small, P^c_{HP} was taken as 252.2 atm, the average derived from the four-parameter VP–T equation [Eq. (11)] and the corresponding state theory estimate based on the 153.2°C boiling point.

The final two constants required in the Tsonopoulos virial coefficient calculations[12] are the hydrogen peroxide critical volume, V^c_{HP}, and the Pitzer acentric factor,[47] ω_{HP}. Here two estimates of V^c_{HP} have been made. The first was made from the Equation (25) (volume in cm³) of Tyn and Calus,[48,49] where V^b is the liquid molecular volume at the normal boiling point and V^c the critical volume.

$$V^b = 0.285(V^c)^{1.048} \tag{25}$$

For water Equation (24) gives V^c_W as 53.7 cm³mol⁻¹ which is 5.9% lower than the experimental value of 57.1 cm³mol⁻¹.[46] When applied to hydrogen peroxide using the liquid density functions discussed above, which gives a molecular volume of 27.6 cm³mol⁻¹ for the boiling point 153.2°C, a V^c_{HP} value of 77.4 cm³mol⁻¹ is obtained. We chose to scale this value up by the deviation noted for water to give a V^c_{HP} value of 82.3 cm³mol⁻¹. Another estimate can be made from corresponding state theory arguments[32–35] that the ratio of the liquid molecular volumes of similar liquids at their atmospheric boiling points are in the ratio of their critical volumes; this gives V^c_{HP} as 83.7 cm³mol⁻¹. The average of these two estimates, 83.0 cm³mol⁻¹, has been used in the present work.

The Pitzer acentric factor, ω_{HP} reflects the noncentral nature of intermolecular forces. It has been defined by Equation (26)[47] where P^s is the vapor pressure calculated from a vapor pressure equation at T with the reduced temperature, T_r, of 0.7 and $T_r = T/T^c$.

$$\omega = -\log_{10}(P^s/P^c)_{T_r=0.7} - 1.000 \tag{26}$$

For water Equation (26) gives a ω value of 0.344, which is the accepted value.[46] Using the seven- and four-parameter VP–T equations for hydrogen peroxide derived below and Equation (26), we calculated values of 0.244 and 0.417, respectively. The former value seems way too low, which indicates that even at a T_r of 0.7 (575.7 K, 242.5°C) the seven-parameter VP–T equation [Eq. (10)] is not valid. One can again draw a comparison with the ammonia–hydrazine pair, for which the ω values are 0.244 and 0.316, respectively.[46] The 0.417 value for ω_{HP} given by the four-parameter VP–T equation [Eq. (11)] then seems reasonable and has been used here. Table 10 summarizes the constants estimated in

Table 10. Constants used in calculations of virial coefficients.

	T_{BP}[a]	T^c[a]	P^c	V^c	ω
water[b]	373.150	647.3	218.3 atm	57.1 cm³mol⁻¹	0.344
hydrogen peroxide	426.305	739.5	252.2 atm	83.0 cm³mol⁻¹	0.417

[a] Temperature in K. [b] Taken from reference [46].

this section and which are required for calculations of the virial coefficients.

It should be kept in mind that all the constants estimated in this section are used to calculate virial coefficients that go into the imperfect gas law correction terms of Equations (6) and (7), which are expected to make only small contributions to the complete chemical potential expressions Equations (3) and (4) at the pressures involved here. To verify this in the present work model calculations were carried out which showed that the imperfect gas correction terms contribute at most 1–2% to the mixture vapor pressures in the temperature and pressure ranges considered. Depending on the mole fraction and temperature, these terms, however, can contribute as much as 20% to a particular, small total chemical potential term.

Calculations of second virial coefficients: For use in the calculation of the second virial cross coefficient, β_{HP-W}, values of the so-called binary critical constants T_{HP-W}, P^c_{HP-W} and ω_{HP-W} are required. The following mixing rules [Eq. (27)–(29)], recommended by Tsonopoulos and Heidman,[12b] have been used.

$$\omega_{HP-W} = 0.5(\omega_W + \omega_{HP}) \tag{27}$$

$$T^c_{HP-W} = (T^c_W T^c_{HP})^{1/2}(1-k_{HP-W}) \tag{28}$$

$$P^c_{HP-W} = \frac{4 \times T^c_{HP-W}(P^c_W V^c_W/T^c_W + P^c_{HP}V^c_{HP}/T^c_{HP})}{(V^{c\,1/3}_W + V^{c\,1/3}_{HP})^3} \tag{29}$$

If two polar substances are very similar in chemical nature and not too different in size, k_{HP-W} can be taken as zero which was done here. The virial coefficients, β_W, β_{HP}, and β_{HP-W}, were calculated from the Tsonopoulos Equation (30),[12] for which [Eq. (31)–(33)] are applicable.

$$\beta_i P^c_i/RT^c_i = f^{(0)}(T_r) + \omega_i f^{(1)}(T_r) + f^{(2)}(T_r) \tag{30}$$

$$f^{(0)}(T_r) = 0.1445 - 0.330/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 - 0.000607/T_r^8 \tag{31}$$

$$f^{(1)}(T_r) = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 - 0.008/T_r^8 \tag{32}$$

$$f^{(2)}(T_r) = -0.0109/T_r^6 \tag{33}$$

In the above equations β_i is the virial coefficient, P^c_i and T^c_i the appropriate critical pressure and temperature, respectively, R the gas constant (units cm³mol⁻¹K⁻¹), ω_i the Pitzer acentric factor, and T_r the reduced temperature, T/T^c_i. Here the pressure units of P^c_i are bars (1.0 atm = 1.01325 bar = 760.0 mm Hg). A program was written to calculate the β_i values as a function of temperature for both water and hy-

drogen peroxide. These results along with the results for these parameters calculated from equations from the original work[8,21] are in the Supporting Information.

[1] S. Uchida, S. Ogawa, M. Yamaguchi, *Japan Sci. Rev., Eng. Sci.* **1950**, *1*, No. 2, 41–49 (in English).

[2] See for example: a) L. F. Keyser, *J. Phys. Chem.* **1982**, *86*, 3439–3446; b) J. J. Lamb, L. T. Molina, C. A. Smith, M. J. Molina, *J. Phys. Chem.* **1983**, *87*, 4467–4470; c) S. P. Sander, *J. Phy. Chem.* **1984**, *88*, 6018–6021; d) G. L. Vaghjiani, A. R. Ravishankara, N. Cohen, *J. Phys. Chem.* **1989**, *93*, 7833–7837.

[3] A. L. Lane, S. P. Sander, Jet Propulsion Laboratory; personal communications.

[4] J. M. Nicovich, P. H. Wine, *J. Geophys. Res.[Atmos.]* **1988**, *93*, 2417–2421.

[5] a) R. W. Carlson, M. S. Anderson, R. E. Johnson, W. D. Smythe, A. R. Hendrix, C. A. Barth, L. A. Soderblom, T. B. McCord, J. B. Dalton, R. N. Clark, J. H. Shirley, A. C. Ocampo, D. L. Matson, *Science* **1999**, *283*, 2062–2064; b) J. F. Cooper, R. E. Johnson, B. H. Mauk, H. B. Garrett, N. Gehsels, *Icarus* **2001**, *149*, 133–159.

[6] a) G. Scatchard, C. L. Raymond, H. H. Gilman, *J. Am. Chem. Soc.* **1938**, *60*, 1275–1278; b) G. Scatchard, C. L. Raymond, *J. Am. Chem. Soc.* **1938**, *60*, 1278–1287; c) G. Scatchard, S. E. Wood, J. M. Mochel, *J. Phys. Chem.* **1939**, *43*, 119–130; d) G. Scatchard, S. E. Wood, J. M. Mochel, *J. Am. Chem. Soc.* **1939**, *61*, 3206–3210; e) G. Scatchard, S. E. Wood, J. M. Mochel, *J. Am. Chem. Soc.* **1940**, *62*, 712–716; f) G. Scatchard, S. E. Wood, J. M. Mochel, *J. Am. Chem. Soc.* **1946**, *68*, 1957–1960; g) G. Scatchard, S. E. Wood, J. M. Mochel, *J. Am. Chem. Soc.* **1946**, *68*, 1960–1963; h) G. Scatchard, G. M. Kavanagh, L. B. Ticknor, *J. Am. Chem. Soc.* **1952**, *74*, 3715–3720; i) G. Scatchard, L. B. Ticknor, *J. Am. Chem. Soc.* **1952**, *74*, 3724–3729; j) G. Scatchard, F. G. Satkiewiez, *J. Am. Chem. Soc.* **1964**, *86*, 130–133; k) G. Scatchard, G. M. Wilson, *J. Am. Chem. Soc.* **1964**, *86*, 133–137.

[7] W. C. Schumb, C. N. Satterfield, R. L. Wentworth, *Hydrogen Peroxide*, ACS Monograph Series, Reinhold Publishing Corp., New York, **1956**, pp. 221–231.

[8] G. M. Kavanagh, PhD thesis, MIT (USA), **1949**.

[9] FMC, Technical Bulletin 67.

[10] M. F. Easton, A. G. Mitchell, W. F. K. Wynne-Jones, *Trans. Faraday Soc.* **1952**, *48*, 796–801.

[11] L. Haar, J. S. Gallagher, G. S. Kell, *NBS/NRC Steam Tables*, Hemisphere Publishing Corp., New York, **1984**.

[12] a) C. Tsonopoulos, *AIChE J.* **1974**, *20*, 263–272; b) C. Tsonopoulos, J. L. Heidman, *Fluid Phase Equilib.* **1990**, *57(3)*, 261-276.

[13] O. Maass, P. G. Hiebert, *J. Am. Chem. Soc.* **1924**, *46*, 2693–2700.

[14] O. Redlich, A. T. Kister, *Ind. Eng. Chem.* **1948**, *40*, 345–348.

[15] For example, see J. M. Prausnitz, R. N. Lichtenthaler, E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed. Prentice Hall, New Jersey, **1999**, pp. 225–264.

[16] For other texts see: a) E. Hala, J. Pick, V. Fried, O. Vilim, *Vapor-Liquid Equilibrium*, Pergamon Press, Oxford, **1967**; b) H. C. Van Ness, M. M. Abbott, *Classical Thermodynamics of Nonelectrolyte Solutions with Applications to Phase Equilibria*, McGraw-Hill, New York, **1982**; c) J. S. Rowlinson, F. L. Swinton, *Liquid and Liquid Mixtures*, 3rd ed., Butterworth Scientific, London, **1982**.

[17] See: H. C. Van Ness, M. M. Abbott, *Classical Thermodynamics of Nonelectrolyte Solutions with Applications to Phase Equilibria*, McGraw-Hill, New York, **1982**, pp. 200—202.

[18] G. M. Wilson, PhD thesis, MIT (USA), **1953**, p 56.

[19] The exponent terms in Equation (5) need to be divided by RT. For the chemical potentials, μ_1^E and μ_2^E, the RT must be $T \times 82.0578/41.2925$, while RT for the imperfect gas correction terms is $760 \times T \times 82.0518$.

[20] F. G. Keyes, *J. Chem. Phys* **1947**, *15*, 602–612.

[21] Calculated from an equation given by: F. G. Keyes, L. B. Smith, H. T. Gerry, *Proc. Am. Acad. Arts Sci.* **1936**, *70*, 319–364.

[22] The data processing package used was "PSI-Plot" available from "Poly Software International," P. O. Box 60, Pearl River, NY 10965 (USA). The version used to fit equations like Equation (5) above must be "Version 3." This version has a choice of three nonlinear curve fitting techniques: Powell, Marquardt—Levelburg, and Simplex methods. Newer versions of this software package only have the Marquardt-Levelburg method; we found that the latter does not give solutions to most iterative equations that have been tried in our work. With "Version 3" sometimes both the Powell and the Marquardt–Levelburg methods will not converge or fail many times in initial fittings where reasonable starting parameters are not known. However, the Simplex method with somewhat arbitrary guesses was found to yield reasonable initial parameters. When the fit was getting close, it was observed that the Simplex method in "PSI-Plot" appears to wander for equations such as Equation (5). Thus, the final fits were always made with the Powell method which always led to stable solutions. It was noted that the final parameters from the Powell method vary slightly with the input parameter estimates. In our work the practice adopted was to use parameter estimates of five significant digits which were iterated until no changes were observed in the fifth decimal place of final parameters. To reduce the possibility of roundoff error, only four decimals points are shown in Table 2 and these are the numbers used in all the simulation data presented. Equation (5) was programmed into the "PSI-Plot" nonlinear least-squared curve fitting script language with the parameters B_0, B_1, B_2, B_3, and P_{HP}. To start, the nominal T value reported in the previous analyses[6h,8] was used. Next T was changed in small increments and improvements in the observed minus calculated mixture vapor pressures were sought. Each change of T causes a change in P_{HP} and P_W. Attempts to incorporate the two required VP–T equations along with Equation (5) proved too cumbersome and appeared to exceed the capability of the nonlinear curve fitting script language in "Version 3" of "PSI-Plot."

[23] S. P. Vango, S. L. Manatt, unpublished work carried out at the Jet Propulsion Laboratory, California Institute of Technology.

[24] In the work of reference [23] the following observations were made that are suggestive of this explanation for mixtures. For solvent mixtures of various mole fractions, the temperature differentials were mole fraction dependent when the energy input, rate of reflux and coolant flow rate were carefully held constant. However, temperature differences were even observed for pure water and pure solvents but they were significantly less than for mixtures. In the analysis of the data in the Jet Propulsion Laboratory work temperature iteration was not done, but the temperature was always taken from a thermocouple at one particular location in the apparatus. Also for the most part pure component vapor pressures were taken from manufacture's tables but in several cases vapor pressures were determined so all these results certainly had errors, based on the observations in the present work, probably of the order of those existing in the original Scatchard, Kavanagh, and Ticknor work[6h,8]

[25] The Scatchard group (references [6h, 8]) stated that the measured vapor mole fractions, Y_i's, could not be measured to nearly the same accuracy as the liquid mole fractions and mixture vapor pressures. However, the Y_i's are calculated accurately from the equation $Y_i = P_i X_i \exp[(X_j^2/RT)(\mu_i^E + IGC_i)]/P$.

[26] a) C. Antoine, *Compt. Rend.* **1888**, *107*, 1143–1145; b) See also: G. W. Thomson, *Chem. Rev.* **1946**, *46*, 1–39.

[27] In the original analyses of the three sets of mixture vapor pressures at the nominal temperatures of "60," "75" and "90"°C it was acknowledged by Scatchard, Kavanagh and Ticknor that the vapor pressures of pure hydrogen peroxide at these latter temperatures

are required.[6h,8] They first obtained these vapor pressures by graphical extrapolations of the mixture vapor pressures to 1.00 mole fraction hydrogen peroxide. There was no mention of what the starting extrapolated pure hydrogen peroxide vapor pressures were. The Redlich–Kister constants were then obtained "using a successive approximation form of the method of least squares." "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 the experimental pressures."[6h,8] The pure hydrogen peroxide vapor pressures resulting from the iterations to a stationary sum of the squares of the vapor pressure residuals were not given. The values for pure hydrogen peroxide vapor pressures at the three nominal temperatures were calculated from the final fit parameters using only "the two measurements most concentrated in hydrogen peroxide. The two values obtained were averaged with double weight being given to the determination more concentrated in hydrogen peroxide …."[6h,8] No mention was made of how many iterations were required or of any estimates of the error. The statement was made that, "The final extrapolation for the vapor pressures was made with least squared constants before they had been temperature smoothed."[6h,8] The meaning of "final extrapolation" is not clear to us. The values for the pure hydrogen peroxide vapor pressures found by Scatchard, Kavanagh, and Ticknor are shown in Table 3 along with the errors of their fits to Equations (8) and (9). Fits were also carried out in the present work using the Wilson[29] approach with a third polar parameter and two gas imperfection terms (with P_{HP} as a parameter and T iteration). Results similar to those from a three parameter Redlich–Kister treatment were obtained for the goodness of fit for the "60" and "75" degree data, but the fit for the "90" degree data was poor and the values for the pure hydrogen peroxide vapor pressures for the "75" and "90" experimental data were substantially different, 38.98 and 79.24 mm Hg, respectively, from those (see Table 3) from the three-parameter Redlich–Kister treatment.

[28] W. Ramsay, S. Young, *Philos. Mag.* **1886**, *21(5)*, 33–51.

[29] G. M. Wilson, *J. Am. Chem. Soc.* **1964**, *86*, 127–130.

[30] P. A. Giguère, O. Maass, *Can. J. Res.* **1940**, *18B*, 181–193.

[31] These same authors presented data at 45 and 60°C but they had serious reservations about its quality as they were plagued by decomposition. Calculations using the parameters derived in the present work gave results in very poor agreement with these latter data sets which seems to confirm the serious experimental problems these authors had at these two temperatures. Our parameters at 60°C should certainly be correct because of the good fit to the data of references [6h, 8].

[32] F. G. Keys, *J. Am. Chem. Soc.* **1938**, *60*, 1761–1764.

[33] See Reference [15] pp. 104–113.

[34] E. A. Guggenheim, *J. Chem. Phys.* **1945**, *13*, 253–261.

[35] G. W. Castellan, *Physical Chemistry*, Addison-Wesley, Palo Alto **1964**, pp. 41–43.

[36] C. F. Curtiss, J. O. Hirschfelder, *J. Chem. Phys.* **1942**, *10*, 491–496.

[37] G. S. Kell, G. E. McLaurin, E. Whalley, *J. Chem. Phys.* **1968**, *48*, 3805–3813.

[38] Several questions regarding the original temperature calibrations arose. The centigrade temperature (International Practical Celsius Temperature) was taken as $t = T - 273.16$ in the original work, whereas now the accepted equation is $t = T - 273.15$ where in both cases T is the International Practical Kelvin Temperature (See: *The International Practical Temperature Scale of 1968, Metrologia* **1969**, *5*, 35–44). This is a very small difference, but as discussed above the quality of the fits to the experimental data is very sensitive to T. The original temperature calibrations of the apparatus were based on EMF measurements with a 20 junction thermocouple system and a water VP–T equation reported by Keyes[20] some 57 years ago. In the present work the recent revised water vapor pressure values (and water liquid densities used below) recommended by Haar, Gallagher and Kell were used.[11] In the present analysis for the temperature determinations from experimental water vapor pressure values (P_w in mm Hg) the new water vapor pressure data for 11 points $\pm$ 5°C about each estimated temperature was fit by a separate Antoine equation[26] of the form $\ln P_w = A + B/(T + C) + $ Corr. where A, B and C are least-square determined constants and Corr. is a very

small correction term obtained graphically from plots of the differences between the pressures from the above equation and the new steam table data.[11] The fit to a quadratic relation in the Celsius temperature with inclusion of all 17 thesis EMF values exhibited average errors significantly greater than ± 0.02°C. Sifting the data easily eliminated six of the thesis EMF points and the resulting 11 points yielded a fit with an average error ± 0.005°C. The stated temperatures for the various runs (44.50, 60.00, 75.00, 90.00 and 105.00°C) (with errors estimates of about ± 0.02°C) were achieved by observing the thermocouple system EMF, while setting the apparatus heater system to give an EMF corresponding to that of the desired temperature as given by the quadratic relation determined from the water VP–T equation. Although the temperatures estimated in the present work (44.495, 60.004, 75.016, 90.031, and 105.050°C with an error estimate of ± 0.005°C) differ only slightly from the thesis ones, the important thing to keep in mind here is that the water vapor pressure differences between the Keyes equation[20] values and an equation derived here based on the new steam table data[11] (old steam equation, 70.034, 149.400, 289.100, 525.724, and 905.700 mm Hg versus new, 70.039, 149.447, 289.307, 526.380, and 907.443 mm Hg) affect the goodness of fit significantly as the water vapor pressures multiply the exponentials of the excess energy terms. The differences in temperature discussed here, however, become unimportant because, as discussed above, the average temperature of a suite of mixtures vapor pressure measurements of different mole fractions made at a particular heater setting dictated by a particular EMF setting can be determined in the fit to the mixture vapor pressure data.

[39] For the Lorentzian and sigmoid curves four parameters are required to be determined from only three data points. The following iterative procedure was used with "PSI-Plot": two parameters were guessed and two parameters were fit to the three data points; in the next stage the fit parameters were input and two parameters guessed originally were fit; repetition of this procedure, while monitoring the least square residuals and the parameters, was stopped when the parameters were unchanged in the sixth decimal place.

[40] The activity coefficients, γ_i values, were calculated at a number of temperatures including 60, 75 and 90°C. Although the differences between the γ_i values calculated from the previous work and the present work are small at 75°C, the latter γ_i values exhibited no anomalies that might reflect on the large Ts_x^E values calculated in this temperature region. This is consistent with the γ_i values coming essentially from g_x^E. The g_x^E values of the previous and present works are close at all temperatures. The equations used to calculate the γ_i values are given in reference [15], pp. 236–237.

[41] See for example: L. Pauling, *The Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithaca, New York, **1948**, pp. 301–304 and p. 333.

[42] We have verified this possibility in one case using the Scatchard and Raymond data on the ethanol-cholorform system.[6b] Possibly the reason it works for the latter data is because there were several measurements for mole fraction greater than 0.9 for both components.

[43] Several typo errors in the experimental data in the thesis,[8] the review,[7] and the original publication[6h] were noted. In Table 1 of the thesis the EMF in run #3 should be 0.035814 v and the temperature should be 44.599°C; the pressures in runs 7 and 8 should be 394.711 and 354.182 mm Hg, respectively; in Table 2 the mole fraction at 60°C of 0.1577 should have a pressure 26.21 mm Hg and the fourth mole fraction should be 0.4221; in reference [7] in Table 16 the mole fraction at 60°C of 0.8423 should have a pressure of 26.21 mm Hg and the eighth mole fraction at 75°C should be 0.7460; in reference [6h] the 44.50 and 105.00°C smoothed pressures should be 27.41 and 415.68 mm Hg, respectively.

[44] W. C. Schumb, *Ind. Eng. Chem.* **1949**, *41*, 992–1003.

[45] C. E. Huckaba, F. G. Keyes, *J. Am. Chem. Soc.* **1948**, *70*, 2578–2500.

[46] For an extensive compilation of boiling points, critical constants, acentric factors, and other molecular constants, see: R. C. Reid, J. M. Prausnitz, B. E. Poling, *The Properties of Gases & Liquids*, 4th ed., McGraw-Hill, New York, **1987**, pp. 656–732.

[47] a) K. S. Pitzer, *J. Am. Chem. Soc.* **1955**, *77*, 3427–3433; b) K. S. Pitzer, D. Z. Lippman, R. F. Curl, C. M. Huggins, D. E. Peterson, *J. Am. Chem. Soc.* **1955**, *77*, 3433–3440.

[48] M. T. Tyn, W. F. Calus, *Processing* **1975**, *21*, 16–17.

[49] See: R. C. Reid, J. M. Prausnitz, B. E. Poling, *The Properties of Gases & Liquids*, 4th ed., McGraw-Hill, New York, **1987**, pp. 53–55.