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**TEMPERATURE DEPENDENCE OF WILSON COEFFICIENTS:
VAPOR-LIQUID EQUILIBRIA OF AQUEOUS AMMONIA**

Paul E. Field

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
Blacksburg, VA 24061-0212

Roger J. Combs

RESEARCH AND TECHNOLOGY DIRECTORATE



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PREFACE

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TEMPERATURE DEPENDENCE OF WILSON COEFFICIENTS: VAPOR-LIQUID EQUILIBRIA OF AQUEOUS AMMONIA

1. INTRODUCTION

Numerous studies of the equilibrium of gaseous ammonia and liquid water have been reported over the past century. They can be divided into two practically mutually exclusive groups based on whether the solution concentration is reported on a molarity (equilibrium constant) or molality (weight or mole fraction) basis. Only in the latter group are the data sufficiently determined and reported to provide pressure, temperature, and composition of both the liquid and vapor phases (P , T , X , Y). Actual measured values as contrasted to empirically smoothed values further narrow the useful information available. To date there has been no analysis of the Wilson equation which provides a direct comparison of all the published data for aqueous ammonia in a concise format. Particular interest, other than the high pressure absorption refrigeration work, relates to the lower pressure, below two atmospheres, analysis of non-ideal behavior in terms of Henry's law or other treatments of activity coefficients such as, in particular, the Wilson equations. There are twenty-seven isothermal sets ranging up to 1.0 MPa (10 atm) having sufficient experimental data to permit evaluation of the Wilson coefficients, W_{12} and W_{21} , provided by eight studies (number of isotherms listed in parentheses): Perman¹ (7), Wilson² (6), Clifford and Hunter³ (4), Rizvi and Heidemann⁴ (2), Inomata⁵ (1), Muller⁶ (1), Kurz⁷ (4), and Harms-Watzenberg⁸ (1).

Even as late as the time of publication of Wilson's original paper⁹ in 1964, the non-linear form of the equations requiring five to ten iterations for solution was an impediment to its application. With the advent of computer power, coefficients for binary systems in a form recast by Orye and Prausnitz¹⁰ were first systematically compiled by Hirata *et al.*¹¹ and Gmehling *et al.*¹² No studies to date have examined the temperature dependence of the Wilson coefficients for the aqueous ammonia system.

2. DATA ANALYSIS

The Wilson coefficient defined by Orye and Prausnitz¹⁰ is given as

$$W_{ij} = (v_j^L/v_i^L) \exp - [(\lambda_{ij} - \lambda_{ji}) / RT] \quad (1)$$

where v_i^L are the pure liquid molar volumes and the λ_{ij} are proportional to the intermolecular interaction energies. The excess Gibbs free energy for an N component system is obtained in terms only of the binary coefficients (*i.e.* N-tuplets are not implied) as

$$\Delta G^{xs}/RT = -\sum_i^N X_i \ln [\sum_j^N X_j W_{ij}] = \sum_i^N X_i \ln \gamma_i \quad (2)$$

then the activity coefficient for a two component system in terms of the Wilson coefficients is related as

$$\ln \gamma_i = -\ln [X_i + W_{ij} X_j] + X_j [W_{ij}/(X_i + W_{ij} X_j) - W_{ji}/(X_j + W_{ji} X_i)] \quad (3)$$

In the search for the "best" pair of W_{ij} coefficients to represent a PTXY data set of a binary system by any of several objective functions, both Hudson and Van Winkle¹³ and Hirata *et al.*¹¹ observed an inverse relationship between W_{12} and W_{21} having constant contours about a minimum in the objective function lying along an hyperbolic path. We have previously shown¹⁴ for several binary aqueous volatile organic compound (VOC) systems of simple alcohols or ketones that better agreement in the average deviation of the vapor mole fractions are obtained by searches over PTXY data using the residual sum of the squares for the excess free energy ($SQ = \sum r_i^2$) as the objective function. Here,

$$r_i = \sum X_i \ln \gamma_i (\text{obs}) - \sum X_i \ln \gamma_i (\text{calc}) \quad (4a)$$

$$\text{with } \gamma_i (\text{obs}) = (Y_i / X_i)(P_T / P_i^o) \quad (4b)$$

where P_T is the total vapor pressure, P_i^o is the vapor pressure of the pure component at the observed temperature that is calculated using an empirical equation, and $\ln \gamma_i (\text{calc})$ is obtained from equation 3.

Unlike the aqueous VOC systems reported previously, minimization of SQ by the usual least squares method of solving two partial derivative equations: $(\delta SQ / \delta W_{ij}) = 0$ was not possible. Iterative solutions of these equations do not converge for any of the aqueous ammonia data sets. As an alternative means of solution, two computerized grid searches were carried out. A preliminary coarse search over the practical range of $0.1 \leq W_{ij} \leq 12.0$ was performed and 120 point data files of W_{21} having the smallest average deviation ($ad = SQ/N$) found for values of W_{12} stepped by increments of 0.1 in each coefficient were obtained for each experimental data set. In all cases a minimum curve for $ad(W_{21})$ versus W_{12} and monotonic dependence of W_{21} on W_{12} was found. The second fine search generated a 200 point data file over a range of two units of W_{12} about the coarse minimum using a commensurate range of W_{21} at increments of 0.01 in each coefficient. More sophisticated search algorithms, such as simplex, were not used because the discreteness of a data set does not guarantee the non-existence of false minima.

Figure 1 illustrates the results of both searches. The saw-tooth behavior of ad vs. W_{12} for the coarse search is typical and an artifact of the step size in W_{21} . The fine curve clearly defines the true minimum within a coefficient precision of 0.01. The data set illustrated is the 30 °C isotherm from Perman and was selected as typical. Deeper and shallower minima are found in the other data sets. In Table 1 the first entry at each temperature for each reference summarizes the results for the search of the W_{ij} pair having the least sum of squares, SQ, for each of the twenty-seven experimental PTXY data sets. The additional two entries which have larger mean sums of squares will be considered in the next section. Normalization of SQ by division of the number of points per set permits comparison between sets. Given temperature, T, and concentration in the liquid state, X, as the independent variables, the pair of Wilson coefficients, W_{ij} , at each temperature measure the non-ideality of the solution. For a given mole fraction of one component, X_i , of a two component system ($X_j = 1 - X_i$), estimations may be made of vapor mole fraction, Y_i , partial pressure, P_i , and total vapor pressure, $P_T = P_1 + P_2$. For a given data set the simplest measure for goodness of fit is the average deviation of the dependent variable, P_i or Y_i , corresponding to the probable error limit (*i.e.* 50 percentile). A second common measure is the standard error obtained from the estimate of the standard deviation and corresponding to an error limit at the 63 percentile. We have included both in order to allow comparison with previous studies, especially references 11 and 12, in both the vapor composition and total vapor pressure. While these statistics

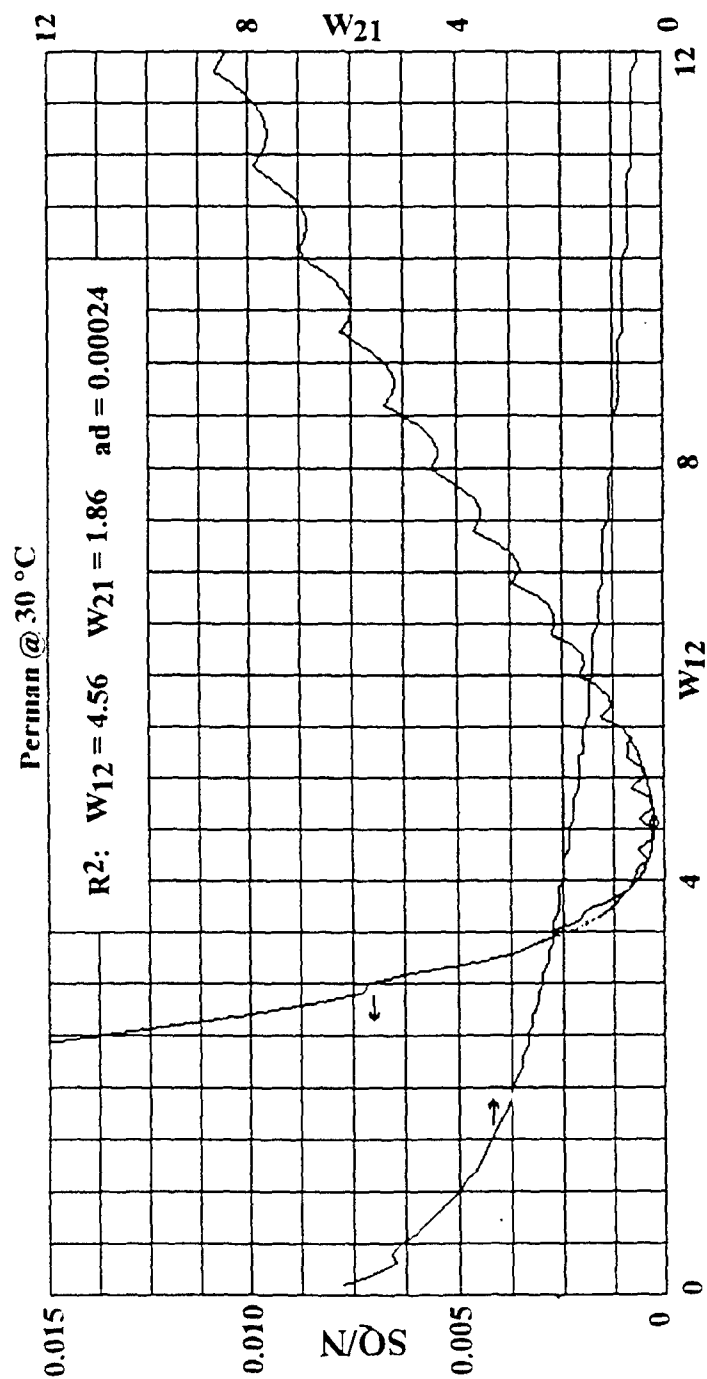


Figure 1. Coarse and fine grid search results of 30 °C isothermal data set (ref. 1) to obtain W_{ij} pair at minimum average deviation of excess free energy objective function, SQ/N.

Table 1. Wilson Coefficient Goodness of Fit

Ref.	T, °C ^a	W ₁₂	W ₂₁	SQ/N ^b	BESE(Y _A)	ad(Y _A) ^c	ad(P _T), kPa ^d	%ad(P _T) ^e
Perman	0.0	4.81	2.78	5.730e-3	0.0187	0.0129	0.43	10.06
		5.40	2.57	6.548e-3	0.0151	0.0114	0.55	10.30
		5.49	2.26	1.672e-2	0.0219	0.0153	0.37	5.20
	10.0	4.93	2.26	3.325e-3	0.0097	0.0067	0.35	3.52
		5.31	2.21	4.493e-3	0.0115	0.0081	0.36	3.94
		5.36	2.08	4.628e-3	0.0084	0.0057	0.29	2.63
	19.9	4.63	2.02	1.579e-4	0.0038	0.0023	0.48	2.52
		5.22	1.92	2.795e-3	0.0086	0.0073	0.33	1.86
		5.23	1.91	2.407e-3	0.0072	0.0060	0.27	1.41
	30.1	4.56	1.86	2.496e-4	0.0033	0.0026	0.39	1.40
		5.12	1.69	5.627e-4	0.0023	0.0016	0.58	1.52
		5.10	1.75	1.155e-3	0.0056	0.0047	1.08	3.02
	40.0	3.87	1.87	4.196e-4	0.0050	0.0041	0.88	1.93
		5.01	1.52	1.700e-3	0.0046	0.0039	1.09	1.66
		4.97	1.61	3.475e-3	0.0094	0.0086	2.63	4.96
	50.0	4.56	1.49	2.887e-5	0.0017	0.0012	0.17	0.38
		4.88	1.39	1.082e-4	0.0034	0.0029	0.37	0.88
		4.83	1.48	9.805e-4	0.0098	0.0091	1.91	3.62
	60.0	6.90	0.88	2.970e-4	0.0056	0.0038	0.59	0.96
		4.73	1.28	1.503e-3	0.0101	0.0080	0.47	0.78
		4.69	1.37	8.829e-4	0.0106	0.0101	1.64	2.88
Wilson	0.0	7.00	2.35	4.404e-2	0.0137	0.0056	54	34.8
		5.40	2.57	5.203e-2	0.0189	0.0074	43	27.7
		5.49	2.26	5.903e-2	0.0250	0.0098	43	30.1
	20.0	5.49	1.70	1.567e-2	0.0054	0.0029	113	32.1
		5.22	1.92	1.621e-2	0.0040	0.0023	111	31.0
		5.23	1.91	1.614e-2	0.0041	0.0023	111	31.0
	40.0	4.13	1.72	1.449e-2	0.0118	0.0051	131	23.0
		5.01	1.52	1.714e-2	0.0101	0.0057	156	28.1
		4.97	1.61	1.830e-2	0.0080	0.0053	158	28.7
	60.0	3.23	1.88	7.868e-4	0.0026	0.0016	81	13.7
		4.74	1.28	7.813e-3	0.0073	0.0063	114	20.2
		4.69	1.37	9.005e-3	0.0067	0.0060	119	21.1
	80.0	2.68	1.92	1.117e-5	0.0005	0.0004	49	7.26
		4.39	1.15	6.412e-3	0.0089	0.0082	80	12.4
		4.38	1.18	6.573e-3	0.0081	0.0071	81	12.2
	90.0	2.77	1.82	2.910e-4	0.0025	0.0024	59	6.96
		4.18	1.13	5.190e-3	0.0151	0.0123	90	12.8
		4.20	1.10	5.402e-3	0.0171	0.0137	89	13.1
Clifford	60.0	3.51	1.65	1.497e-3	0.0185	0.0148	1.33	2.24
		4.74	1.28	2.031e-3	0.0211	0.0154	0.73	9.93
		4.69	1.37	3.071e-3	0.0210	0.0178	2.43	3.80
	80.0	6.47	0.76	2.720e-4	0.0099	0.0073	3.94	2.74
		4.39	1.15	8.228e-4	0.0130	0.0102	1.33	0.95
		4.38	1.18	5.731e-4	0.0120	0.0095	2.31	1.75
	90.0	7.64	0.49	1.439e-4	0.0095	0.0068	0.80	0.75
		4.18	1.13	1.584e-4	0.0097	0.0062	0.76	0.72
		4.20	1.10	1.698e-4	0.0100	0.0083	0.36	0.39

Table 1. Wilson Coefficient Goodness of Fit (Continued)

Ref.	T, °C ^a	W ₁₂	W ₂₁	SQ/N ^b	BESE(Y _A)	ad(Y _A) ^c	ad(P _T), kPa ^d	%ad(P _T) ^e
Clifford	100.0	2.37	1.64	1.968e-5	0.0034	0.0030	0.75	0.60
		3.95	1.13	2.505e-5	0.0051	0.0051	0.52	0.43
		3.99	1.04	1.590e-4	0.0102	0.0097	1.48	1.22
Kurtz	40.0	4.91	1.59	3.689e-3	0.0185	0.0110	0.88	2.53
		5.01	1.52	4.076e-3	0.0214	0.0138	0.35	0.86
		4.97	1.61	3.956e-3	0.0179	0.0120	1.47	4.38
	60.0	5.12	1.20	8.420e-4	0.0080	0.0058	3.97	3.20
		4.73	1.28	9.969e-4	0.0084	0.0059	2.79	2.24
		4.69	1.37	1.353e-3	0.0102	0.0080	6.44	5.90
	79.9	6.94	0.61	7.167e-4	0.0153	0.0122	8.07	4.17
		4.39	1.15	1.129e-3	0.0127	0.0110	3.85	1.99
		4.38	1.18	1.319e-3	0.0149	0.0123	5.28	3.00
	100.5	4.33	0.97	7.424e-5	0.0036	0.0027	5.68	2.15
		3.93	1.13	4.123e-4	0.0087	0.0078	11.5	4.36
		3.98	1.04	2.295e-4	0.0073	0.0063	1.12	0.42
Harms- Watzenberg	100.0	4.71	1.17	4.450e-2	0.0332	0.0184	389	19.2
		3.95	1.13	4.995e-2	0.0545	0.0288	245	11.2
		3.99	1.04	5.194e-2	0.0604	0.0315	233	10.3
Muller	100.0	3.49	1.29	1.285e-4	0.0041	0.0029	27.2	4.70
		3.95	1.13	2.686e-4	0.0047	0.0043	30.8	5.09
		3.99	1.04	1.091e-3	0.0137	0.0113	24.0	4.46
Rizvi	32.4	7.86	1.09	6.073e-2	0.0204	0.0124	171	43.5
		5.09	1.65	6.820e-2	0.0216	0.0121	130	35.9
		5.07	1.72	6.787e-2	0.0198	0.0115	131	36.7
	68.6	5.99	1.38	2.246e-2	0.0315	0.0192	237	37.5
		4.60	1.21	5.004e-2	0.0688	0.0420	151	21.5
		4.56	1.28	4.515e-2	0.0642	0.0394	156	23.0
	86.5 ^f	14.84	0.10	3.757e-2	0.0570	0.0320	610	38.5
		4.26	1.13	8.398e-2	0.0893	0.0549	218	15.3
		4.26	1.13	8.433e-2	0.0900	0.0552	217	15.1
	Inomata 59.7 ^f	1.13	3.05	2.017e-3	0.0007	0.0006	77.5	15.4
		4.74	1.28	8.035e-2	0.0169	0.0112	207	21.5
		4.70	1.37	8.422e-2	0.0183	0.0119	211	22.7

NOTES:

^aFor each isotherm. First entry: based on minimized residual sum of squares (SQ) of excess free energy of individual isotherm; Second entry: group (25 isotherms) fitted Dif S and Sum S functions to parabolic temperature dependence ($a+bT+cT^2$); Third entry: group fitted Dif S and Sum S functions to linear temperature dependence ($a + bT$).

^bMean value of the calculated residual excess free energy.

^cAverage Deviation of Ammonia Vapor Mole Fraction: $\Sigma[Y_{\text{obs}} - Y_{\text{calc}}]/N$.

^dAverage Deviation of Total Vapor Pressure, kPa: $\Sigma[P_{\text{obs}} - P_{\text{calc}}]/N$.

^eAverage Deviation of relative Total Vapor Pressure, %: $\Sigma\{[P_{\text{obs}} - P_{\text{calc}}]/P_{\text{obs}}\}/N$.

^fOutliers: not used in Dif S or Sum S fitting.

provide a succinct measure of the range within which 50% (or 63%) of the values will fall with respect to the mean, they may mask significant details of individual datum. We illustrate this in the comparison of results section.

Because the total range of the mole fraction, $0 \leq Y_i \leq 1$, is small (*i.e.* essentially over one order of magnitude) absolute values of the error limits for the vapor mole fraction are comparable over all sets and is shown in Table 1 to be on the order of 1 mole per cent. Total vapor pressure, on the other hand, spans three orders of magnitude, and relative error limits are more applicable. The absolute and relative average deviations of the total vapor pressure are given in Table 1. While absolute errors range over three orders of magnitude, relative errors only vary by a factor of 10 in the range of 2 to 20%.

3. EVALUATION OF RESULTS

In examining these results for the interdependence of W_{12} and W_{21} , a distinctive temperature dependence becomes obvious. In a plot of the "best" (minimized) values of W_{12} versus W_{21} , there is a clear hyperbolic dependence of the distribution of the W_{ij} pairs over the entire liquid water range 0 to 100 °C according to the temperatures of the isotherms. Assuming a simple hyperbolic function of $W_{12}W_{21} = f(T)$ and substituting equation 1 for both coefficients, the pure molar volume terms cancel and one obtains:

$$W_{12} W_{21} = \exp [(\lambda_{11} + \lambda_{22} - 2\lambda_{12}) / RT] \quad (5a)$$

Tassios¹⁵ identified λ_{ij} with the negative molal energy of vaporization at P and T of the pure component i and as such is related to Hildebrand's solubility parameter¹⁶

$$\delta_i = (\Delta U_i^{\text{vap}}/v_i)^{1/2}$$

The relationship of λ_{ij} to the heat of vaporization assumes ideal vapor with $\Delta(PV) = RT$ per mole:

$$\lambda_{ij} = -\Delta U_{ij}^{\text{vap}} = -(\Delta H_{ij}^{\text{vap}} - RT)$$

Orye and Prausnitz¹⁰ noted the relative temperature independence of $(\lambda_{ij} - \lambda_{ji})$ which really only asserts that the two terms closely follow the same temperature dependence. We can further factor out the temperature of the individual terms if the terms $\Delta H_{ij}/T$ are identified with the molar entropies of vaporization, ΔS_i for the pure components, and $\Delta S_{12} = \Delta S_{21}$ for the solution, then

$$W_{12} W_{21} = \exp - [(\Delta S_1^{\text{vap}} + \Delta S_2^{\text{vap}} - 2\Delta S_{12}^{\text{vap}})/R] \quad (5b)$$

As the product of coefficients corresponds to a sum of terms in the exponential, so the ratio of coefficients yields a difference in the entropies of the pure components with the elimination of the solution entropy term but the retention of the squared pure molar volume ratio:

$$W_{12} / W_{21} = (v_2^L/v_1^L)^2 \exp - [(\Delta S_1^{\text{vap}} - \Delta S_2^{\text{vap}})/R] \quad (6)$$

Because the right side of equation 6 is not dependent on the solution properties, it implies an independent correlation between the two coefficients. To simplify the subsequent analysis, the exponential quantities normalized to the gas constant R (quantities in brackets) in equations 5b and 6 will be referred to as Sum S and Dif S respectively.

The temperature dependence of both Sum S and Dif S were determined by linear least squares analysis of $\ln(W_{12} W_{21})$ versus T(K) and $\ln(W_{12} / W_{21})$ versus T(K) respectively. Both linear ($a + bT$) and parabolic ($a + bT + cT^2$) fits were tested using the Fisher F test criterion for the significance in the reduction of the variance. Although the linear fit of Dif S failed at the 99% confidence level and the parabolic fit failed at the 95% level, both forms have been employed in the subsequent treatment as described below. Figure 2 shows the W_{12} versus W_{21} plot with isotherms computed at 10 °C intervals over the normal liquid water range using the parabolic (three parameter) Sum S fit. The "best" pairs for 26 of the data sets used in the analysis are plotted and show a distinctive temperature correlation. "Tie lines" corresponding to constant values of Dif S (in units of R) are shown extending over the temperature range from the normal boiling point of ammonia (-33 °C) to approximately +130 °C where all these curves converge. The very small range for the values of Dif S between +0.5R and +1.5R clearly illustrates the sensitivity of this function to the experimental measurements. The empirical equations obtained for 25 of the 27 data sets are:

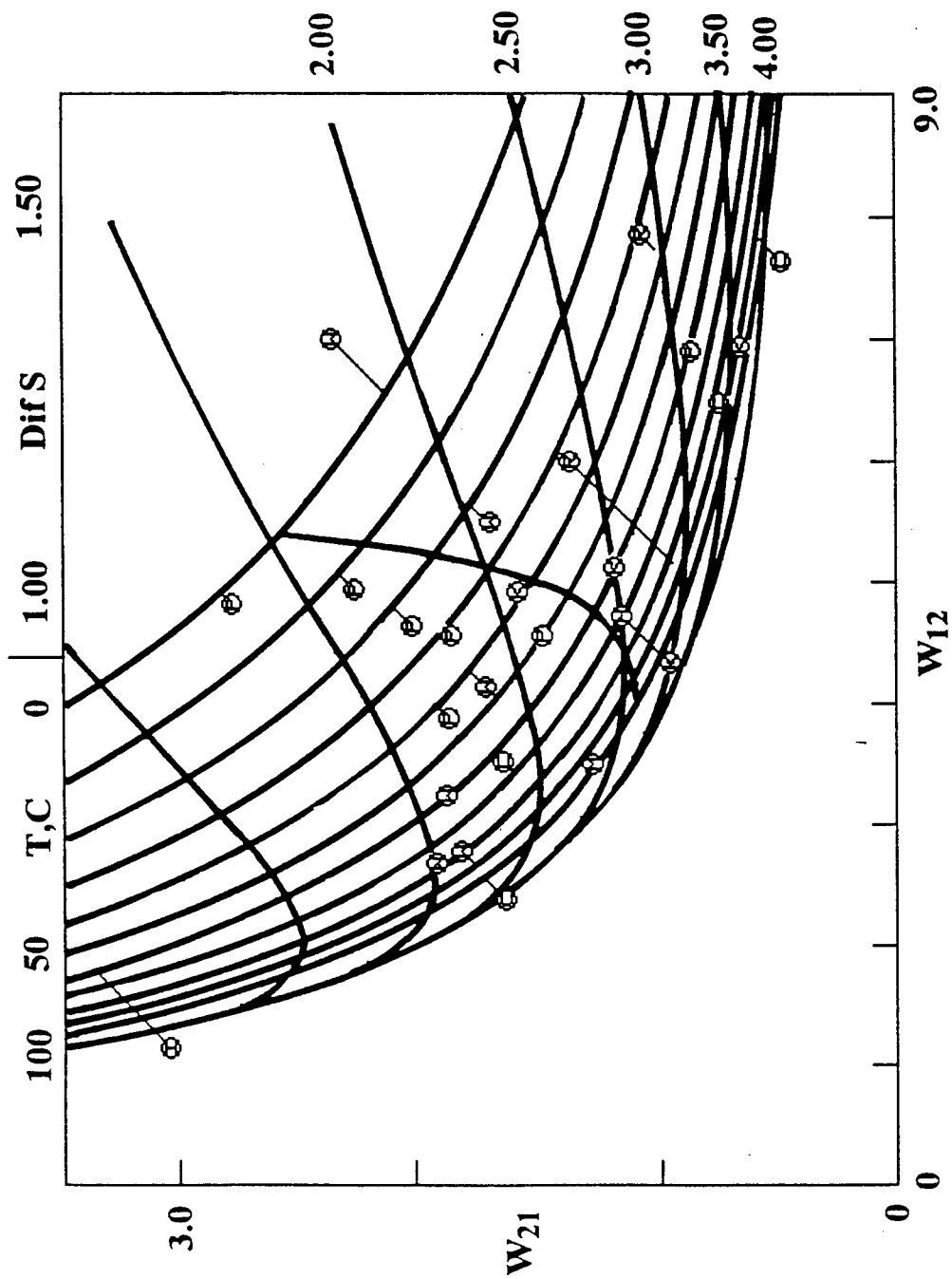


Figure 2. Distribution of Primary (experimental PTXY) isothermal data sets' W_{ij}

pairs relative to the Sum S computed temperature curves, curves of constant Dif S values, and the combined entropy functions predicted temperature dependence: 45° links correlate data to appropriate isotherm. Key [ref.]: C[3], H[8], I[5], K[7], M[6], P[1], R[4], W [2].

$$\begin{aligned}
& \text{Sum } S = (+5.52 \pm 0.28) - (0.01098 \pm 0.00085) T, & (7a) \\
\text{or} & = 11.82 - 0.0500 T + 0.597E-4 T^2 ; & (7b) \\
\text{and} & \text{Dif } S = (-1.17 \pm 1.34) + (0.0104 \pm 0.0040) T, & (8a) \\
\text{or} & = -9.47 + 0.0617 T - 0.785E-4 T^2 ; & (8b)
\end{aligned}$$

where the uncertainties listed for the linear forms are the standard errors.

Tabulated values of the thermodynamic properties (including entropies) of the saturated liquid and vapor phases of both pure components and their solutions at 0.1 intervals in mole fraction and at 10 degree temperature intervals from well below the normal boiling point of ammonia to well above that of water were published by Scatchard and co-workers¹⁷ using graphical interpolation methods over 50 years ago and more recently by Tillner-Roth and Friend¹⁸ employing computer optimization techniques. Although the solution behavior of these two sources differs significantly, the values for the pure components differ negligibly. Pure molar entropies of vaporization, $\Delta S_{i\text{vap}} = (S_{i\text{vapor}} - S_{i\text{liquid}})$, calculated from these tables are included in Table 2. The corresponding difference and sum of the pure molar entropies of vaporization are identified as Dif S (taken ammonia – water) and Sum*S in the column headings. Note that Sum*S differs from the Wilson equation Sum S by the solution term, $2\Delta S_{12\text{vap}}$, given in equation. 5b. Also included in Table 2 are the molar volume ratios. These were obtained from empirical equations as function of (Celsius) temperature for the pure molar *saturated* liquid volumes (m^3/kmol) for ammonia¹⁹ and water²⁰ as given in Table 3. Table 3 also includes empirical expression for the temperature dependence of the pure vapor pressures (kPa) for ammonia²¹ and water.²² The subsequent parabolic expressions for the pure molar entropies of vaporization as a function of (Kelvin) temperature are so highly correlated one is inclined to suspect the tables were generated from analytical expressions of the same form. The Fisher F test for Dif S for 8 degrees of freedom was 2450 while that for Sum S was 194 compared to values at the 99% (95%) confidence interval of 11 (5.3), both well in excess of the higher level. These expressions are:

Table 2. Temperature Dependence of Pure Component Entropy Functions

T °C	V _{H2O} /V _{NH3}	ΔS _{H2O} ^{vap} /R	ΔS _{NH3} ^{vap} /R	Dif S	Sum*S
0	0.6764	19.84	9.46	-10.38	29.30
10	0.6615	18.96	8.87	-10.09	27.83
20	0.6471	18.14	8.29	- 9.85	26.43
30	0.6326	17.37	7.73	- 9.64	25.10
40	0.6183	16.65	7.19	- 9.46	23.84
50	0.6038	15.98	6.66	- 9.32	22.64
60	0.5890	15.34	6.13	- 9.21	21.47
70	0.5733	14.74	5.60	- 9.14	20.34
80	0.5564	14.17	5.07	- 9.10	19.24
90	0.5375	13.62	4.52	- 9.10	18.14
100	0.5153	13.11	3.93	- 9.18	17.04

**Table 3. Empirical Temperature Dependence of Pure Liquids
Vapor Pressure (kPa) and Molar Volume (liters/mole)**

NH ₃ :	$P^0_1 = (101.325 / 760) \exp [(\ln(10))(7.74396 - (1113.928 / (t+262.741)))]$ $V^L_1 = 0.01703 (4.283 + 0.813055 (133 - t)^{1/2} - (8.2861E-3)(133 - t) / (1 + 0.424805 (133 - t)^{1/2} + (1.5938E-2)(133 - t))$
H ₂ O:	$P^0_2 = 100 * \exp [6.357118 - 8858.842 / T + 607.5633 T^{-0.6}]$ $V^L_2 = 18.02 / (999.83952 + 16.945176 t - (7.9870401E-3)t^2 - (46.170461E-6)t^3 + (105.56302E-9)t^4 - (280.54253E-12)t^5) / (1 + (16.897850E-3)t)$

Note: T represents degrees Kelvin, while t represents degrees Celsius.

$$\text{Sum}^*\text{S} = (+62.06 \pm 0.67) - (0.1214 \pm 0.0020) T, \text{ or} \quad (9a)$$

$$= 84.30 - 0.2604 T + 2.152E-4 T^2 ; \quad (9b)$$

$$\text{and} \quad \text{Dif S} = (-13.45 \pm 0.55) + (0.0122 \pm 0.0017) T, \text{ or} \quad (10a)$$

$$= -32.38 + 0.1306 T - 1.832E-4 T^2 . \quad (10b)$$

It was because of this high degree of correlation that the parabolic expressions for the empirical Dif S and Sum S in equations 7b and 8b were adopted in spite of a lower than 95% correlation.

The difference equations for Sum S (*i.e.* equation 9 – equation 7) and for Dif S (*i.e.* equation 10 – equation 8) evaluated at 25 °C intervals between 0 and 100 °C, are listed in Table 4. For this comparison, because the curves of the literature values are so highly correlated and more temperature sensitive, they provide a better insight into the nature of the differences. The linear differences have been included to illustrate that they do not exhibit any noteworthy differences from the curves. The difference in the Sum S curves:

$$\Delta \text{SumS} = \text{Sum}^*\text{S} - \text{SumS} = 2\Delta S_{12} / R$$

equals twice the entropy of vaporization from the saturated solution, ΔS_{12} . It can be seen to be strongly temperature dependent: decreasing by 40% over the normal liquid water range and exceeding the mean of the pure components by about R. The value of ΔS_{12} thus determined seems reasonable.

The difference in the Dif S curves is much more intriguing. The determination of the difference in the entropies of vaporization of ammonia and water can be obtained:

$$\text{Dif S} = [\Delta S_{\text{NH}_3(T)^{\text{vap}}} - \Delta S_{\text{H}_2\text{O}(T)^{\text{vap}}}] / R$$

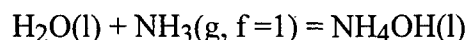
from literature values, Dif S(lit), or empirically, Dif S(emp), from the ratio of Wilson coefficients, $W_{12}/W_{21} = \exp(-\text{Dif S})$ where in both cases the temperature dependence is observed to obey a simple parabolic relation:

$$\text{Dif S} = a + b T + c T^2$$

Table 4. Differences between Literature and Experimental Entropy Functions

T °C	$\Delta \text{DifS}(\text{curve})$	$\Delta \text{DifS}(\text{line})$	$\Delta \text{SumS}(\text{curve})$	$\Delta \text{SumS}(\text{line})$
0	-11.90	-11.78	26.61	26.38
25	-11.68	-11.73	23.57	23.62
50	-11.58	-11.69	20.73	20.86
75	-11.61	-11.64	18.08	18.10
100	-11.78	-11.60	15.62	15.34

Although one might expect that these quantities would be equal, it has been found that there is an essentially temperature independent constant difference equal to $-11.69R$. The origin of this difference may be attributed to a difference in the reference state such that the thermodynamic process includes a step for the actual solution process that is not included in the theoretical calculation. For example, in a detailed analysis of the thermodynamics of ammonia, water and ammonium hydroxide, Hildenbrand and Giauque²³ report the entropy of the (hypothetical) reaction:



at 0 °C as $-12.09R$ and at 25 °C as $-11.67R$. It may be fortuitous, but the entropy of this reaction at 25 °C is equal to the difference found in the Dif S terms and also has a correspondingly small temperature coefficient. The difference attributed to this step:

$$\text{Dif S (lit)} - \text{Dif S (emp)} = \Delta S_{\text{rNH}_4\text{OH}} / R$$

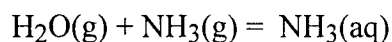
thus

$$\text{Dif S (emp)} = [\Delta S_{\text{NH}_3}^{\text{vap}} - \Delta S_{\text{H}_2\text{O}}^{\text{vap}} - \Delta S_{\text{rNH}_4\text{OH}}] / R$$

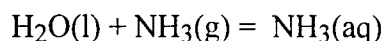
would be explained by the formation of a chemical compound (ammonium hydroxide) in solution, a step clearly not considered in the Wilson theory of interaction.

Alternatively, the magnitude of this difference is very close to the Trouton's Rule value for the molar entropy of vaporization: $10.9R$, corresponding to the entropy of volume expansion of a mole of ideal gas, but of opposite sign. The Wilson theory is concerned with the energy of interaction brought about by bringing the interacting

molecules within range from a zero energy state corresponding to the attenuated gases and represented by the reaction:



Over the normal temperature range of liquid water, the actual solution process would be:



The difference in entropy of these two processes is obviously the entropy of condensation of water:

$$\begin{aligned}\Delta S_p/R &= \text{Dif } S(\text{lit}) - \text{Dif } S(\text{emp}) \\ &= [(S_{\text{NH}_3^{\text{aq}}} - S_{\text{H}_2\text{O}^{\text{g}}} - S_{\text{NH}_3^{\text{g}}}) - (S_{\text{NH}_3^{\text{aq}}} - S_{\text{H}_2\text{O}^{\text{l}}} - S_{\text{NH}_3^{\text{g}}})]/R \\ &= [S_{\text{H}_2\text{O}^{\text{l}}} - S_{\text{H}_2\text{O}^{\text{g}}}] / R = -\Delta S_{\text{H}_2\text{O}^{\text{vap}}} / R\end{aligned}$$

Unfortunately, although the second interpretation might be more chemically satisfying, the numerical magnitude of the entropy of vaporization of water listed in Table 2 over the normal liquid temperature range varies from 20R to 13R compared to the observed difference of 12R. The upper limit at the normal boiling point compares favorably (for water) with both Trouton's Rule and ΔS_p . It is also equal to the low temperature end of the range of ΔS_{12} (given in Table 4 as $\Delta \text{Sum } S = 2 \Delta S_{12} / R$) which varies from 13R to 8R. Until other strongly interacting systems can be similarly examined, further analysis is hardly warranted.

4. COMPARISON OF RESULTS

There are four classes of data to be analyzed with the temperature dependent Wilson coefficients: (1) primary data: the unsmoothed PTXY sets used to evaluate the temperature dependence of the coefficients; (2) refined data: PTXY sets reported from smoothed experimental data; (3) secondary data: PTXY data of sets having three or fewer isothermal points or whose mole fractions had to be calculated from concentration units that require solution density assumptions; and (4) partial data: underdetermined results which reported only the Partial (*N.B.* not Total) vapor pressure of ammonia and the liquid state concentration.

Representation of individual measurements in each of the data sets is best made with isothermal curves taking the liquid mole fraction as the independent variable plotted against either the vapor mole fraction or the vapor pressure. As can be seen in Table 1 there is no apparent correlation of the goodness of fit between these two dependent variables. Because of the large deviation from ideality (ammonia's high vapor pressure over the liquid water temperature range), the vapor concentration of ammonia, Y_1 , rises rapidly with increasing liquid mole fraction and exceeds 90 mole % at X_1 around 30%. Because the vapor pressure of water rises exponentially over its liquid range, the higher temperature isotherms increase more slowly. Figure 3 incorporates 173 of the primary data in this range (excluding Wilson's and Rizvi's data to be discussed below.) The radius of the plotted circles in this graph corresponds to ± 1.5 mole % in Y_1 . The letter in each plotted circle (unless otherwise noted) is the initial of the surname of the primary author of the reference. In almost all cases the points lie on their respective isotherms. Notable exceptions are Harms (encircled H) 100 °C at $X_1 = 0.10$ and Innomata (encircled I) and Clifford (encircled C) both 60 °C and $X_1 = 0.20$. All three are anomalous in Y_1 although not in P_T . Perman (encircled P) 0 °C at $X_1 = 0.05$ deviates slightly in Y_1 as well as in P_T . For Kurz's data (encircled K), several measurements at each temperature were at fixed X_1 with scatter in the measured Y_1 . The vertical center of each cluster appears to lie within the same error limit on each isotherm as the data from the other sets. This vertical scatter is not observed in the vapor pressure.

There are a total of 285 individual primary measurements, 262 are presented in a $\log_{10} P_T$ versus X_1 plot in Figure 4. Nine of the remainder lie above the upper limit of $X_1 = 0.75$ and fourteen lie above the upper limit of $\log_{10} P_T > 4$. The radius of the circles correspond to a relative error of $\pm 6\%$ parallel to the ordinate. All points which do not lie within a radius of their isotherm are connected by vertical lines. The three isotherms of Rizvi (encircled R) are at 32.4, 68.8 and 86.5 °C and are not anchored since the isothermal curves are at 10 °C multiples. Of the eight studies of 27 isothermal sets examined, three covering ten isotherms differ significantly from the computed isothermal curves based on the temperature dependent Wilson coefficients. These are Wilson (encircled W), Rizvi (encircled R), and Innomata (encircled I). As noted in Table 1, two of these sets, Rizvi at 86 °C and Innomata at 60 °C, had "best" Wilson coefficients which were so far removed from the others that they were rejected as outliers in the least square

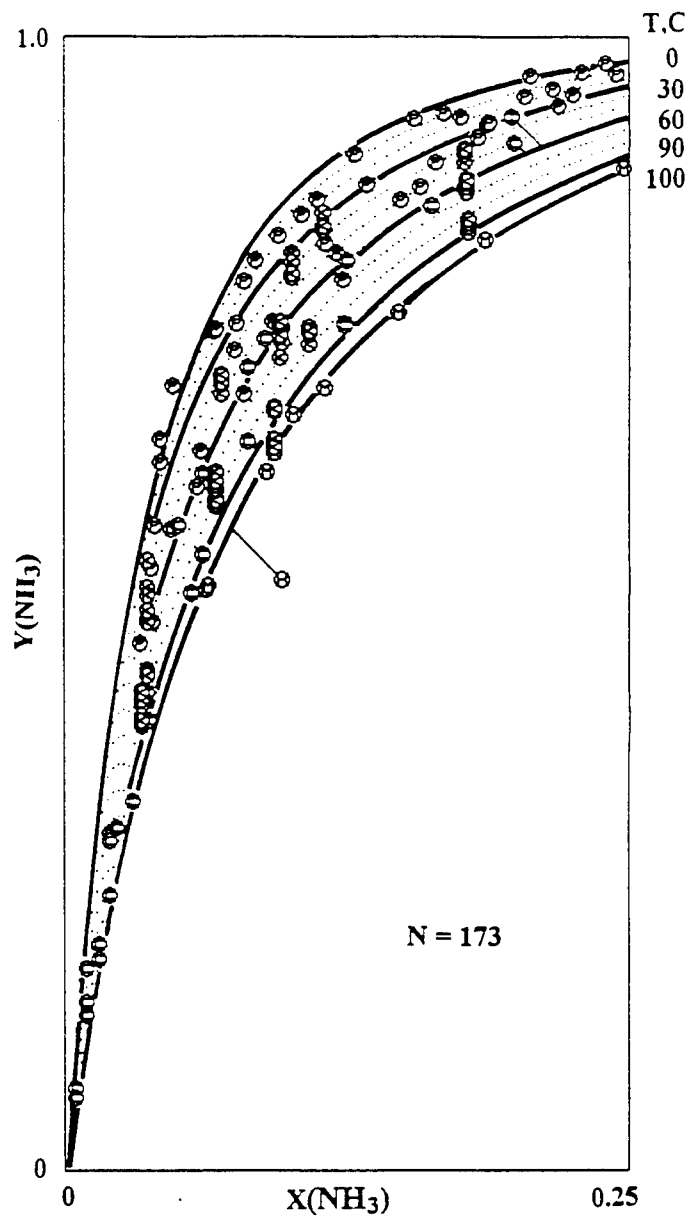


Figure 3. Distribution of all individual Primary isothermal vapor compositions as a function of corresponding liquid composition relative to the predicted isothermal curves in 10 °C intervals: three 45° links correlate data whose deviations exceed radii to appropriate isotherm. Key [ref.]: C[3], H[8], I[5], K[7], M[6], P[1], R[4], W[2].

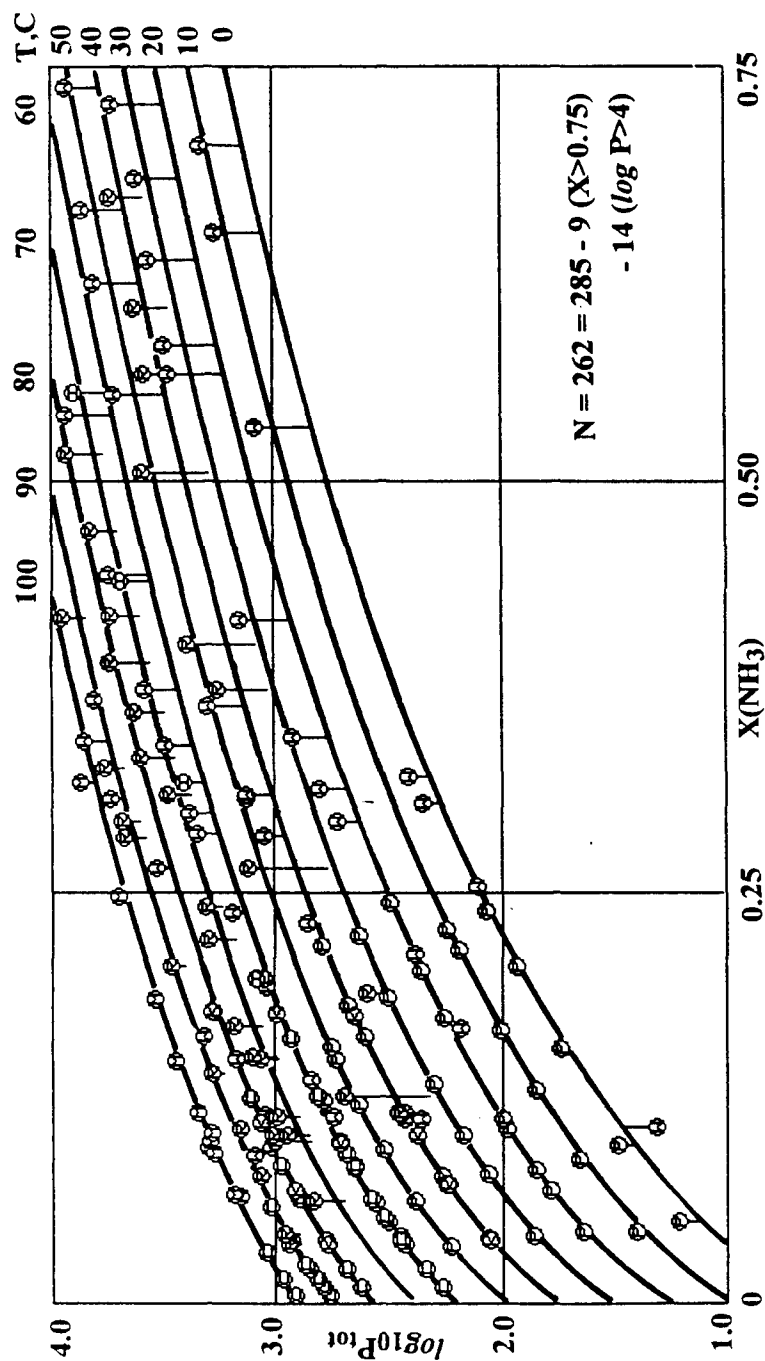


Figure 4. Distribution of all individual Primary isothermal total pressure ($\log[P(\text{Pa})]-2.1249$) as a function of corresponding liquid composition relative to the predicted isothermal curves in 10 Celsius degree intervals: vertical links correlate data to appropriate isotherm. Key [ref.]: C [3], H [8], I [5], K [7], M [6], P [1], R [4], W [2].

temperature dependence evaluations. It can be seen in the figure that these also comprise all of the points at $X_1 > 0.3$ for which we have seen in Figure 3 that $Y_1 > 0.9$. Rizvi's deviations being just as large (and positive) below $X_1 = 0.3$ would indicate a systematic deviation that is independent of concentration whereas Wilson's deviations tend to become increasingly negative as both temperature and concentration decrease. It remains to be seen whether these data have significantly biased the Wilson coefficient predictions at large X_1 .

We have avoided incorporating refined data in the analysis of the temperature dependence of the Wilson coefficients because of an anomaly noted in the distribution of the "best" coefficients of such sets. There are five sources of smoothed data. In addition to tabulating his raw data, Wilson² provided tables at 32 °F and from 40 °F to well above the normal boiling point at 10 °F (11.1 °C) temperature intervals and concentration intervals of 5 mole % from 0 to 100% in pressures of precision 0.01 psi. Wucherer²⁴ provided only tables of smoothed data from which we replotted isobars of X_1 at P of 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 atm. and Y_1 at 0.2, 0.3, 0.4, and 0.5 and interpolated isothermal sets ($N=6$) at 10 °C intervals from 10 to 60 °C. Tillner-Roth and Friend¹⁸ also evaluated and made corrections to Wucherer's data. Macriss and co-workers²⁵ published PTXY tables that were smoothed by relying on Wilson's and Wucherer's tables for consistency. Their 60 °C data is included for later reference to published Wilson coefficients. The fourth source was Gillespie *et al.*²⁶ who listed both measured and smoothed pressure isotherms at three temperatures below the normal boiling point of water. These sets of W_{12} and W_{21} are shown plotted in Figure 5 on the same computed curves as Figure 2. The Wilson data clearly appears to parallel the curves of constant $\text{Dif } S$ as those of Gillespie (encircled G) might also be construed, but both sets of Wucherer's values (replotted as encircled R and corrected as encircled C) appear to run perpendicularly to the $\text{Dif } S$ curves. The $\log P_T - X_1$ graph of the Wilson data is even more illuminating as shown in Figure 6. The isotherms at 0, 10, 21, 32, 43, 54, and 60 °C show the same increasing positive deviation with increasing X_1 above 30 mole % and reasonable agreement below that value. The difference is, that unlike Wilson's primary data, they do not negatively deviate in the more dilute concentrations. In fact the smoothing appears to be practically linear in the log plot as though the original smoothing followed an exponential curvature. The two sources of Wucherer's refined data are presented in

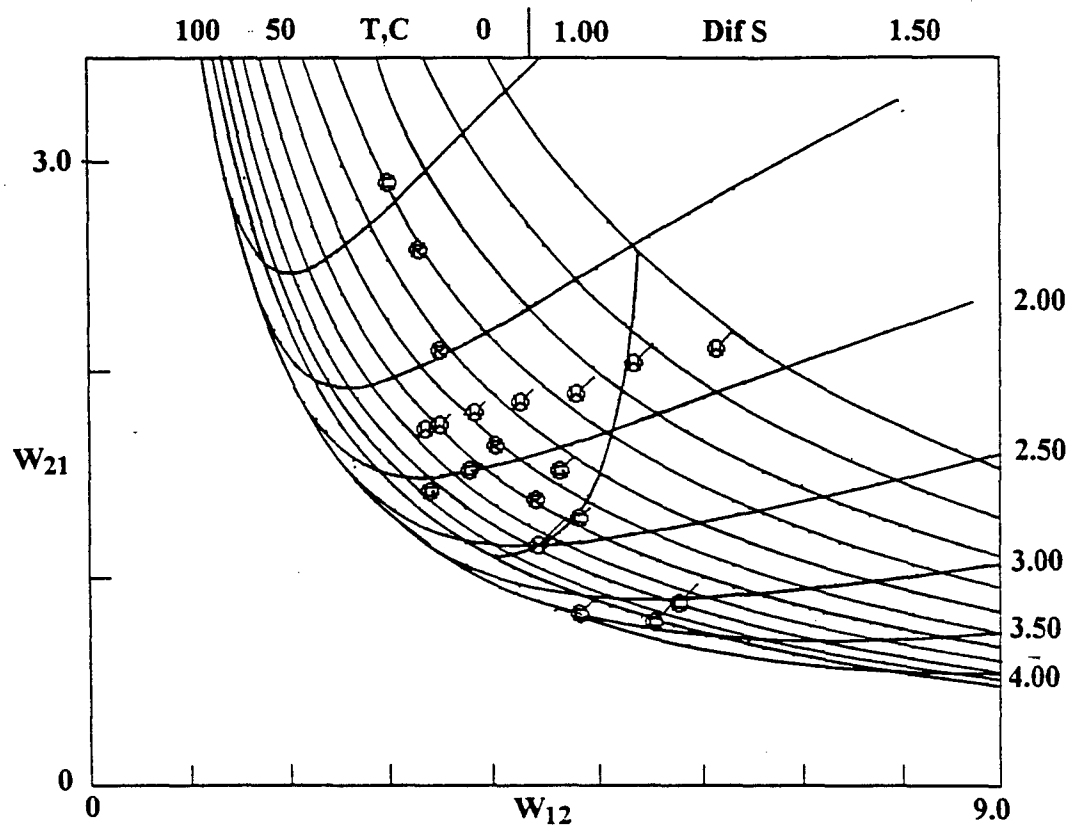


Figure 5. Distribution of Refined (smoothed PTXY) isothermal data sets' W_{ij} pairs relative to the Sum S computed temperature curves, curves of constant Dif S values and the combined entropy functions predicted temperature dependence: 45° links correlate datum to appropriate isotherm. Key [ref.]: C[18], G[26], M[25], R[24], W[2].

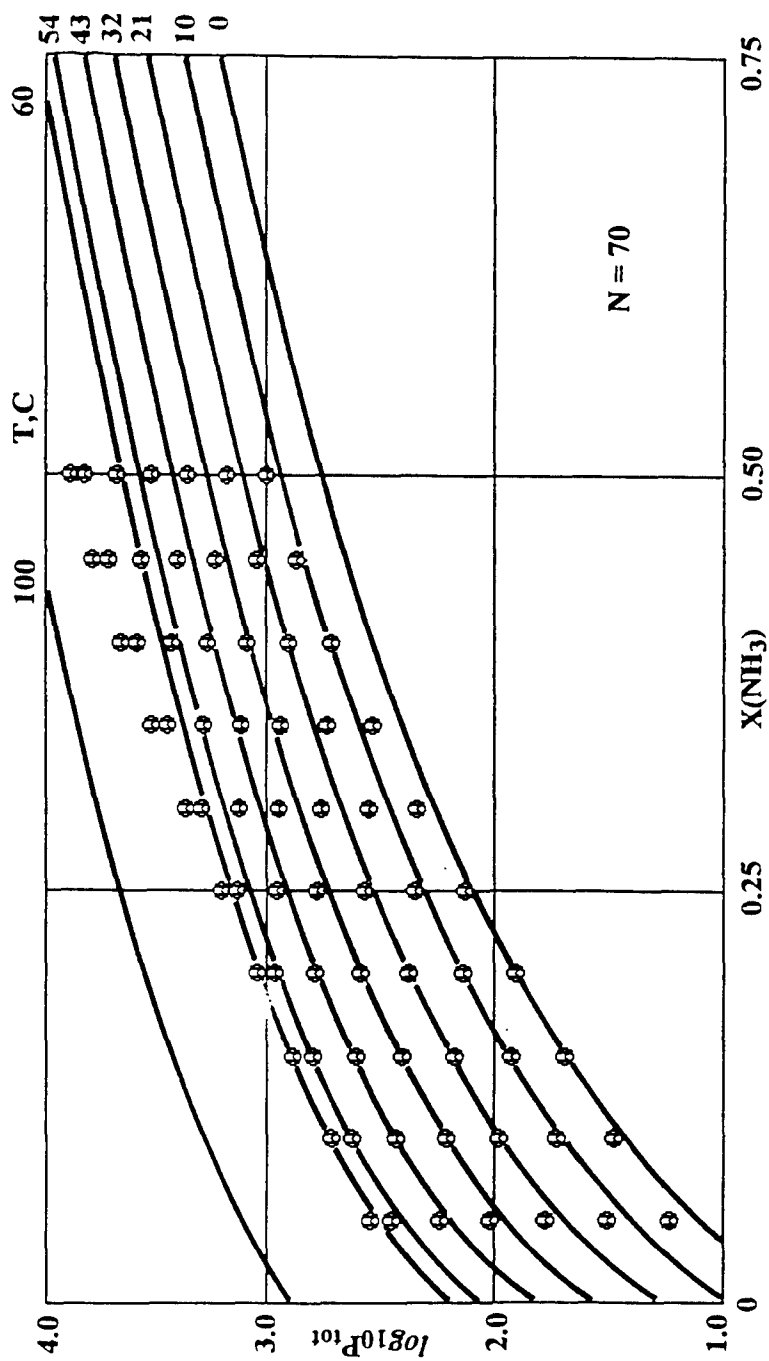


Figure 6. Distribution of all Wilson's Refined (smoothed PTXY) isothermal total pressures ($\log[P(\text{Pa})]-2.1249$) as a function of corresponding liquid composition relative to the predicted isothermal curves. Key [ref.]: W [2].

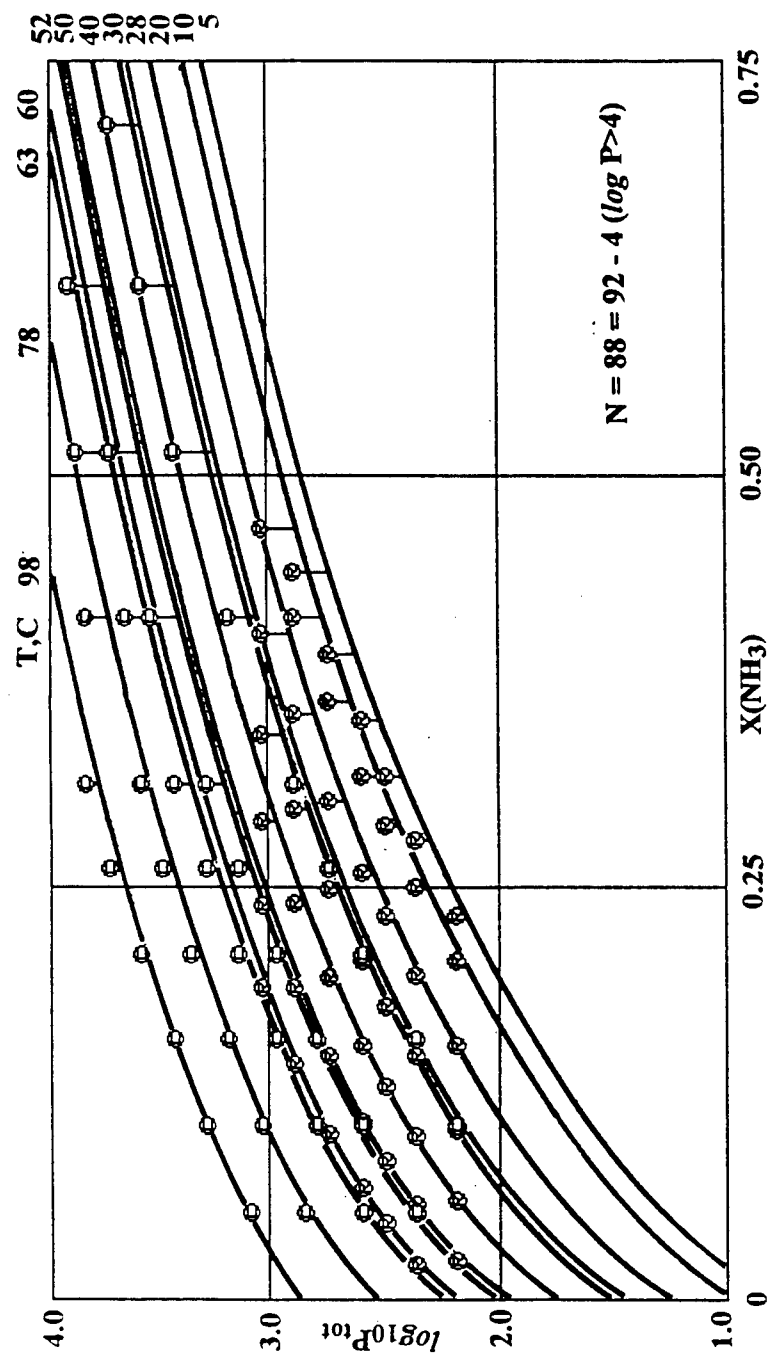


Figure 7. Distribution of all Wucherer's Refined (smoothed PTXY) isothermal total pressures ($\log[P(Pa)]-2.1249$) as a function of corresponding liquid composition relative to the predicted isothermal curves: vertical links correlate data to appropriate isotherm. Key [ref.]: C[18], R[2].

$\log P_T - X_1$ isotherms in Figure 7. The effect of the correction by Tillner-Roth and Friend (encircled C) can be compared where their values overlap with the other (encircled R). There is again increasing positive deviations with increasing concentration, although they would appear to be in quite good agreement below $X_1=0.25$ with the "corrected" values generally giving a slight improved agreement with the computed isotherms.

The third class of published VLE data is presented in Figure 8. These 80 data include three isotherms each of Gillespie *et al*²⁶, Neuhausen and Patrick²⁷, four isotherms of one to three points each of Harms-Watzenberg that were too small to search for "best" coefficients, and two isobars at 1 atm. pressure of Polak and Lu²⁸ and Sako²⁹. As all of Neuhausen's concentrations but two have $X_1 > 0.3$ we again observe that these are the concentrations in which $Y_1 > 0.9$ and are underestimated by the Wilson temperature dependence. On the other hand, most of those at the lower mole fractions lie well within the 6% error limit. Sako's concentrations all lie below $X_1=0.03$ and are essentially isothermal at 99 °C; Polak's concentrations range sufficiently to cover temperatures between 90 °C ($X_1=0.02$) and 99 °C. Both data sets lie well within the precision limits shown.

The final class consists of isotherms at 0, 10, 18, 25 and 35 °C with concentrations given in molarity and partial pressures of ammonia only. They include the four isotherms of Morgan and Maas³⁰, nine points at four temperatures of Hougén³¹, and a 25 °C isotherm at $X_1 < 0.03$ of Scheffer and DeWijs³² shown in Figure 9. In addition to their molarity values, Morgan and Maas included solution densities permitting conversion to mole fraction. Solution densities for the molarities of Macriss and of Scheffer and DeWijs were taken from the empirical equations given by Sohnel and Novotny³³: $\rho(t) = \rho_1(t) + M(-6.880 - 0.011989 t + 9.711e-5 t^2) + M^{3/2}(0.01843 - 4.392e-3 t - 1.126e-6 t^2)$, where $\rho_1(t) = 999.65 + 0.20438 t - 0.061744 t^{3/2}$ is the density of pure water (kg/m³). It should be noted that the pressure scale is lower by an order of magnitude from the previous figures and all isotherms approach the ordinate asymptotically rather than equaling the vapor pressure of pure water as the ammonia concentration decreases to zero. Positive deviations are noted to exceed the error limit at $X_1 > 0.3$ in this case also. Excellent agreement with the data of Scheffer and DeWijs (encircled I) in the most dilute regime at partial pressures below 10 torr and at 25 °C are shown in the Inset of Figure 9. The data of Morgan and Maas (encircled M) below 25 °C at $X_1 < 0.1$ show more positive deviations from the curves.

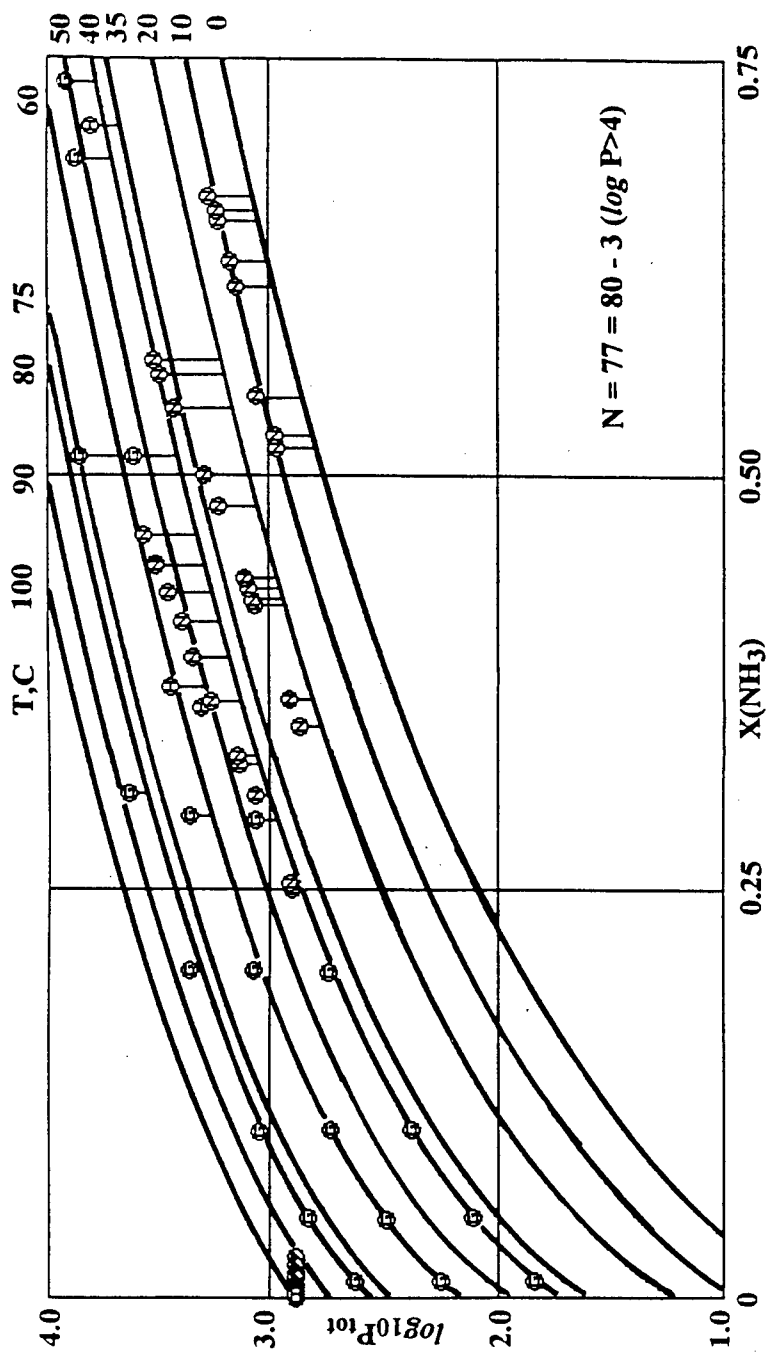


Figure 8. Distribution of all Secondary isothermal total pressures ($\log[P(\text{Pa})]$)-2.1249) as a function of corresponding liquid composition relative to the predicted isothermal curves: vertical links correlate data to appropriate isotherm. Key [ref.]: G[26], H[8], I[29], N[27], P[28].

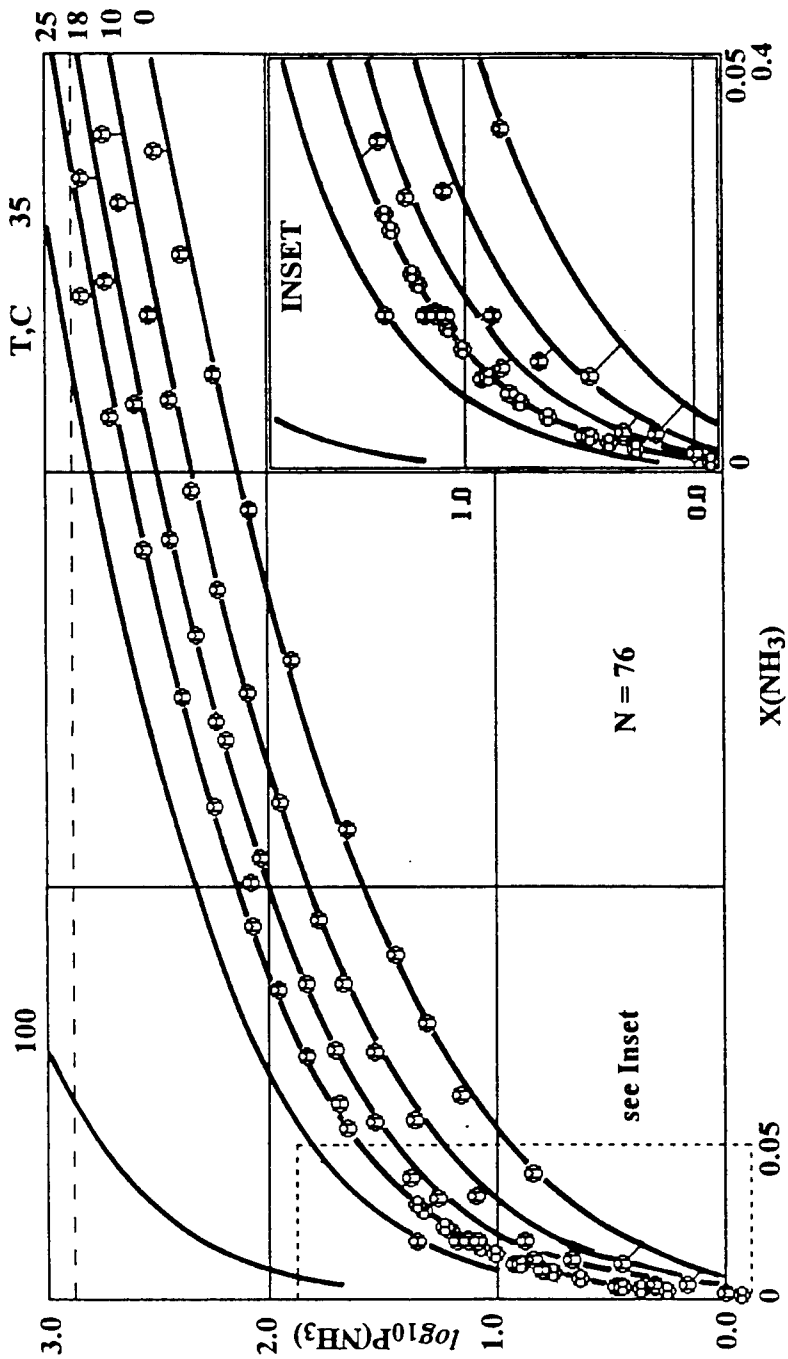


Figure 9. Distribution of all Partial isothermal ammonia vapor pressures ($\log[P(\text{Pa})]-2.1249$) as a function of corresponding liquid composition relative to the predicted isothermal curves: 45° links correlate data to appropriate isotherm. Key [ref.]: H[31], I[32], M[30].

5. REPORTED WILSON COEFFICIENTS

Only three determinations have been reported. Each was at a different temperature of 0, 60 or 100 °C. An evaluation of errors and comparison to our results is presented in Table 5. Hirata *et al.*¹¹ (*op. cit.* p. 799) evaluated a 0 °C isotherm of Wilson's smoothed data using the same objective function (SQ) used in this report and given by equation 4a. These authors also noted that an alternate means from the least squares equations of finding the minimum had to be employed, although their specific method is not detailed. In this case, as in all three cases, the least mean SQ is obtained by the grid search. The grid search result also yields the best fit in terms of the vapor mole fraction, however the best fit in terms of saturation pressure is obtained by Hirata's coefficients by a margin of 5% less than a relative error of 21% for the other two methods.

Table 5. Literature Wilson Coefficient Comparison

Ref.	T, °C ^a	W ₁₂	W ₂₁	SQ/N ^b	BESE(Y _A)	ad(Y _A) ^c	ad(P _T), kPa ^d	%ad(P _T) ^e
Hirata	0.0	6.13	2.12	5.105e-3	0.0137	0.0062	14.9	20.5
		2.907	3.415	6.800e-2	0.0314	0.0148	6.1	16.1
		5.40	2.57	1.061e-2	0.0291	0.0114	14.1	21.2
Edwards	60.0	4.43	1.17	2.120e-2	0.0109	0.0051	173	15.5
		6.23	0.52	2.528e-2	0.0223	0.0099	220	21.4
		4.73	1.28	2.356e-2	0.0031	0.0025	200	17.5
Sako	100.0	4.26	1.86	4.624e-4	0.0067	0.0047	0.57	0.56
		2.279	1.320	1.144e-3	0.0053	0.0038	0.48	0.47
		3.95	1.13	0.945e-3	0.0033	0.0002	0.25	0.24

NOTES:

^aThe W_{ij}'s for each isotherm are given in the following order. First entry: based on minimized residual sum of squares (SQ) of excess free energy of individual isotherm. Second entry: literature cited coefficients. Third entry: Dif S and Sum S entropy functions fitted to parabolic temperature dependence (a+bT+cT²).

^{b-c} See Table 1.

In the remaining two cases, the best fit in vapor composition is obtained from the entropy functions. The best fit in saturation pressure for these two cases is either the grid search (at 60 °C) or the entropy functions (100 °C). The Wilson coefficients at 60 °C were evaluated by Edwards *et al.* ³⁴ based on the smoothed data given by Macriss and co-workers.²⁵ Numeric values were not provided except as a plotted function of the unsymmetric (Henry's Law) activity coefficient of ammonia versus the liquid mole fraction. The values given in Table 5 were obtained by interpolating the curve in comparison to the published data of Macriss and solution of two equations cited by Edwards in relation to the initial slope ($X_1=0$) and final intercept ($X_1=1$) of their Figure 2. The Wilson coefficients evaluated at 100 °C by Sako *et al.* ²⁹ were based on the 100 °C data of Clifford and Hunter.³ Although they do not specify their method of evaluation, their values (2.28, 1.32) are close to those that we obtained (2.37,1.64) by the grid search for the same data set. Their data is isobaric, however their concentration range was so small that it was effectively isothermal as well. The comparison in Table 5 is to their data not that of Clifford and Hunter. The coefficients obtained from the entropy functions yields better results in both Y and P than either of the others.

6. CONCLUSIONS

The extension of Wilson's model for non-ideal solution behavior for aqueous ammonia treats the interaction in terms of the temperature dependence of the partial molal entropies of solution and the molar entropies of the pure components. It provides excellent agreement in the solution concentration region where the vapor composition is changing rapidly ($0 < Y_1 \leq 0.9$) over the entire normal liquid water temperature range. With selection of a temperature (K), computation of the Wilson coefficients for that temperature requires first calculating the pure molar volumes (and vapor pressures) using empirical equations such as those given in Table 3. Secondly, the Sum S and Dif S functions are evaluated, equations 7b and 8b respectively. If the constants obtained are A and B, as

$$\begin{aligned} W_{12} * W_{21} &= \exp - [\text{Sum S}] = A \\ &= \exp [-(11.82 - 0.0500 T + 0.597E-4 T^2)], \end{aligned}$$

$$\begin{aligned} \text{and} \quad W_{12}/W_{21} &= (v_2^L/v_1^L)^2 \exp -[\text{Dif } S] = B \\ &= (v_2^L/v_1^L)^2 \exp [-(-9.47 + 0.0617 T - 0.785E-4 T^2)] ; \end{aligned}$$

$$\text{then} \quad W_{12} = [A*B]^{1/2}$$

$$\text{and} \quad W_{21} = [A/B]^{1/2}.$$

Once the Wilson coefficients are obtained for a given temperature, then for any liquid composition, X_1 ($X_2=1-X_1$), the activity coefficients of each component may be evaluated using equation 3. Finally, using the previously evaluated pure vapor pressures, the vapor composition can be determined from $P_i = \gamma_i X_i P_i^0$ and $Y_1 = P_1/P_T$ where $P_T = P_1 + P_2$.

Corresponding to an application of the central limit theorem, this study incorporated all primary experimental measurements uncovered in the literature in an effort to obtain the most evenly biased representation. All other data were compared to these results. It has been found that the analysis leads to very good agreement below $Y_1=0.9$ for all cited studies except Wilson's and Rizvi's. Although, as has been noted above, Wilson's results have been utilized by some, it has also been criticized by others including Guillevic *et al.*³⁵ and Tillner-Roth and Friend¹⁸ (who also are critical of Rizvi's data). Rizvi and Heidemann⁴ also discuss the criticism of Wilson's data. We are inclined to agree with that criticism. It is difficult to assess the cause for the disagreement at the higher vapor compositions: $Y_1 > 0.9$ for ($0.3 < X_1 < 1.00$.) Smolen *et al.*³⁶ along with Guillevic and co-workers have also discussed the difficulty of measuring vapor concentrations of ammonia above 0.2 mole fraction. Rizvi and Heidemann observe the greatest difficulty is encountered in determining the vapor composition with the uncertainty in the amount of water being very significant. Because the very small slope in this region may give rise to error in the determination, the consistent underestimation of all the data sets in this region may be the fault of either experimental measurement or the entropy functions. It may be that improved empirical expressions for the entropy functions, Dif S and Sum S, are required by incorporating additional temperature terms, such as used in empirical heat capacity equations (*e.g.* a $1/T$ term). This neither mitigates the utility of these computations for vapor compositions below 90 mole % nor the validity of the model to incorporate temperature dependence employing the entropy functions.

In reference to the Flory-Huggins origins of the Wilson model, Danner and Gupte³⁷ noted its basis on "entropic considerations." We have found no elaboration of any thermodynamic treatment of vaporization entropies in reference to the interaction parameters of the Wilson model in the literature. In 1996, thirty-two years after his model's inception, Wilson³⁸ predicted that developments in the next 20 years would include "accurate methods for deriving non-ideal VLE parameters from volume of mixing, heat of mixing, or other mixture properties." We believe that the mixture property of value is the entropy.

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