Comparison of Experiments 14 and 15 show that the reaction rate at 153°C is higher by 2.2×10^{-7} mol/s, very close to the rate of the thermal reaction at this temperature as measured in Experiment 12a.

Additional data were obtained at longer forechamber distances as shown for Experiments 16, 17, 18 and 19 in Table 2. In these cases, it is expected that transmission of radiation through the grid would not be significant since the increased path lengths insure that only negligible amounts of radiation should penetrate through the chlorine gas to reach the grid surface. Nonetheless, the thin grid data do show that the rate is larger than that for the thick grid, as expected because of radical deactivation effects, but still decreasing with forechamber length. It may be that the flow pattern in the rear chamber differs somewhat due to grid thickness and this factor contributes to the observed rate. Some experiments were also made to check the effect of total flow rate and molar ratio of the feed gases on the rate of reaction, but these did not indicate any significant trends.

It should be noted that Richard (1982) has recently reported studies made with a reactor of comparable design but illuminated with a high-pressure mercury lamp. His results indicate rates similar to those reported by Dworkin (1977) and also show that there is an optimum flow rate for each forechamber length at which the rate goes through a maximum.

Comparison of the reaction rates found in this work with those observed previously by Dworkin indicate that his rates were approximately 10 times higher, despite an incident intensity which was only 1/4 of that in this work. His reactor diameter was twice that used here and his grid contained 2.5 times as many openings per unit area. The difference in rate suggests that an increased reactor surface to volume ratio in the present smaller diameter case has a pronounced influence on radical termination rates. The effect of hole distribution in the grid similarly may reflect a change in radical termination rates as the number of holes per unit area is changed. However, such conclusions must remain speculative at present in the absence of additional data.

This study has demonstrated clearly that chlorine radicals can indeed be transported through small-diameter holes in a relatively thick piece of teflon in sufficient number to initiate measurable reactions in a dark reactor zone. The measurements have shown that thin, apparently opaque, teflon diaphragms can transmit significant amounts of near UV radiation and this fact should be considered in the design and analysis of future two-zone reactors. The potential of the two-zone reactor concept for photoreactions which are subject to deposit and by-product formation remains considerable. However, its benefits may also be achieved by appropriate control of the reactor flow pattern.

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Simplest Equation of State for Vapor-Liquid Equilibrium Calculation: a Modification of the van der Waals Equation

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There is evidence in the literature (Döring and Knapp, 1980; Lira et al., 1981; Adachi et al., 1983a) that practically identical results in vapor-liquid equilibrium (VLE) calculations can be obtained from various cubic equations of state, in spite of their differences in representing pure-component properties, and these results are frequently comparable to those obtained from more complex equations of state. In applying these cubic equations to VLE calculations, the general practice is to treat the cohesion parameter a temperature-dependent in addition to the inclusion of an adjustable binary interaction coefficient k_{ij}.

It is less costly to use a simpler equation, especially when the required number of iterative calculations is large, as in the VLE calculations for multicomponent systems. The objective of this work is, therefore, to obtain a suitable but simplest possible equation for VLE calculations.

We attempted to develop and compare three generalized temperature functions for representing Ω_a, which is related to the parameter a by $a = \Omega_a R^2 T_c{}^2 / P_c$. The performance of several selected cubic equations has been evaluated. The VLE values used as the basis for the evaluation are limited to binary mixtures of normal fluids, which are important to petroleum and cryogenic industries.

SELECTION OF EQUATIONS FOR EVALUATION

The Redlich-Kwong (RK) (1949) equation as modified by Soave (SRK) (1972) and the Peng-Robinson (PR) equation (1976) are two of the currently popular equations.

More recently, Martin (1979) made a detailed analysis of volume-cubic equations of state and concluded that the Clausius (1880) type equation is the best of the simpler cubic equation for representing volumetric data of pure fluids. Joffe (1980) subsequently introduced a Soave-type temperature function into the Martin equation and applied it to VLE and density calculations. Adachi et al. (1983b) evaluated 16 two-term three-parameter equations of state from the viewpoint of suitable representation of saturated properties and liquid-phase densities (with reduced densities less than or equal to 3), and concluded that the best equation is a three-parameter RK equation, which is of the form suggested by Fuller (1976) and by Usdin and McAuliffe (1976) but with all the parameters generalized in terms of the acentric factor ω and with only one of the parameters considered temperature-dependent.

It appears that further consideration and evaluation of these equations are of interest. The results obtained from the four-parameter cubic equation proposed by Adachi et al. (1983a) are also included for comparison.

However, any evaluation or consideration without including the truly simplest cubic equation of state, the van der Waals (VDW) (1873) equation itself, would be unsatisfactory. Perhaps its shortcomings in representing pure-component properties prevented any stimulation of interest to modifying it for VLE calculations. Its capability in such calculations is therefore uncertain. For this reason, it is evaluated in this work.

TEMPERATURE-DEPENDENT FUNCTIONS FOR Ω_a

Our experience indicated that the parameter values which are capable of predicting vapor pressures of pure substances would in general be suitable for VLE calculations. In this work, vapor pressures of pure components are reproduced by treating Ω_a temperature-dependent with all other parameters kept constant at their critical point values.

In addition to the Soave-form temperature function (S),

$$\Omega_a = \Omega_{ao}[1 + m(1 - T_r^{0.5})]^2 \tag{1}$$

a logarithmic form (L)

$$\Omega_a = \Omega_{ao} 10^{m(1 - T_r)} \tag{2}$$

and a polynomial form (P)

$$\Omega_a = A_o + A_1/T_r + A_2/T_r^2 + A_3/T_r^3 \tag{3}$$

were also considered for the representation of Ω_a. The quantity Ω_{ao} in these equations represent the values of Ω_a at the critical point.

The vapor pressures for ten normal alkanes from methane to decane, generated from the correlation of Gomez-Nieto and Thodos (1978), were used for the evaluation of Ω_a. An attempt was made to generalize the coefficients of Eqs. 1–3 in terms of ω. The vapor pressure values recalculated from these expressions are compared with those obtained from the correlation of Gomez-Nieto and Thodos in the reduced temperature range from 0.5 to 0.98 at 0.02 intervals. The deviations obtained from the VDW, Clausius, and Martin equations are found to be identical. The L form is only suitable for the VDW equation. The S form is not very suitable for the VDW equation, but acceptable for other equations. For the VDW equation, the deviations obtained from the L form are much lower than those obtained from the S form but slightly higher than those obtained from the P form. Other than the VDW equation, the overall differences between the results obtained from the S and P forms are not considered significant (less than 1% in average absolute deviations). The overall average absolute deviation obtained from the L form of the VDW equation is slightly lower than those obtained from the S form of the other equations.

VLE CALCULATIONS

The VLE values for 27 binary systems at 80 isothermal conditions for a total of 844 data points were selected as the basis for comparison. A bubble-point calculation precedure was followed for all the isotherms. The calculated values of system pressure, P, and equilibrium vapor composition, y, were compared with the experimental values reported in the literature. In the calculation, the conventional mixing rules

$$a_{\text{mixture}} = \sum\sum x_i x_j a_{ij} \tag{4}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{5}$$

$$b_{k,\text{ mixture}} = \sum_i x_i b_{ki},\ k = 1,2,3 \tag{6}$$

$$c_{\text{mixture}} = \sum_i x_i c_i \tag{7}$$

were adopted. A comparison of the calculated results is summarized in Table 1. The differences in the calculated P and y values from all the equations included in the comparison are not at all significant. Furthermore, the VDW equation appears to have the smallest deviations when the L- or P-form temperature-dependent function for Ω_a was used.

It should also be mentioned that the VLE values calculated from the modified Martin equation and the Clausius equation were identical to those obtained from the VDW equation. The reason for obtaining identical vapor pressure values for pure components and identical VLE values for mixtures is not coincidental, but is due to the controlling role of Ω_a.

The k_{ij} values of Eq. 5 were obtained by minimizing the P values. A number of the isotherms studied involve a supercritical

TABLE 1. COMPARISON OF CALCULATED VAPOR PRESSURE P AND VAPOR MOLE FRACTION y VALUES

Binary Systems	Data Points	Soave-Form Temperature Function					Polynomial Form	Logarithmic Form
		SRK	PR	3 par. RK	4 par.	VDW	VDW	VDW
		Average Absolute Deviations of $\Delta P/P$, %						
13 Hydrocarbon–Hydrocarbon	403	2.12	2.19	1.98	2.01	2.10	2.21	2.00
4 N_2–Hydrocarbon	100	6.06	6.45	6.32	6.21	6.04	6.20	5.91
3 H_2S–Hydrocarbon	91	2.71	2.84	2.72	3.08	2.69	2.71	2.72
7 CO_2–Hydrocarbon	193	2.53	2.49	2.55	2.51	2.54	2.45	2.47
	Overall Avg.	2.79	2.88	2.76	2.79	2.77	2.83	2.69
		Average Absolute Deviations of Δy						
13 Hydrocarbon–Hydrocarbon	373	0.0088	0.0115	0.0108	0.0101	0.0100	0.0093	0.0095
4 N_2–Hydrocarbon	100	0.0155	0.0126	0.0164	0.0128	0.0165	0.0167	0.0166
3 H_2S–Hydrocarbon	91	0.0111	0.0115	0.0111	0.0106	0.0115	0.0108	0.0110
7 CO_2–Hydrocarbon	165	0.0088	0.0107	0.0087	0.0097	0.0076	0.0069	0.0072
	Overall Avg.	0.0109	0.0115	0.0112	0.0105	0.0106	0.0099	0.0101

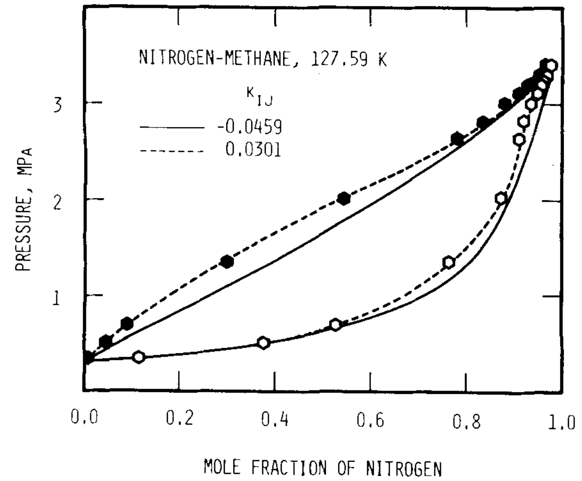

Figure 1. Comparison of calculated VLE values for the system nitrogen-methane at 127.59 K using two k_{12} values: ——, two data points near the critical excluded; - - -, four data points near the critical excluded.

component. Nonconvergence occasionally occurred in the calculation for those data points located in the vicinity of the critical point of the binary mixture. An adjustment of k_{ij} value by excluding some points in that region would improve very much the representation of the remaining data points. A typical example of such an improvement is shown in Figure 1, in which the representation of the VLE data for the system nitrogen-methane at 127.59 K (Stryjek et al., 1974) by means of two different k_{ij} values is depicted. It should be mentioned that whenever nonconvergence calculation occurred in the use of the VDW equation, it also occurred in the use of all the other equations tested.

In conclusion, the van der Waals equation

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2} \tag{8}$$

is capable of calculating VLE values. A generalized logarithmic-form temperature function proposed for representing Ω_a,

$$\Omega_a = (27/64)10^{m(1-T_r)} \tag{9}$$

with

$$m = 0.228165 + 0.791981\omega - 0.648552\omega^2 + 0.654505\omega^3 \tag{10}$$

makes it possible to achieve the same satisfactory results for VLE calculations as those obtained from the currently popular cubic equations of state.

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NOTATION

a,b,c = parameters
A_0,A_1,A_2,A_3 = coefficients
m = function of ω
P = pressure
R = universal gas constant
T = temperature
x = liquid mole fraction
y = vapor mole fraction

Greek Letters

α = constant
ω = acentric factor
Ω_a = $aP_c/R^2T_c^2$

Subscripts

c = critical
i,j,ij = component identification
k = constant identification

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