METHOD OF EVALUATION OF THE CONSTANTS

The constants in the BWR equation were evaluated by a least-squares technique outlined by Brough, Schlinger, and Sage (*4*), minimizing the sum of squares of deviations in the calculated pressure values. Details of the method are outlined elsewhere (*4, 11*). Although the least-squares technique was used, the minimization of maximum and average-absolute deviations was taken into consideration also.

RESULTS AND DISCUSSION

Table I gives the values of the constants, the range of temperature and pressure used in the evaluation of the constants, and other information. A set of constants for NO is reported earlier by Opfell, Schlinger, and Sage (*8*). Table I shows the two sets of constants for NO. A comparison of the degree of fit for the two sets of constants is shown in Table II. Although the disagreement between the two sets of constants is large, Opfell, Schlinger, and Sage have used wider temperature and pressure ranges. However, in the limited range considered in the present work, the set of constants obtained gives a better representation of the *P-V-T* data. Further, Opfell, Schlinger, and Sage minimized the sum of the squares of the deviations in compressibility as compared with pressure used in this work. The accuracy of any fit depends on several things such as the primary data used, the number of points used, the weight put on the points, the range of temperature and pressure used, the criterion on which the fit is obtained, the dependent and the independent variables chosen, etc. Therefore, each set of constants should be judged by its own merit depending on its use and not solely by some criterion such as standard deviation, as this has no reflection on the accuracy of the fit.

In the case of oxygen and nitric oxide, although the principle of least-squares was used, both average-absolute and maximum deviations were minimized, also, and the maximum deviation for different values of γ was 1%. Included in Table II are the maximum and average-absolute deviations for each isotherm, and the values of the pressures at which the maximum deviations occurred. In the case of $N_2O_4 \rightleftarrows 2NO_2$, the γ value chosen was the one which gave a minimum value for the maximum and average-absolute deviations, and for which the sum of the squares of the deviations was close to the minimum value also. This is shown in Table III.

Table III. Effect of γ on Various Deviations for $N_2O_4 \rightleftarrows 2NO_2$

γ	Av.-Abs. Dev., %	Max. Dev., %	Sum of the Squares of Dev.
0.0380	2.95	17.72	46.45
0.0400	1.25	8.20	20.76
0.0405	1.75	10.15	18.00
0.0410	1.21	5.70	19.04
0.0420	1.27	6.23	18.77
0.0440	1.36	7.00	18.40

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Solid-Liquid Solubility Determination by Variable Heating Rates

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In a recent paper Satterfield and Houlard (*3*) have shown that the visual determination of solid solubility in liquids by static methods avoids errors due to overshoot of the true solubility temperature in the dynamic method. The existence of such an overshoot has been well recognized in the literature of solubility determination. Unfortunately, the static method frequently involves considerable time in the location of the precise temperature at which the last crystal of solid dissolves only after prolonged isothermal agitation. (This is especially true in the case of highly viscous solutions.) Satterfield and Houlard recommend 3 hours of isothermal agitation at the solubility temperature. Heric and Posey (*2*) have made isothermal solubility determinations from the direction of undersaturation, and they considered 12 hours of agitation advisable to assure saturation of the solution by the solid solute. The uncertainty of the results of the latter work was estimated to be 0.0005 in mole fraction solute at saturation.

In presenting an argument for the greater accuracy of the static method, Satterfield and Houlard have provided at least tentative evidence that the dynamic method may also be suited, with proper usage, to precise solubility determination. This communication points out this evidence, with the hope that the method may prove to be a useful technique.

Table I, taken from the publication of Satterfield and Houlard (*3*), presents the argument proposed here. Listed there for each system are the ratios of the saturation temperature overshoot to the heating rate—i.e., the overshoot per unit heating rate—both for each heating rate and the average for all heating rates in a system. [The two values in parentheses there have been omitted in averaging because

Table I. Static and Dynamic Solubility in Benzene

Heating Rate, °C./Min.	Solute: *m*-Terphenyl		Biphenyl	*p*-Terphenyl	
	Mole Fraction Solute				
	0.2805	0.3841	0.6137	0.01047	0.00689
	Overshoot per Unit Heating Rate, Min.				
0.02	(2.5)	10.0	2.5	8.0	7.0
0.03	10.0	...	2.7	...	7.0
0.04	8.5	...	2.5	..	10.5
0.05	...	...	(4.0)	7.0	11.0
0.10	...	12.0	2.0	8.0	9.0
Av. ± st. dev.	9.2± 1.1	11.0± 1.4	2.4± 0.3	7.7±0.6	8.8±1.9
	Limiting Saturation Temperature by Dynamic Method, ° C.				
	37.87± 0.03	48.79±0.03	45.40± 0.01	48.82± 0.01	37.01± 0.04
	Saturation by Static Method, ° C.				
	37.85	48.81	45.40	48.81	37.05
	Difference in Saturation Temperatures, Static Minus Dynamic				
	−0.03	+0.02	0.00	−0.01	+0.04

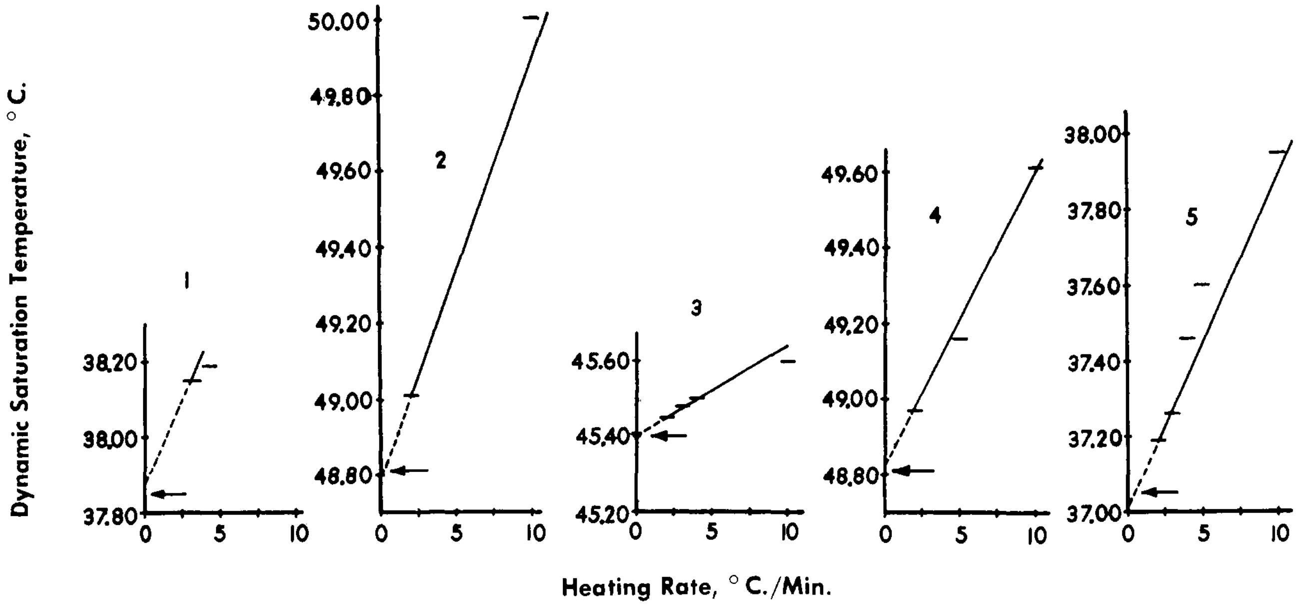

Figure 1. Dynamic saturation temperature vs. heating rate

Static saturation temperature is indicated by arrow

1. 0.2805 mole fraction *m*-terphenyl
2. 0.3841 mole fraction *m*-terphenyl
3. 0.6137 mole fraction biphenyl
4. 0.01047 mole fraction *p*-terphenyl
5. 0.00689 mole fraction *p*-terphenyl

of excessive departure from what must be presumed, on the basis of the limited number of observations, to be a normal distribution. The decision is based on the Dean and Dixon *Q* test (*1*).] The "limiting dynamic saturation temperature" has been obtained by subtracting from the lowest listed saturation temperature by the dynamic method (*3*) the product of the average overshoot per unit heating rate and the lowest listed heating rate. This is illustrated in Figure 1. In the first listed system the second heating rate entry was used because the first entry appears to be atypical, as noted above. The limiting dynamic saturation temperature is the apparent value at a zero heating rate, corresponding to an isothermal (static) solubility determination.

The results by the true static and extrapolated dynamic measurements agree within the standard deviation of the latter. This agreement compares favorably with many of the more precise literature values of solubility. The precision of the extrapolation method undoubtedly is dependent upon uniformity of conditions, such as uniform stirring rate, uniform particle size of the solid solute, a precisely controlled heating rate, and a reproducible initial state for the heating runs.

While the present argument is in terms of overshoot temperature and heating rate, which requires a knowledge of the static temperature of saturation, in general, it would not be necessary to know the static temperature to apply the method—that is, the saturation temperature at the zero heating rate could similarly be obtained by extrapolating the dynamic solubility temperatures, directly, rather than the overshoot.

The present method bears a clear resemblance to the corrective procedure for eliminating the effect of supercooling on freezing point measurements. There a time-temperature plot is extrapolated through the region of supercooling back to a temperature corresponding to the onset of crystallization. In the present situation a time-related function-solubility temperature plot is extrapolated through the region of superheating (the overshoot) to the temperature onset of homogeneity. The time-related function is the heating rate.

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Nitrogen Constants for the Benedict-Webb-Rubin Equation of State

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A new set of Benedict-Webb-Rubin constants for nitrogen is presented. These constants were developed to represent gas phase *P-V-T* behavior over the full BWR density range to twice the critical, in the temperature range below 373° K. The over-all accuracy is very satisfactory, especially in the higher density region, where the earlier constants of Stottler and Benedict are not applicable. Accuracy of the constants in representing wide-range mixture data also has been demonstrated, using previously published argon constants and combining rules, and recent Ar–N_2 *P-V-T* data.

THE Benedict-Webb-Rubin equation of state (*3, 4*) was developed originally to represent the behavior of light hydrocarbons and their mixtures to twice the critical density. The equation subsequently has been applied to a number of other substances (*9, 11, 13, 14*). As has been discussed elsewhere (*9*), it is not possible to determine a unique set of constants for this equation that will correlate accurately liquid-vapor phase behavior as well as gas phase *P-V-T* behavior over a wide range of temperature and pressure. Several solutions to this problem have been proposed in these references: One or more of the coefficients are varied for use in the different regions of the *P-V-T* surface; various modifications in the functional representation are utilized; individual sets of constants are developed, one based on vapor pressure data and another on gas phase *P-V-T* data.

Currently, two sets of nitrogen constants are available for the BWR equation. Stottler and Benedict (*13*), using the originally proposed graphical technique, fit the equation to *P-V-T* data for a maximum density of 1.25 ρ_c. To improve vapor pressure correlation, they adjusted the constant C_0 at two temperatures. Lin and Naphtali (*9*) have presented a set of nitrogen constants determined from vapor pressure data by means of a least squares technique. In addition, they modified one temperature exponent in the equation.

It would be desirable to have available a set of nitrogen constants for the unmodified equation that represent *P-V-T* behavior over the full density range of the equation. Such constants, in addition to increasing the range of applicability for nitrogen calculations, would be especially useful in correlating wide-range mixture data, and also for phase equilibria correlations not requiring nitrogen vapor-pressure prediction (*12*). The constants from (*13*) are not applicable above 1.25 ρ_c, and for temperatures below about 200° K., begin to give appreciable errors above 1.0 ρ_c. The other set (*9*), intended for *K*-factor prediction, are not suitable for wide-range *P-V-T* calculations.

EVALUATION OF THE CONSTANTS

For the reasons discussed above, a new set of nitrogen constants was developed for the unmodified BWR equation of state, covering the full density range shown in Figure 1. The experimental *P-V-T* data used in the final evaluation (*1, 2, 5, 6, 7, 10*) are shown on the plot, and include recent low temperature data. The range is 100° to 373° K., and from low density to 2.0 ρ_c (to saturated vapor below T_c).

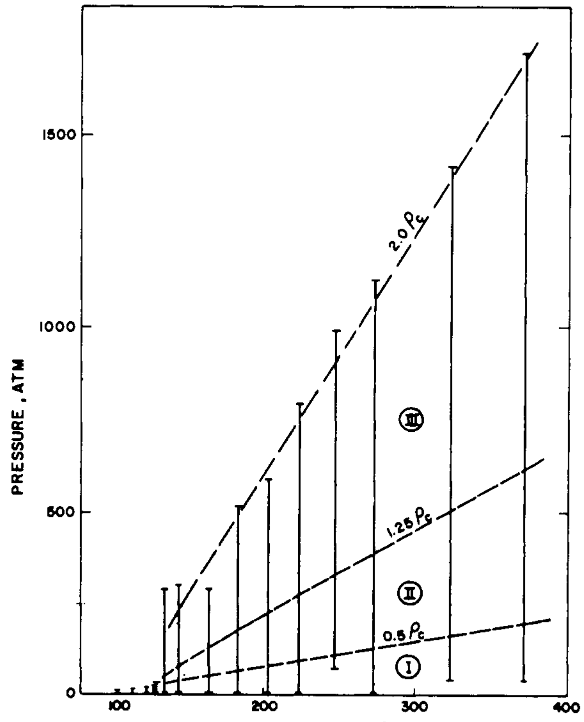

Figure 1. Range of experimental data

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