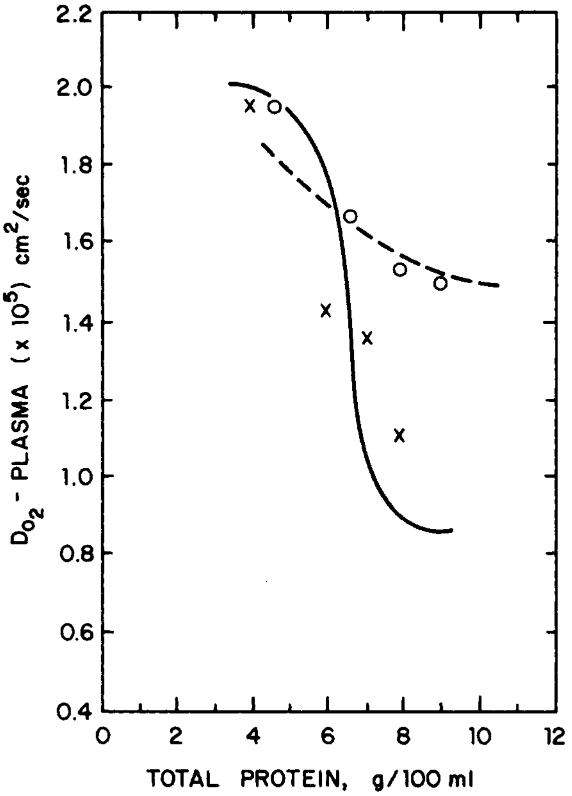

Figure 1. - - - -, data from Goldstick et al., 1976; ——, data from Navari et al., 1971; *x*, plasmas having normal transferrin levels; 0, plasmas having elevated transferrin levels. Standard deviations for all points is ±0.05 × $10^5 \cdot cm^2/s$.

TABLE 1. TRANSFERRIN LEVEL VS. OXYGEN DIFFUSIVITY

Total Protein Concentration of Plasma, g/100 mL	% Increase in Diffusivity If Transferrin Level Elevated
4	0
6	18
7	15
8	35

Blood plasma is really a very complex system, and, although this paper has pointed out how a particular protein, transferrin, may cause an apparent increase in oxygen transport in this system, it is obvious that other constituents in plasma can have different effects. It would appear that more study is needed before a definitive answer can be made as to the factors controlling the diffusivity through plasma.

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Simple and Accurate Vapor Pressure Equations for the Near Critical Region

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Vapor pressure is an important thermodynamic property used in the chemical process industry. Many equation forms have been presented to correlate experimental data (Miller, 1964; Reid et al., 1977), many of which require numerous parameters or coefficients. Also, many of the simpler equations have relatively high percentage errors (Miller, 1964). More recently, equations containing five or more coefficients, many of which are nonlinear, have been developed that fit the data very well, but are overly complex to work with.

Vapor pressure equations based on theories describing the universality of critical point behavior have been one of the more recent developments. The purpose of this article is to present empirical values of certain critical exponents from scaling theory that describe the vapor pressure curvature at and near the critical point. These values are used in the general form of the vapor pressure equation derived from scaling theory and produce a simple, but highly precise, equation. Three related forms of the equation are developed and applied, all of which have only linear coefficients to be determined.

THEORY

A basic universality has been observed in the region of a phase transition critical point in many physical systems, and this similarity

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of physical behavior in the critical region has led to the scaling theory (Levelt Sengers et al., 1977). Stanley (1971) gives an extensive development of simple scaling theory, which predicts a divergence of the second derivative of the vapor pressure with respect to temperature at the critical point (CP) as

$$d^2P_r/dT_r^2 \sim T_r^{-\theta} \quad (T_r \geq 0) \tag{1}$$

where $T_r = 1 - T/T_c$ and $P_r = P/P_c$. A large discrepancy in the supposed universal value of θ has developed in the literature as described by Walton et al. (1978). Therefore, for engineering purposes, an empirical value of θ must be deduced in order to develop vapor pressure equations that can fit experimental data precisely.

VAPOR PRESSURE EQUATION

An empirical, though theoretically consistent, vapor pressure equation can be deduced from Eq. 1 knowing that the scaling relation holds only in the asymptotic limit as the CP is approached. To extend this to a useable range, the scaling relation can be cast in the form of an expansion about the CP, one particular form of which is given by Moldover (1978). An alternate formulation using a series of correction terms gives the following form to the scaling relation (Walton et al., 1978):

$$(d^2P_r/dT_r^2) = C_1T_r^{-\theta}\left(1 + \sum_{j=1}^{\infty} c_jT_r^{j\eta}\right). \tag{2}$$

Truncation of the infinite sum after the second correction term leaves

$$(d^2P_r/dT_r^2) = C_1T_r^{-\theta} + C_2T_r^{\eta-\theta} + C_3T_r^{2\eta-\theta}. \tag{3}$$

Integration twice yields

$$P_r = 1 - \Psi_cT_r + C_1'T_2^{2-\theta} + C_2'T_r^{2+\eta-\theta} + C_3'T_r^{2+2\eta-\theta} \tag{4}$$

where the reduced slope of the critical isochore at the CP

$$\Psi_c = (T_c/P_c)(\delta P/\delta T)_{\rho c|T=T_c} = -(dP_r/dT_r)_{|T_r=0} \tag{5}$$

and unity are constants of integration. Also, C_1', C_2', and C_3' are constants that have absorbed the exponent effects from the integration. Similar equations have been obtained by others (e.g., Hastings and Levelt Sengers, 1977), but were used primarily for the purpose of evaluating θ, rather than correlating data.

PROCEDURE

To apply Eq. 4, or shorter forms of it, the effective values of the exponents θ and η were needed. Once the values for these components had been determined, a linear least-square procedure was used to determine the coefficients that produced the best weighted fit to the experimental data.

Exponent Selection

The values of θ and η were obtained by analysis of the research done by Walton (1977) in conjunction with other results described by Walton et al. (1978). By varying the values of θ and η, Walton was able to obtain a mapping of the three dimensional error surface (the weighted sum of the squared deviations) for seven compounds, where θ and η are nonlinear parameters. The empirical values of θ and η were obtained by comparing the regions of these plots that obtained the best fit to the data and choosing those values that were in this region for all the compounds. Examples of two of these plots are given by Walton et al. (1978).

Curve Fit Method

Once the values of θ and η were obtained, a weighted linear least-squares analysis was used to obtain the coefficients for three modified forms of Eq. 4. These were

$$P_r - 1 = A_1T_r + A_2T_r^{2-\theta} \tag{6}$$

$$P_r - 1 = A_1T_r + A_2T_r^{2-\theta} + A_3T_r^{2+\eta-\theta} \tag{7}$$

$$P_r - 1 = A_1T_r + A_2T_r^{2-\theta} + A_3T_r^{2+\eta-\theta} + A_4T_r^{2+2\eta-\theta} \tag{8}$$

The equations were fit for the vapor pressure data of ethane (Douslin and Harrison, 1973), ethylene (Hastings and Levelt Sengers, 1977), and water (Osborne et al., 1933) for the temperature ranges from the critical temperature to 10% below $T_c(T_r = 0 - 0.1)$ and 23% below $T_c(T_r = 0 - 0.23)$.

As in the work by Walton et al. (1978), the relative error in the pressure measurements were assumed to be normally distributed, which led to a weighting factor of

$$W_i = [(P_{r,i} - 1)/P_{r,i}]^2 \tag{9}$$

This weighting factor agrees with Verbeke (1970), who observed that the errors in pressure in the critical region depend on $(P_c - P)$ rather than P alone.

RESULTS AND DISCUSSION

Exponent Values

By following the procedure outlined under Exponent Selection, the empirical values of θ and η were found to be 0.2 and 2, respectively. Walton (1977) found that the objective function which was being minimized by the least-squares procedure was extremely flat, thereby allowing a large range in the exponent values that obtained excellent fits to the experimental data. In particular, θ values ranged from 0.08 to 0.34 for various compounds, equation forms, and temperature ranges. This coincides with the large range reported in the literature, from 0.1 (Hastings and Levelt Sengers, 1977) to 0.5 (Baehr et al., 1976). By studying the regions of minimal error, a consistent value of $\theta = 0.2$ and $\eta = 2$ was found to provide an excellent fit to the data for each compound. Therefore, these values represent an empirical universal set that can be used to correlate experimental vapor pressure data for various compounds and thereby eliminates the time consuming nonlinear search for a particular exponent value that may apply only to that compound and for only one particular temperature range. When the number of terms in the vapor pressure equation are determined by the temperature range desired, this set of exponent values is independent of the temperature range.

It should be noted that these values of θ and η are not the universal theoretical values. The theoretical value of θ is 0.1 (Vicentini-Missoni et al., 1969) and η is 0.5 (Wegner, 1972), based on extended scaling theory. These are the asymptotic values and theoretically apply only within a very small range from the CP and at zero gravity (Eubank et al., 1980; Balfour et al., 1980).

Curve Fit Results

Tables 1, 2, and 3 give the statistical results when the vapor pressure data of ethane, ethylene, and water were correlated, respectively. The temperature range of the data is defined by $T_{\min}$ as the lower bound and the critical temperature as the upper bound

TABLE 1. CORRELATION CHARACTERISTICS OF ETHANE VAPOR PRESSURE DATA

Data Reference: Douslin and Harrison (1973)

$T_c = 305.33$ K

$P_c = 4{,}871.76$ kPa

$T_{\min}$ (K)	$T_{r,\max}$	Eq.	s_p (kPa)	$\overline{ABS} \times 10^6$	max ABS $\times 10^6$
278.15	0.089018	6	0.616	123	233
		7	0.0372	7.58	13.0
		8	0.215	2.97	11.5
238.15	0.220024	6	8.59	3560	6470
		7	0.695	284	593
		8	0.180	70	154

TABLE 2. CORRELATION CHARACTERISTICS OF ETHYLENE VAPOR PRESSURE DATA

Data Reference: Hastings and Levelt Sengers (1977)

$$\left.\begin{array}{l} T_c = 282.344\ \mathrm{K} \\ P_c = 5{,}039.0\ \mathrm{kPa} \end{array}\right\}\ \text{Moldover (1974)}$$

$T_{\min}$ (K)	$T_{r,\max}$	Eq.	s_p (kPa)	$\overline{ABS} \times 10^6$	max ABS $\times 10^6$
258.15	0.085690	6	0.384	63.9	145
		7	0.0781	13.8	28.7
		8	0.0765	12.8	25.5
219.65	0.222048	6	8.28	3050	6880
		7	0.596	219	430
		8	0.125	47	88.7

TABLE 3. CORRELATION CHARACTERISTICS OF WATER VAPOR PRESSURE DATA

Data Reference: Osborne et al. (1933)

$$\left.\begin{array}{l} T_c = 647.30\ \mathrm{K} \\ P_c = 22{,}128.7\ \mathrm{kPa} \end{array}\right\}\ \text{Osborne et al. (1939)}$$

$T_{\min}$ (K)	$T_{r,\max}$	Eq.	s_p (kPa)	$\overline{ABS} \times 10^6$	max ABS $\times 10^6$
583.15	0.099104	6	11.9	631	1,190
		7	1.47	74.5	150
		8	0.714	29.6	94.8
503.15	0.222694	6	85.6	9,750	20,900
		7	10.1	1,180	2,090
		8	2.91	340	592

(note: $T_r = 0$ at T_c). The weighted standard deviation of the pressure, s_p, is defined by

$$s_p = \left[\frac{N}{N-K} \frac{\sum_{i=1}^{N} W_i (P_i - P_{i,\mathrm{calc}})^2}{\sum_{i=1}^{N} W_i} \right]^{1/2} \tag{10}$$

where the first term corrects the weighted sum by a factor that considers the number of coefficients, K, being used to fit the data. The average of the absolute relative errors, $\overline{ABS}$, is defined by

$$\overline{ABS} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{P_i - P_{i,\mathrm{calc}}}{P_i} \right| \tag{11}$$

the max ABS is the maximum absolute relative error for any particular data point used in the correlation. Finally, Table 4 gives the coefficients for some of the equations used for each compound.

The precision of these simpler forms of the vapor pressure equation is comparable to or better than the more complex ones used by the experimentalists. For ethane, Douslin and Harrison (1973) used two different equations, one having six coefficients and the other having five coefficients (one being non-linear), which had a maximum relative error of 0.00015. When Eq. 8, which has four linear coefficients, was used to correlate the same data, the same maximum relative error was found (Table 1, $T_{\min} = 238.15$ K). Similar comparisons were found for the ethylene and water data.

TABLE 4. COEFFICIENTS FOR SELECTED VAPOR PRESSURE EQUATIONS

$T_{r,\max}$	Eq.	Coefficient	Compound		
			Ethane	Ethylene	Water
0.10	6	A_1	−6.425142	−6.336086	−7.75703
		A_2	9.634207	9.357967	13.8065
	8	A_1	−6.4487997	−6.3489827	−7.8434629
		A_2	9.9641695	9.5305312	14.974427
		A_3	−25.060126	−8.2516286	−86.706623
		A_4	405.25531	−474.69520	2066.0226
0.22	8	A_1	−6.435963	−6.345229	−7.790893
		A_2	9.812158	9.508525	14.31971
		A_3	−14.85904	−13.19129	−36.80110
		A_4	49.50856	39.88720	149.9169

Comparisons between Eqs. 6–8 for a fixed temperature range show that an improvement of one order of magnitude is obtained as the number of terms in the equation is increased from two to four, as expected. Alternately, the accuracy decreases by about one order of magnitude as the temperature range of the data used is extended from 10% below the critical temperature to about 23% below T_c. This is also expected since the equation was derived from critical point behavior and its precision will decrease as the lower temperature bound moves further from the critical point. Thus, these equations should only be used in the near critical region. In particular, Eq. 6 is recommended for use within 10% of the critical temperature, Eq. 7 within 15%, and Eq. 8 within 20%, though it should be noted that Eq. 8 may still retain its high precision beyond the 20% limit, but this will depend on the particular compound that is being considered.

CONCLUSIONS

This study has concerned itself with obtaining simple, yet highly precise, forms of a vapor pressure equation based on an empirical extension of the scaling theory while past studies have been primarily interested in the precise values of the scaling law exponents. It has been shown that an optimal empirical set of the critical exponent values of θ and η equal to 0.2 and 2, respectively, will produce precise reproduction of experimental vapor pressure data in the near critical region. By using these values in Eq. 6, 7 or 8, the weighted linear least-squares correlation method can be applied, producing vapor pressure equations that have 98% confidence intervals of less than 0.2% error when used over the recommended temperature range.

NOTATION

A_1, A_2, A_3, A_4 = linear coefficients of vapor pressure equations
C_1, C_2, C_3 = constant coefficients in Eq. 3
$C_1', C_2' C_3'$ = constant coefficients in Eq. 4
c_j = constant coefficient j in Eq. 2
K = number of free parameters to be found in a particular equation
N = total number of data points
P = vapor pressure, kPa
P_c = critical pressure, kPa
s_p = standard deviation of calculated vapor pressure, kPa
T = temperature, K
T_c = critical temperature, K
$T_{\min}$ = minimum data temperature used in curve fit, K
T_r = reduced temperature, $(T_c - T)/T_c$
$T_{r,\max}$ = maximum value of T_r for data used in curve fit
W = weighting factor defined by Eq. 9

Greek Letters

α = critical exponent of the isochoric heat capacity
η = second order critical exponent of the vapor pressure curvature
θ = primary critical exponent of the vapor pressure curvature
ρ_c = critical density, kg-mol/m^3
Ψ_c = dimensionless slope of vapor pressure curve at CP, Eq. 5

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Diffusion of n-Decane in 5A Zeolite Crystals

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In a recent paper Caro, Kärger and Bülow (1980) showed that the rate of adsorption of n-decane from the liquid phase into 5A zeolite crystals is controlled by a surface blocking effect rather than by intracrystalline diffusion. We have measured the sorption of n-decane from the vapour phase into Linde 5A zeolite crystals at much higher temperatures (250–323°C). A typical set of experimental uptake curves is shown in Figure 1. The uptake rate was found to be essentially independent of the quantity and configuration of the zeolite crystal sample indicating the absence of any significant bed diffusion or heat transfer limitations.

For a diffusional process, in the long time region, the fractional uptake (m_t/m_∞) is given by:

$$1 - m_t/m_\infty \approx (6/\pi^2)\exp(-\pi^2 Dt/r^2) \tag{1}$$

while for a surface barrier limited process:

$$1 - m_t/m_\infty \approx \exp(-3\alpha t/r) \tag{2}$$

where D is the intracrystalline diffusivity; r, the equivalent radius of the crystal; α, the barrier coefficient; and t, time. It is evident that the form of the uptake curves shown in figure 1 is consistent with the diffusion model (Eq. 1) rather than the surface barrier model (Eq. 2) since the zero time intercepts of the extrapolation of the long time region of the semilog arithmic plot of $(1 - m_t/m_\infty)$ vs. t are all close to $6/\pi^2$.

The diffusivity shows the usual strong positive concentration dependence (Figure 2). Corrected diffusivities (D_o) calculated according to the expression:

$$D = D_o(dlnp/dlnc) \tag{3}$$

where $dlnp/dlnc$ is the non-linearity correction factor derived from the equilibrium isotherm are essentially independent of concentration, as observed previously for n-heptane and other light hydrocarbons in 5A zeolite. (See, for example, Doetsch, Ruthven and

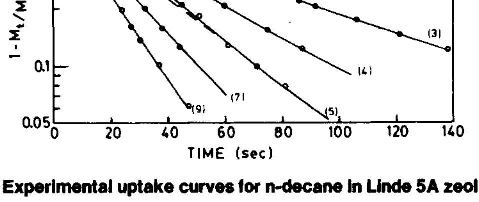

Figure 1. Experimental uptake curves for n-decane in Linde 5A zeolite crystal (mean diameter 3.6 µm). The curves are for the following pressure steps (in Pa): (2): 1.86–10.6; (3): 10.6–19.0; (4): 19.0–33; (5): 33–44; (7): 56–71; (9): 82–97.

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