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Generalized Vapor Pressure Behavior of Substances Between Their Triple Points and Critical Points

Several approaches are utilized for the estimation of the parameters associated with the normalized vapor pressure equation

$$\ln P_R = \alpha + \frac{\beta}{T_R^m} + \gamma T_R^7$$

to develop a capability for the prediction of vapor pressures consistent with the theorem of corresponding states. In this development, conditions and restrictions associated with the critical point and the normal boiling point were used to establish the vapor pressure parameters α, β, γ, and m. For the evaluation of these parameters, five different approaches were applied, and vapor pressures calculated with each of them were compared with corresponding experimental values presented in the literature. These comparisons were further examined using the results of four other well-known vapor pressure equations available in the literature.

This evaluation included 138 substances of all types and involved a total of 7,633 literature reported vapor pressure values to show that improved results are possible through the involvement of the generalized vapor pressure equation of this investigation.

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SCOPE

The perennial involvement of the vapor pressure behavior of substances makes it mandatory that simple and exacting relationships be established that are capable of predicting vapor pressures over the complete liquid region included between the triple point and the critical point of a substance. In this context, a generalized vapor pressure equation, consistent with the theorem of corresponding states, has been examined and tested to show that improved results are possible with it. The capability of this generalized relationship permits the calculation of vapor pressures that find use in vapor-liquid equilibria of both simple and complex mixtures, the estimation of latent heats of vaporization over the complete liquid range, and thermodynamic properties associated with the saturated vapor-liquid state. In addition, the analysis associated with this study constitutes a basis for evaluating parameters that find use in the application of the theorem of corresponding states for both gases and liquids.

CONCLUSIONS AND SIGNIFICANCE

Average percent deviations resulting from the use of this generalized vapor pressure equation are smaller than those obtained from corresponding relationships available in the literature. The capability of the vapor pressure equation examined in this study has been extensively tested using 138 substances and involving a total 7 633 vapor pressure values reported in the literature. One of the proposed schemes for estimating the vapor pressure

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parameters of this generalized vapor pressure equation yields an overall average deviation of 1.05%, while the other four approaches for the estimation of these parameters yielded deviations of 1.42, 1.43, 1.55, and 1.58%. Using the capability of four well-established methods available in the literature, these deviations were found to be 1.52, 1.71, 2.28, and 3.39%.

The last 30 yrs. have witnessed, among other developments, concerted efforts to account for the vapor pressure behavior of substances at low pressures and also at pressures sufficiently high to approach in the limit the critical state of these substances. Attempts to generalize the dependence of the vapor pressure function are reported in the literature in the early work of Gamson and Watson (1944) which presents as a compromise of simplicity and accuracy, the vapor pressure function in reduced coordinates through the relationship

$$\log P_R = -\frac{A(1-T_R)}{T_R} - e^{-20(T_R-b)^2} \tag{1}$$

Parameters A and b were evaluated for over forty compounds, comprising representative members of organic series and a few miscellaneous inorganic substances. Values for parameter b were found to range from 0 for methane and hydrogen cyanide up to 0.358 for pentatetracontane ($C_{45}H_{92}$), with values of 0.163 and 0.243 for such polar substances as water and methanol, respectively. Near the critical point, Equation (1) becomes linear where the contribution of the exponential term becomes negligible. However, in the low pressure region, this term properly accommodates the nonlinear behavior of actual vapor pressure data to produce deviations from experimental data that were claimed to be generally less than 2% for pressures varying from the critical point down to 0.1 mm.

The nonlinear nature of the vapor pressure function in the low pressure region is well represented by the Rankine-Kirchhoff relationship which, in its reduced form, becomes

$$\ln P_R = A + \frac{B}{T_R} + C \ln T_R \tag{2}$$

Equation (2) follows from the integration of the Clapeyron equation that on the assumption the liquid molar volume can be neglected, the vapor behaves ideally and the latent heat of vaporization is linearly dependent on temperature. Although these assumptions are only approximate, and in particular fail near the critical point, Equation (2) holds very well over a wide range of temperatures. In many respects, Equations (1) and (2) describe ostensibly vapor pressure functions of a similar nature, with both exhibiting a linear dependence of ln P_R on $1/T_R$ in the vicinity of the critical point.

The true nature of the complete vapor pressure function was not recognized until 1950. At that time, Thodos (1950) pointed out that the ln P vs. $1/T$ dependence of this function, in the high pressure region, was not actually linear, but instead it curved towards the critical point. With this characteristic property, the vapor pressure behavior for real substances can be represented as an elongated S shaped function, which is characterized with a reversal in curvature in the vicinity between the normal boiling point and the critical point of a substance. This overall behavior of the vapor pressure function was later corroborated from the studies of Waring (1954).

Attempts to take into account the reversal of curvature of the vapor pressure function in the high pressure region have been reported in the literature. Using semitheoretical arguments, Frost and Kalkwarf (1953) attempt to account for this inflection point with the development of the transcendental vapor pressure relationship

$$\ln P = A + \frac{B}{T} + C \ln T + D\frac{P}{T^2} \tag{3}$$

In their development, they assumed that the latent heat of vaporization depends linearly on temperature, that the molar volume of the liquid state can be neglected, as did Rankine (1851) and Kirchhoff (1858), but that the volumetric dependence of the saturated vapor can be represented by a van der Waals' type of behavior. In Equation (3), $D = a/R^2$, where a is the van der Waals constant $a = 27R^2T_c^2/64P_c$. Reynes and Thodos (1962) normalize Equation (3) to produce the generalized vapor pressure function

$$\ln P_R = a + \frac{b}{T_R} + c \ln T_R + 0.1832 \frac{P_R}{T_R^2} \tag{4}$$

in which the coefficient 0.1832 represents a universal constant for this function.

Another approach to account for the reversal in curvature is suggested by Riedel (1954), who proposes the relationship in reduced form

$$\ln P_R = A + \frac{B}{T_R} + C \ln T_R + DT_R^6 \tag{5}$$

to define the vapor pressure explicitly in terms of temperature. In this connection, Riedel (1954) utilizes properties consistent with the vapor pressure function to produce the parameters of Equation (5). In this regard, the parameter $\alpha = d \ln P_R/d \ln T_R$ is introduced which when evaluated at the critical point becomes the constant $\alpha_c = (d \ln P_R/d \ln T_R)_c$, a characterization parameter for a substance. This parameter is commonly referred to as the Riedel parameter. As the critical point is approached along the saturation line, Plank and Riedel (1948) postulate a trivial dependence of α on T_R and therefore propose the boundary condition $(d\alpha/dT_R)_c = 0$. This boundary condition of Plank and Riedel (1948) is not shared by Goodwin (1969) who suggests that $(d^2P/dT^2)_c$ may be unbounded. In this connection, Zia and Thodos (1974) have utilized the high vapor pressure data of Beattie and Kay (1937), Kay (1938), and Young (1898) for n-heptane in order to verify the practical involvement of this Riedel-Plank condition at the critical state. The treatment by Zia and Thodos (1974) shows that a plot of log P_R vs. log T_R becomes linear in the neighborhood of the critical point, indicating that the Riedel-Plank boundary condition appears to be applicable. Equation (5), coupled with the α_c parameter and the boundary condition $(d\alpha/dT_R)_c = 0$, possesses simplicity and is capable of reproducing vapor pressures accurately.

Another vapor pressure relationship that has been cited frequently in the literature is due to Miller (1964). The form of the function suggested by Miller involves a third-order polynomial in temperature which, in its simplified form, can be expressed as

$$\ln P_R = \frac{1}{T_R}(A + BT_R + CT_R^2 + DT_R^3) \qquad (6)$$

In using Equation (6), Miller utilizes the Riedel parameter α_c and the Riedel-Plank restriction $(d\alpha/dT_R)_c = 0$ to eliminate two constants from this equation. Equation (6) is referred to by Reid and Sherwood (1966) as the Riedel-Plank-Miller equation, and they express a high regard for its ability to represent the vapor pressure behavior of substances.

In attempting to generalize the vapor pressure function, Thek and Stiel (1966) propose a relationship which can be expressed as

$$\ln P_R = \frac{1}{T_R}(A + BT_R + CT_R^2 + DT_R^3 + ET_R \ln T_R + FT_R^n) \qquad (7)$$

These investigators also utilize the Riedel and Riedel-Plank conditions to simplify Equation (7) in order to present a final generalized relationship. Zia and Thodos (1974) apply their development to the behavior of thirty-three hydrocarbons of all types and utilize the vapor pressure function

$$\ln P_R = A + \frac{B}{T_R} + \frac{C}{T_R^2} + DT_R^8 \qquad (8)$$

to represent the dependence of vapor pressure on temperature between the triple point and critical point of these hydrocarbons. Their treatment included normal alkanes, from methane through dodecane, a number of iso-alkanes, olefins, naphthenes, and aromatics.

Interest in this direction is expressed through the studies of Gómez-Nieto and Thodos (1977*a*, 1977*b*) who attempt to maintain mathematical simplicity without sacrificing accuracy and propose the relationship

$$\ln P_R = \alpha + \frac{\beta}{T_R^m} + \gamma T_R^7 \qquad (9)$$

In their studies, they utilize experimental data over the complete liquid region, whenever possible, to account for the vapor pressure behavior of *n*-alkanes ranging from methane through eicosane and nonpolar substances in general (Gómez, Nieto and Thodos, 1977*a*) and the treatment of compounds possessing polar and hydrogen bonding characteristics (Gómez-Nieto and Thodos, 1977*b*). Equation (9) has been shown to represent the vapor pressure behavior of substances in a generalized manner within classes of compounds. However, this expression could prove more utilitarian if its application were extended to encompass substances of all types in a more comprehensive manner so as to produce a generalized approach for the prediction of vapor pressures for all types of substances. Such an analysis will require that the prediction of the parameters of Equation (9) be reestablished using more generalized arguments commensurate with the theorem of corresponding states.

THIRD CORRELATING PARAMETERS

Attempts to account for the deviation of properties predicted from the involvement of reduced temperature and reduced pressure using the theorem of corresponding states have been proposed through the introduction of an additional third correlating parameter. In this connection, Meissner and Seferian (1951) suggest this parameter to be the critical compressibility factor $z_c = P_c v_c / RT_c$. The involvement of this parameter requires that the coexisting pressure, volume, and temperature of a substance at the critical point be available with a high degree of accuracy. The value of z_c as a third correlating parameter was extensively investigated by Lydersen et al. (1955) for seventy-one different compounds. However, since z_c requires for its calculation knowledge of the critical volume, this parameter cannot be properly estimated from the vapor pressure behavior of a substance at the critical point.

On the other hand, third correlating parameters derived from the vapor pressure behavior of substances have been suggested in the literature. In this context, Pitzer (1955), and Pitzer et al. (1955) introduce the acentric factor ω as a correlating parameter to account for the nonspherical nature of a molecule. This parameter can be visualized to express the deviation of the intermolecular potential function of a substance from that of simple spherical molecules. The acentric factor is defined through the vapor pressure function at $T_R = 0.700$ as

$$\omega = -\log P_R|_{T_R=0.700} - 1.000 \qquad (10)$$

and ranges from 0 for spherically symmetric atoms such as argon, krypton, and xenon to 0.600 for such hydrogen bonded polar molecules as pentanol. Another characterization parameter associated with the vapor pressure function is that suggested by Riedel (1954) who proposes the slope α of the vapor pressure function at the critical temperature as the correlating parameter needed to account for the behavior of different substances through the corresponding states principle. This parameter, defined as

$$\alpha_c = \left.\frac{d \ln P_R}{d \ln T_R}\right|_{T_R=1.00} \qquad (11)$$

utilizes the conditions surrounding the critical point of the vapor pressure function for its numerical evaluation. The Riedel parameter α_c is a fundamental third parameter and requires for its establishment only two variables for its definition at the critical point.

Since the acentric factor ω and the Riedel parameter α_c are properties derived from the vapor pressure function, the constants α, β, γ, and exponent m of Equation (9) become indispensable requirements for the calculation of these parameters. In this connection, the vapor pressure parameters reported by Gómez-Nieto and Thodos (1977*a*) for inorganic substances, hydrocarbons of all types, and polar and hydrogen bonding substances (Gómez-Nieto and Thodos, 1977*b*) have been consulted. These parameters resulted from an exhaustive literature search of vapor pressure data, a careful screening of these data for internal consistency, and a critical analysis of their behavior using a nonlinear regression technique. The vapor pressure parameters derived from this regression analysis are presented elsewhere (Gómez-Nieto and Thodos, 1977*a*, *b*), and these values have been used to calculate both the Pitzer acentric factor ω and the Riedel parameter α_c. The Pitzer acentric factor ω follows directly from Equation (10), while the Riedel parameter can be shown to be $\alpha_c = -\beta m + 7\gamma$. Values of ω and α_c calculated from these original vapor pressure parameters are presented in Table 1 for the inorganic, polar, and hydrogen bonded substances, in Table 2 for saturated alkanes, and

TABLE 1. PHYSICAL PROPERTIES AND SUMMARY OF DEVIATIONS RESULTING FROM DIFFERENT METHODS USED IN THE ESTIMATION OF VAPOR PRESSURES FOR INORGANIC, POLAR, AND HYDROGEN BONDING SUBSTANCES

										Average percent deviation								
										Present study					Methods available in literature			
Monatomic	M	T_b, °K	T_c, °K	P_c, atm	s	ω	α_c	T_{Ri}	No. of points	Method A	Method B	Method C	Method D	Method E	Riedel	R-P-M	T-S	Z-T
Helium	4.00	4.22	5.20	2.24	3.4913	−0.3877	3.902	—	57	1.01	1.23	0.52	0.82	2.59	6.48	228.22	44.37	10.14
Neon	20.18	27.09	44.40	26.19	5.1108	−0.0369	5.695	0.629	62	0.34	0.23	0.42	0.34	0.30	0.69	0.52	0.50	0.42
Argon	39.94	87.30	150.60	48.00	5.3391	−0.0017	5.835	0.745	171	0.26	0.25	0.22	0.30	0.28	0.32	0.38	0.40	0.27
Krypton	83.70	119.93	209.40	54.27	5.3532	−0.0021	5.787	0.747	95	0.87	0.61	0.74	0.85	0.84	0.52	0.88	0.64	0.79
Xenon	131.30	165.05	289.75	57.64	5.3661	0.0030	5.816	0.745	74	0.44	0.10	0.16	0.29	0.26	0.26	0.32	1.17	0.23
Diatomic																		
n-Hydrogen	2.02	20.38	33.24	13.22	4.0905	−0.2256	4.529	—	53	1.46	1.42	2.08	2.08	10.76	2.45	2.99	13.68	2.09
Nitrogen	28.02	77.35	126.15	33.52	5.5669	0.0384	6.007	0.774	118	0.47	0.47	0.48	0.53	0.48	0.54	0.56	0.87	0.56
Oxygen	32.00	90.18	154.77	50.14	5.4659	0.0191	5.919	0.767	22	4.71	2.98	2.24	2.27	2.19	2.56	2.28	16.29	2.41
Carbon monoxide	28.01	81.20	133.20	34.50	5.5293	0.0388	5.837	0.817	74	4.91	4.70	4.96	5.08	4.98	4.65	4.74	4.01	5.13
Nitric oxide	30.01	121.40	180.20	64.00	8.5865	0.5854	9.704	0.840	129	0.57	0.57	0.57	0.70	0.60	0.49	0.66	0.66	0.70
Fluorine	38.00	85.00	144.31	51.47	5.6474	0.0493	6.115	0.779	125	0.45	0.50	0.33	0.54	0.34	0.68	1.15	2.11	0.55
Chlorine	70.91	238.60	417.20	76.10	5.7874	0.0739	6.282	0.800	45	2.73	2.96	2.71	2.83	2.72	2.80	2.77	2.88	2.92
Bromine	159.83	331.90	584.20	102.00	6.0841	0.1579	8.350	0.737	42	2.13	7.29	2.24	2.15	2.23	2.10	1.36	2.34	1.82
Polyatomic																		
Carbon dioxide	44.01	185.29	304.16	72.85	6.6845	0.2241	6.824	0.859	69	0.33	0.13	0.74	0.70	0.86	0.42	1.88	1.27	0.89
Nitrous oxide	44.02	184.70	309.70	71.70	6.3130	0.1583	6.361	0.863	22	2.32	2.25	2.38	2.38	2.38	2.35	2.64	2.74	2.40
Carbon disulfide	76.13	319.37	552.20	78.00	5.9763	0.1223	7.037	0.746	63	2.66	0.16	2.98	2.86	2.97	3.17	2.41	2.36	2.59
Sulfur trioxide	80.06	317.50	491.46	84.00	8.0868	0.4500	7.801	0.903	32	7.04	6.96	7.85	7.81	8.30	7.79	8.57	7.69	8.06
Carbon tetrachloride	153.84	349.90	556.40	45.00	6.4501	0.1926	6.859	0.829	46	1.34	1.15	0.88	0.86	0.91	0.96	1.73	0.52	1.04
Polar																		
Ammonia	17.03	239.80	405.50	111.30	6.8195	0.2517	6.961	0.849	90	3.07	2.25	1.88	1.98	1.82	1.76	1.09	1.84	1.53
Acetone	58.08	329.27	508.10	46.39	7.0648	0.3076	7.267	0.854	87	2.55	2.59	2.19	2.35	1.91	2.36	1.19	2.46	1.97
Diethyl ether	74.12	307.50	466.74	35.90	6.9146	0.2805	7.135	0.860	54	0.34	0.44	0.46	0.35	0.75	0.35	1.51	3.24	0.61
Acetic acid	60.05	391.05	594.80	57.10	7.7630	0.4407	8.300	0.819	70	6.20	4.08	5.37	5.52	4.67	5.43	4.18	1.16	5.08
Phenol	94.11	454.90	692.40	60.50	7.8581	0.4461	7.493	0.986	20	0.96	2.25	0.79	0.82	0.74	0.75	0.97	4.79	0.74
Phosgene	98.92	281.15	455.20	56.00	6.5023	0.1954	6.467	0.890	37	1.81	2.42	1.72	1.74	1.68	1.73	1.22	1.30	1.58
Methyl fluoride	34.03	194.80	317.80	58.00	6.4307	0.1899	6.667	0.830	35	1.55	1.32	1.00	1.01	0.98	1.28	0.62	1.55	0.81
Ethyl fluoride	48.06	235.45	375.31	49.62	6.5729	0.2169	6.835	0.830	46	2.02	1.76	1.49	1.54	1.41	1.79	1.03	1.49	1.33
Difluorodichloromethane	120.92	243.35	384.95	40.71	6.3699	0.1756	6.973	0.817	25	2.45	4.49	2.51	2.49	2.54	2.97	3.71	2.79	2.56
Methyl chloride	50.49	248.94	416.30	65.90	6.2297	0.1597	6.969	0.789	54	1.83	1.99	1.71	1.70	1.70	1.85	1.70	3.13	1.59
Ethyl chloride	64.52	285.37	460.40	52.00	6.4421	0.1903	6.782	0.829	29	0.52	0.43	0.47	0.49	0.44	0.61	0.63	1.25	0.32
Chloroform	119.39	334.35	536.60	54.00	6.5944	0.2055	6.603	0.876	46	2.09	2.64	2.11	2.16	2.08	1.95	2.43	3.65	2.07
Fluorobenzene	96.10	358.20	559.80	44.60	6.7478	0.2487	6.950	0.856	32	0.62	0.91	0.52	0.55	0.55	0.50	1.36	2.17	0.62
Chlorobenzene	112.56	404.86	632.40	44.60	6.7573	0.2511	7.189	0.833	69	0.91	0.86	0.70	0.74	0.69	0.86	1.29	1.44	0.74
Piperidine	85.15	379.37	594.00	44.10	6.6927	0.2283	6.837	0.869	22	3.65	2.35	3.15	3.06	3.28	2.83	4.00	3.88	3.39
Aniline	93.12	457.30	698.80	52.60	7.5037	0.3836	7.390	0.917	44	1.26	2.59	1.24	1.39	0.89	1.31	0.55	4.21	1.04
Hydrogen chloride	36.49	188.20	324.60	81.50	6.0718	0.1248	6.529	0.790	48	1.42	0.82	1.13	1.10	1.14	1.27	0.74	0.64	0.98
Hydrogen sulfide	34.08	211.60	373.60	88.90	5.8615	0.0684	6.164	0.838	31	8.17	7.95	8.29	8.44	8.27	8.12	8.95	10.69	8.65
Sulfur dioxide	64.06	263.19	430.70	77.80	6.8412	0.2561	7.096	0.844	58	1.48	0.86	0.86	0.94	0.77	0.81	1.14	3.33	0.70
Hydrogen bonding																		
Water	18.02	373.15	647.31	218.17	7.3297	0.3438	7.589	0.835	79	7.65	4.76	5.70	5.96	5.23	4.53	1.14	12.57	4.95
Methanol	32.04	337.66	512.64	79.91	8.4539	0.5647	8.438	0.899	74	6.24	5.00	4.32	4.26	3.40	4.19	2.97	6.46	3.75
Ethanol	46.07	351.47	513.92	60.68	8.8828	0.6455	8.295	—	78	3.15	4.15	2.03	1.79	1.63	1.53	1.49	1.65	1.45
1-Propanol	60.09	370.36	536.71	51.02	8.7548	0.6211	7.943	—	73	1.82	0.74	3.53	3.75	5.16	3.49	4.06	5.42	4.13
1-Butanol	74.12	390.88	562.98	43.55	8.5717	0.5905	7.775	—	75	4.53	1.62	5.85	5.96	7.28	5.64	6.11	9.77	6.28
1-Pentanol	88.15	411.13	582.90	38.30	8.7256	0.6294	8.664	0.913	67	3.29	3.18	4.53	4.77	6.36	4.35	4.43	10.33	5.16

Table 2. Physical Properties and Summary of Deviations Resulting from Different Methods Used in the Estimation of Vapor Pressures for Saturated Alkanes

										Average percent deviation								
										Present study					Methods available in literature			
Normal alkanes	M	T_b, °K	T_c, °K	P_c, atm	s	ω	α_c	T_{Ri}	No. of points	Method A	Method B	Method C	Method D	Method E	Riedel	R-P-M	T-S	Z-T
Methane	16.04	111.67	191.04	46.06	5.3885	0.0077	5.886	0.741	182	0.30	0.25	0.28	0.22	0.28	0.65	0.63	1.41	0.24
Ethane	30.07	184.53	305.43	48.20	5.9151	0.0958	6.295	0.802	138	0.67	0.64	0.63	0.57	0.64	0.83	0.84	1.03	0.49
Propane	44.09	231.10	369.98	42.01	6.2199	0.1511	6.567	0.821	160	0.72	0.73	0.70	0.69	0.70	0.85	0.71	0.99	0.60
Butane	58.12	272.65	425.17	37.47	6.4773	0.1985	6.779	0.835	104	0.58	0.68	0.60	0.61	0.58	0.70	0.59	0.83	0.54
Pentane	72.15	309.22	469.78	33.31	6.7520	0.2526	7.150	0.834	127	0.75	0.63	0.88	0.97	0.75	1.18	0.50	1.05	0.78
Hexane	86.17	341.89	507.86	29.94	7.0019	0.3008	7.416	0.842	152	0.63	0.69	0.76	0.89	0.63	1.07	0.67	0.70	0.72
Heptane	100.20	371.59	540.17	27.00	7.2647	0.3509	7.663	0.850	155	0.46	0.39	0.52	0.67	0.40	0.98	0.42	0.37	0.46
Octane	114.22	398.82	569.37	24.64	7.4936	0.3957	7.751	0.870	133	1.58	0.59	0.45	0.48	1.29	0.64	0.49	1.47	0.53
Nonane	128.25	423.95	593.80	22.60	7.7824	0.4517	8.175	0.861	51	0.65	0.05	0.45	0.62	0.46	1.19	1.24	0.73	0.32
Decane	142.28	447.27	616.10	20.73	8.0316	0.5011	8.489	0.861	50	1.08	0.41	0.43	0.52	0.75	1.17	1.65	1.06	0.29
Undecane	156.30	469.04	636.00	19.18	8.2983	0.5539	8.756	0.865	50	1.15	0.05	0.84	0.85	0.66	1.61	2.59	1.17	0.58
Dodecane	170.33	489.44	653.90	17.83	8.5739	0.6073	9.157	0.860	52	1.16	0.23	1.42	1.28	0.49	2.14	3.68	1.19	1.03
Tridecane	184.36	508.59	670.10	16.64	8.8543	0.6614	9.470	0.860	45	1.20	0.34	2.19	1.83	0.31	2.78	5.01	1.22	1.58
Tetradecane	198.38	526.72	684.90	15.58	9.1438	0.7150	9.982	0.852	42	1.09	0.39	3.03	2.38	0.17	3.36	6.11	1.08	2.16
Pentadecane	212.41	543.78	698.20	14.64	9.4507	0.7708	10.485	0.847	41	1.08	0.75	4.20	3.08	0.39	4.17	7.66	1.03	2.88
Hexadecane	226.44	559.94	710.40	13.79	9.7653	0.8260	10.915	0.844	47	0.72	0.10	6.10	4.34	0.74	5.57	9.88	0.73	4.16
Heptadecane	240.46	574.97	721.30	13.14	10.1209	0.8847	11.549	0.838	31	0.46	0.25	7.51	5.05	0.87	6.16	10.84	1.00	4.88
Octadecane	254.49	589.27	731.20	12.31	10.4228	0.9361	12.053	0.837	31	0.38	0.44	8.98	5.67	0.32	6.84	12.17	1.31	5.53
Nonadecane	268.51	602.85	740.30	11.67	10.7764	0.9892	12.664	0.833	31	0.81	0.48	11.43	6.97	1.34	8.16	14.08	2.10	6.85
Eicosane	282.54	615.85	748.70	11.09	11.1536	1.0471	13.291	0.831	31	1.70	1.08	14.07	8.14	5.10	9.35	15.89	3.09	8.03
iso-alkanes																		
2-methylpropane	58.12	261.42	409.20	36.36	6.3566	0.1787	6.885	0.814	40	0.14	0.89	0.16	0.17	0.15	0.42	0.53	2.02	0.17
2-methylbutane	72.15	301.00	460.56	33.48	6.6232	0.2288	7.150	0.820	51	0.53	0.26	0.77	0.85	0.65	1.08	0.21	1.99	0.61
2,2-dimethylpropane	72.15	282.65	433.00	31.74	6.5000	0.2060	6.950	0.823	21	0.07	0.02	0.13	0.14	0.12	0.27	0.03	0.65	0.09
2-methylpentane	86.17	333.42	498.70	29.98	6.8599	0.2723	7.257	0.841	45	0.30	0.24	0.08	0.18	0.12	0.45	0.32	1.02	0.06
3-methylpentane	86.17	336.43	504.01	31.30	6.9136	0.2841	7.517	0.821	45	1.02	0.05	1.30	1.42	1.09	1.64	0.87	1.43	1.18
2,2-dimethylbutane	86.17	322.89	486.14	31.04	6.7946	0.2646	7.659	0.798	51	2.47	0.29	2.83	2.96	2.63	3.19	2.28	3.91	2.69
2,3-dimethylbutane	86.17	331.14	500.52	31.43	6.7402	0.2510	7.274	0.824	44	0.30	0.19	0.71	0.80	0.57	1.03	0.26	2.04	0.59
2-methylhexane	100.20	363.20	532.20	27.09	7.0904	0.3162	7.349	0.862	51	1.13	0.06	0.45	0.28	0.81	0.19	0.64	0.56	0.56
3-methylhexane	100.20	365.00	535.42	28.05	7.1408	0.3264	7.597	0.841	51	0.24	0.06	0.80	0.97	0.41	1.31	0.57	0.93	0.68
3-ethylpentane	100.20	366.62	541.10	29.21	7.0908	0.3168	7.584	0.836	49	0.31	0.09	0.88	1.05	0.53	1.37	0.56	0.97	0.75
2,2-dimethylpentane	100.20	352.35	519.76	27.90	7.0058	0.3020	7.619	0.824	49	0.77	0.20	1.32	1.47	1.04	1.80	1.05	2.38	1.21
2,3-dimethylpentane	100.20	362.93	537.87	29.28	7.0060	0.3011	7.524	0.832	51	0.38	0.07	1.01	1.17	0.71	1.48	0.65	1.75	0.88
2,4-dimethylpentane	100.20	353.65	522.27	27.10	6.9203	0.2834	7.160	0.863	50	1.82	0.52	1.05	0.91	1.31	0.53	1.33	1.29	1.17
3,3-dimethylpentane	100.20	359.21	531.52	29.99	7.0900	0.3207	8.120	0.792	50	3.86	0.44	4.26	4.42	3.94	4.68	3.92	3.89	4.14
2,2,3-trimethylbutane	100.20	354.03	528.66	30.03	6.8976	0.2836	7.723	0.802	50	2.23	0.15	2.81	2.94	2.58	3.23	2.39	3.97	2.68
2-methylheptane	114.22	390.80	561.96	24.69	7.3208	0.3614	7.437	0.885	51	1.72	0.49	0.75	0.56	1.27	0.11	0.61	0.10	0.84
3-methylheptane	114.22	392.08	564.02	25.42	7.3778	0.3792	7.745	0.855	51	0.42	0.15	0.41	0.59	0.15	1.03	0.54	0.34	0.30
4-methylheptane	114.22	390.86	562.01	25.33	7.3808	0.3729	7.729	0.857	31	0.42	0.21	0.35	0.53	0.18	0.88	0.48	0.24	0.26
3-ethylhexane	114.22	391.68	566.60	26.22	7.3144	0.3598	7.709	0.852	31	0.48	0.09	0.31	0.49	0.17	0.81	0.31	0.31	0.21
2,2-dimethylhexane	114.22	379.99	550.27	25.35	7.2143	0.3412	7.645	0.847	31	0.50	0.24	0.34	0.52	0.08	0.86	0.33	1.36	0.26
2,3-dimethylhexane	114.22	388.76	564.97	26.35	7.2174	0.3412	7.584	0.852	31	0.67	0.03	0.20	0.38	0.22	0.69	0.15	0.88	0.11
2,4-dimethylhexane	114.22	382.58	554.56	25.43	7.1985	0.3378	7.520	0.858	31	1.06	0.13	0.17	0.04	0.58	0.36	0.19	1.02	0.25
2,5-dimethylhexane	114.22	382.25	554.07	24.76	7.1397	0.3961	7.257	0.884	31	2.68	0.41	1.62	1.45	2.01	1.07	1.64	0.48	1.70
3,3-dimethylhexane	114.22	385.12	558.81	26.91	7.3004	0.3584	8.111	0.813	31	2.33	0.32	2.96	3.14	2.51	3.42	2.91	2.62	2.87
3,4-dimethylhexane	114.22	390.87	568.53	27.24	7.2709	0.3517	7.797	0.836	31	0.68	0.30	1.41	1.59	0.97	1.87	1.31	1.26	1.31
2-methyl, 3-ethylpentane	114.22	388.80	568.30	27.24	7.1578	0.3998	7.612	0.843	31	0.35	0.18	0.52	0.69	0.14	0.98	0.35	1.28	0.43
3-methyl, 3-ethylpentane	114.22	391.41	572.71	28.74	7.2501	0.3497	8.164	0.801	31	3.35	0.86	3.97	4.14	3.57	4.37	3.77	3.38	3.88
2,2,3-trimethylpentane	114.22	382.99	561.68	27.96	7.1390	0.3280	7.934	0.812	31	1.73	0.06	2.47	2.63	2.11	2.88	2.24	2.93	2.37
2,2,4-trimethylpentane	114.22	372.39	543.64	25.49	7.0417	0.3087	7.500	0.838	51	0.15	0.13	0.85	1.01	0.52	1.43	0.73	3.31	0.75
2,3,4-trimethylpentane	114.22	386.62	567.91	27.46	7.0648	0.3120	7.464	0.845	51	0.48	0.13	0.52	0.69	0.19	1.05	0.30	2.07	0.41

TABLE 3. PHYSICAL PROPERTIES AND SUMMARY OF DEVIATIONS RESULTING FROM DIFFERENT METHODS USED IN THE ESTIMATION OF VAPOR PRESSURES FOR MONOOLEFINS, DIOLEFINS, ACETYLENES, NAPHTHENES, AND AROMATICS

										Average percent deviation								
										Present study					Methods available in literature			
	M	T_b, °K	T_c, °K	P_c, atm	s	ω	α_c	T_{Ri}	No. of points	Method A	Method B	Method C	Method D	Method E	Riedel	R-P-M	T-S	Z-T
Monoölefins																		
Ethene	28.05	169.44	283.10	50.50	5.8467	0.0826	6.271	0.802	82	0.46	0.65	0.55	0.67	0.53	0.39	0.70	0.35	0.78
Propene	42.08	225.45	365.00	45.60	6.1712	0.1419	6.582	0.816	61	0.29	0.43	0.28	0.30	0.28	0.44	0.73	0.35	0.43
1-butene	56.10	266.89	419.60	39.70	6.4337	0.1902	6.799	0.829	61	0.27	0.22	0.27	0.29	0.24	0.53	0.65	0.47	0.18
2cis-butene	56.10	276.89	430.20	41.00	6.7067	0.2481	7.601	0.792	44	3.04	0.23	2.78	2.89	2.64	2.91	1.84	0.38	2.60
2trans-butene	56.10	274.03	430.20	41.00	6.5162	0.2105	7.213	0.801	46	1.74	0.33	1.67	1.74	1.59	1.87	0.81	0.83	1.45
1-pentene	70.13	303.12	464.20	34.95	6.6876	0.2407	7.234	0.820	39	0.66	0.14	0.76	0.84	0.65	0.98	0.22	0.86	0.64
2cis-pentene	70.13	310.09	474.80	35.95	6.7440	0.2494	7.215	0.830	45	0.22	0.33	0.31	0.40	0.17	0.57	0.30	0.16	0.17
2trans-pentene	70.13	309.50	473.90	35.88	6.7403	0.2483	7.114	0.837	45	0.36	0.25	0.45	0.54	0.31	0.71	0.15	0.10	0.31
1-hexene	84.16	336.64	503.80	31.22	6.9295	0.2856	7.390	0.835	44	0.31	0.05	0.58	0.71	0.37	0.94	0.16	0.63	0.47
1-heptene	98.18	366.79	537.50	28.11	7.1683	0.3311	7.500	0.853	51	0.18	0.44	0.51	0.73	0.11	1.03	0.25	0.35	0.39
1-octene	112.21	394.43	566.80	25.50	7.4111	0.3785	7.714	0.862	49	0.55	0.39	0.29	0.47	0.32	0.91	0.45	0.11	0.18
Diolefins																		
Propadiene	40.06	238.65	385.37	52.47	6.4418	0.1888	6.810	0.822	31	4.99	4.73	4.82	4.84	4.81	4.98	4.52	4.36	4.67
1,2-butadiene	54.09	284.00	445.99	45.56	6.6956	0.2428	6.981	0.821	31	4.21	4.09	3.97	4.07	3.86	4.01	3.03	1.14	3.79
1,3-butadiene	54.09	268.74	425.20	42.70	6.4481	0.1945	7.004	0.812	60	1.08	0.63	1.00	1.06	0.93	1.16	0.57	0.54	0.85
1,2-pentadiene	68.12	318.01	486.92	39.07	6.9007	0.2803	7.400	0.822	31	2.38	1.38	2.28	2.42	2.07	2.44	1.47	0.22	2.12
1,3cis-pentadiene	68.12	317.22	485.71	38.34	6.8652	0.2739	7.459	0.817	31	1.80	0.40	1.75	1.89	1.56	1.93	0.96	0.32	1.60
1,3trans-pentadiene	68.12	315.18	482.61	38.09	6.8520	0.2730	7.547	0.808	31	2.37	0.49	2.33	2.46	2.14	2.50	1.55	0.40	2.18
1,4-pentadiene	68.12	299.12	458.00	36.70	6.7826	0.2579	7.241	0.824	43	2.54	1.63	2.46	2.61	2.25	2.61	1.48	0.67	2.31
2,3-pentadiene	68.12	321.42	492.12	39.72	6.9324	0.2859	7.703	0.815	31	0.93	1.48	0.81	0.96	0.58	0.96	0.29	2.10	0.64
Acetylenes																		
Ethyne	26.04	188.42	309.65	61.60	6.4046	0.1823	7.057	0.810	42	0.80	0.74	0.57	0.58	0.57	0.68	0.63	1.30	0.51
Propyne	40.06	249.94	394.75	47.63	6.6683	0.2251	6.863	0.857	33	1.07	1.03	1.41	1.34	1.51	1.41	2.48	5.37	1.57
1-butyne	54.09	281.23	441.63	43.96	6.6334	0.2166	6.421	0.942	45	2.57	0.46	2.81	2.69	2.95	2.77	4.13	6.06	3.05
2-butyne	54.09	300.12	471.33	47.25	6.7585	0.2487	7.018	0.846	27	0.84	0.82	0.66	0.74	0.55	0.80	0.21	1.88	0.48
1-pentyne	68.12	313.32	479.76	37.68	6.8319	0.2595	6.902	0.881	28	1.94	0.66	1.97	1.82	2.18	1.75	2.84	3.94	2.15
2-pentyne	68.12	329.21	504.06	39.82	6.9370	0.2811	7.089	0.866	28	0.94	1.49	0.91	0.98	0.81	0.96	0.79	2.75	0.84
Naphthenes																		
Cyclopropane	42.08	240.30	406.70	57.20	5.8437	0.0683	5.789	0.889	14	4.33	1.61	4.05	4.28	4.05	3.60	4.03	1.67	4.53
Cyclobutane	56.10	284.60	464.40	50.29	6.2014	0.1579	6.622	0.820	22	5.74	5.93	5.38	5.46	5.40	5.25	6.54	4.49	5.83
Cyclopentane	70.13	322.41	512.10	44.60	6.4550	0.1916	6.702	0.843	58	0.39	0.44	0.19	0.21	0.19	0.27	1.01	0.27	0.30
Methylcyclopentane	84.16	344.96	534.20	37.54	6.6087	0.2226	7.027	0.834	47	0.96	0.88	0.48	0.40	0.58	0.27	1.14	0.49	0.65
Ethylcyclopentane	98.18	376.62	570.80	33.66	6.8198	0.2630	7.173	0.844	51	0.95	0.31	0.16	0.04	0.36	0.28	0.79	0.88	0.32
Cyclohexane	84.16	353.89	553.20	40.00	6.5498	0.2101	6.878	0.840	108	1.05	0.62	0.63	0.61	0.68	0.52	1.20	0.53	0.75
Methylcyclohexane	98.18	374.08	570.90	34.18	6.7125	0.2447	7.243	0.824	51	0.39	0.59	0.48	0.59	0.33	0.83	0.16	2.32	0.31
Ethylcyclohexane	112.21	404.93	603.40	30.90	6.9998	0.2992	7.494	0.833	38	0.15	0.04	0.85	1.00	0.57	1.21	0.41	1.73	0.73
Cycloheptane	98.18	391.94	588.40	36.10	7.1549	0.3346	8.474	0.783	16	2.76	0.17	2.98	3.07	2.77	3.34	2.64	1.88	2.88
Cyclooctane	112.21	424.30	620.20	32.90	7.5663	0.4117	9.443	0.773	16	4.42	0.45	4.65	4.74	4.26	5.06	4.50	2.89	4.55
Aromatics																		
Benzene	78.11	353.25	562.20	48.60	6.5656	0.2123	7.013	0.829	143	0.66	0.80	0.53	0.50	0.57	0.59	1.04	1.08	0.65
Toluene	92.13	383.78	593.50	41.56	6.8205	0.2569	6.769	0.902	108	0.63	1.87	0.85	0.92	0.76	0.96	0.67	0.87	0.73
Ethylbenzene	106.16	409.33	616.10	36.51	7.1222	0.3220	7.759	0.823	51	1.22	0.08	1.81	1.99	1.46	2.11	1.13	0.25	1.64
o-xylene	106.16	417.56	632.10	36.83	7.0191	0.2990	7.313	0.853	51	0.64	0.25	0.19	0.34	0.13	0.46	0.57	0.95	0.09
m-xylene	106.16	412.25	625.10	35.91	6.9358	0.2806	6.956	0.891	51	2.22	0.27	1.29	1.13	1.55	0.97	2.01	1.45	1.47
p-xylene	106.16	411.50	618.20	35.01	7.0787	0.3119	7.439	0.846	51	0.10	0.50	0.78	0.95	0.45	1.12	0.17	0.36	0.61
Naphthalene	128.16	491.10	749.70	39.20	6.9673	0.2898	7.666	0.826	47	2.49	2.92	0.85	0.70	1.10	0.75	1.69	1.05	1.03
1-methylnaphthalene	142.19	517.79	764.30	34.49	7.4372	0.3811	7.934	0.838	48	0.42	1.04	2.09	2.28	1.54	2.44	1.66	0.16	1.91
2-methylnaphthalene	142.19	514.20	764.30	34.49	7.2796	0.3488	7.478	0.868	48	1.70	0.87	0.35	0.53	0.18	0.68	0.23	0.79	0.23

in Table 3 for unsaturated hydrocarbons including naphthenes and aromatics.

So far, no significance has been attached to the inflection point of the vapor pressure function when represented as ln P_R vs. $1/T_R$. An a priori consideration of this point suggests that it could well represent an additional third correlating parameter to complement the existing ω, α_c, and z_c parameters. In order to establish this point, the second derivative of Equation (9) with respect to $1/T_R$ is equated to zero to yield

$$T_{Ri} = \left[-\beta \frac{m(m-1)}{56\gamma} \right]^{\frac{1}{m+7}} \tag{12}$$

Using the original values of constants β and γ and exponent m with Equation (12), the reduced temperature at the inflection point T_{Ri} was calculated and is reported in Tables 1, 2, and 3 for each substance included in this study. Since it is not the intent of this investigation to pursue a study of third correlating parameters, no further involvement will be dealt with this inflection point, except the reporting of the best estimate of this value for each substance.

GENERALIZED TREATMENT OF THE VAPOR PRESSURE FUNCTION

The vapor pressure function expressed through Equation (9), when applied at the critical point, yields the condition that $\alpha + \beta + \gamma = 0$. This condition permits the elimination of α from Equation (9) to express this relationship as follows:

$$\ln P_R = \beta \left[\frac{1}{T_R^m} - 1 \right] + \gamma [T_R^7 - 1] \tag{13}$$

The generalized application of Equation (13) requires that parameters β, γ, and m be established from properties associated with the vapor pressure function. In this connection, the normal boiling point can be used to evaluate one of these three parameters. The remaining two parameters must then be obtained from additional information associated with the vapor pressure function or specific correlations capable of predicting these parameters using as an independent variable a property of the substance. This analysis in its comprehensive treatment requires the involvement of several schemes, each of which must be tested extensively in order to establish approaches capable of producing the prediction of vapor pressures with minimum deviations.

In this analysis, the normal boiling point has been used as a condition to be satisfied by the vapor pressure equation. Since β is the coefficient of the term associated with the reciprocal reduced temperature, this term contributes most significantly to the vapor pressure function in the low pressure region, and therefore the involvement of the normal boiling point to establish this parameter properly extends the application of the function in the low pressure region. Therefore, the involvement of the normal boiling point leaves parameters m and γ to be established. Parameter m has been found to depend on the characterization parameter $s = T_b \ln P_c/(T_c - T_b)$ in the following manner:

$$m = 2.4186 - \frac{7.0109}{s} + \frac{380{,}900}{s e^{123.21/s}} \tag{14}$$

Therefore, the application of the normal boiling point condition with a capability for predicting parameter m leaves parameter γ to be established. In this connection, it should be noted that since parameter γ is associated with the high pressure region of the vapor pressure function, this parameter should be evaluated from high vapor pressure information. Therefore, several approaches for the estimation of γ are considered and are presented in the following schemes of correlation.

Method A

Using semitheoretical arguments, Frost and Kalkwarf (1953) indicate that the vapor pressure function in the high pressure region can be associated with the van der Waals constant $a = 27R^2T_c^2/64P_c$. This suggests that parameter γ could be related to the ratio T_c^2/P_c. From this critical state ratio for all the substances of this study, including helium and hydrogen, the following dependence was found:

$$\gamma = 0.0016 \left[4\,872.2 + \frac{T_c^2}{P_c} \right]^{1/2} + 3.864 \times 10^{-5} \left[\frac{T_c^2}{P_c} \right]^3 - \frac{0.13}{e^{0.187M}} \tag{15}$$

The term $0.13/e^{0.187M}$ of Equation (15) is of significance only with the quantum gases, helium, hydrogen, and neon, and can be ordinarily neglected. Values of γ calculated with the use of Equation (15) and values for the parameter m obtained through Equation (14), in conjunction with the normal boiling point condition to evaluate β, were used to establish the parameters of the vapor pressure Equation (13). Using these parameters, vapor pressures were calculated and compared with corresponding experimental values reported in the literature to produce an overall average deviation of 1.43% (7 633 points) for 138 substances included in this study. The percent average deviation for each substance and the number of literature values considered in these comparisons are summarized in Tables 1, 2, and 3.

Method B

This approach utilizes the Riedel parameter α_c to evaluate parameter γ through the expression

$$\gamma = \frac{\alpha_c + m\beta}{7} \tag{16}$$

where values of α_c used are those reported in Tables 1, 2, and 3, parameter m was calculated from Equation (14), and parameter β was established from the normal boiling point condition. The vapor pressure parameters, thus derived, were used to calculate vapor pressures which when compared with corresponding experimental values produced an overall average deviation of 1.05% (7 633 points) for the 138 substances considered. Specific percent average deviations, resulting from this approach are included for each substance in Tables 1, 2, and 3.

Method C

The Riedel-Plank restriction, $[d^2 \ln P_R/d(\ln T_R)^2]_c = 0$, when applied to Equation (13), produces for γ the relation

$$\gamma = -\beta \left(\frac{m}{7} \right)^2 \tag{17}$$

If we use Equation (17) for parameter γ, Equation (14) for parameter m and the normal boiling point condition for parameter β, vapor pressures are again calculated and compared with corresponding experimental values to obtain an overall average deviation of 1.58% (7 633 points) for all the 138 substances included in this study. Individual deviations for each substance are presented in Tables 1, 2, and 3.

Method D

This approach utilizes the Riedel-Plank restriction that produces Equation (17). In addition, the involvement of the normal boiling point with Equation (17) expresses Equation (13) in terms of parameter m only. A non-linear regression was applied to this expression to obtain values of m compatible with these restrictions. These new values of m were then correlated with parameter s to yield the following simpler relationship:

$$m = 2.4889 - \frac{7.4539}{s} \qquad (18)$$

If we use Equation (18) for the estimation of parameter m and Equation (17) for parameter γ in conjunction with the normal boiling point condition for parameter β, vapor pressures are calculated and compared with corresponding experimental measurements to produce an overall average deviation of 1.55% (7 633 points) for all the 138 substances considered in this study. Again, the individual average deviations are presented in Tables 1, 2, and 3.

Method E

Since method D does not exhibit an improvement over method C, and since both methods utilize the same restrictions to calculate parameters β and γ, it can be concluded that Equation (18) does not offer a significant improvement over Equation (14) for the evaluation of parameter m. Also, it can be deduced that if any improvement is to be realized, it will require a modification of the Riedel-Plank restriction expressed through Equation (17). A plot of $49\gamma/\beta$ vs. m^2 exhibited a nonlinear dependence which can be represented mathematically as

$$\gamma = -\frac{\beta}{49}\left[1 + 0.165m^{5.52}\right] - \frac{2.07}{M^{2.18}} \qquad (19)$$

If we use Equation (19) to calculate parameter γ and Equation (14) to calculate parameter m in conjunction with the normal boiling point condition, vapor pressures are calculated and compared with corresponding experimental values to produce an overall average deviation of 1.42% (7 633 points) for all the substances included in this study. Once more, the individual deviations associated with each substance are presented in Tables 1, 2, and 3.

COMPARISON WITH OTHER VAPOR PRESSURE EQUATIONS

The results of this study have been compared with those produced by methods available in the literature considered to be most reliable. In this regard, the methods of Riedel (1954), Miller (1964), Thek and Stiel (1966), and Zia and Thodos (1974) have been selected for comparison. The equation of Frost and Kalkwarf (1953) has been excluded from this evaluation since their method has not been generalized and also because of its implicit nature in pressure.

The method for applying in a generalized manner the Riedel equation [Equation (5)] is outlined by Reid and Sherwood (1966). This approach has been adopted in these comparative evaluations using the 7 633 points representing the vapor pressure behavior of the 138 substances to produce for this comparison an overall average deviation of 1.71%. The average deviation associated with each substance is presented in Tables 1, 2, and 3.

The method of Miller (1964) is based on the form of the vapor pressure function expressed by Equation (6) and utilizes the same conditions and restrictions postulated by Plank and Riedel (1948). Because of this involvement, Reid and Sherwood (1966) coin the resulting expression as the Riedel-Plank-Miller equation and suggest details for its application. Following this approach, vapor pressures calculated with this equation were compared again with experimental values to produce the deviations included in Tables 1, 2, and 3. This method yields an overall deviation of 3.39% (7 633 points) for the 138 substances of this study.

The approach suggested by Thek and Stiel (1966) has also been included in this comparison. Their method utilizes the vapor pressure function expressed by Equation (7). Thek and Stiel (1966) suggest a procedure which was used for the evaluation of the constants of this equation. Using their recommended procedure, values of vapor pressure were calculated and compared with experimental measurements to produce an overall average deviation of 2.28% (7 633 points) for the 138 substances included in this study. Specific deviations associated with each substance are given in Tables 1, 2, and 3.

A final comparison involves the use of the vapor pressure equation of Zia and Thodos (1974) expressed through the form given by Equation (8). Using an interlocking relationship between coefficients C and D for this equation, coupled with the Riedel-Plank restriction at the critical point $[d^2 \ln P_R / d(\ln T_R)^2]_c = 0$, the resulting generalized form derived from Equation (8) was applied to the calculation of vapor pressures which, when compared with corresponding experimental values, produced the average deviations presented for each substance in Tables 1, 2, and 3. For the 138 substances, an overall average deviation of 1.52% (7 633 points) resulted from the use of this approach.

GENERAL COMMENTS

The methods developed within the framework of this study and those available in the literature have produced average deviations for the substances included in this study that make possible an appraisal of the merits associated with each of them. Methods A, B, C, D, and E structure criteria for the capability of Equation (9) to represent the vapor pressure behavior of substances over their complete region included between the triple point and the critical point. The various restrictions applied to the evaluation of the constants of this equation establish the procedure already outlined for each method. The comparisons indicate that method B is capable of producing minimum deviations (overall average deviation = 1.05%); however, this method requires that the Riedel parameter α_c be available with a high degree of accuracy. Methods A and E produce deviations of 1.43 and 1.42%, respectively. These deviations are slightly smaller than those encountered with methods C and D which were found to be 1.58 and 1.55%, respectively.

The methods already available in the literature, which were considered in these comparisons, produced overall average deviations that ranged from 1.52% for the Zia-Thodos method (Z-T) to 3.39% for the Riedel-Plank-Miller method (R-P-M). If the excessive deviation of 228.22% due to helium is excluded from the evaluation of the Riedel-Plank-Miller method, the overall average deviation reduces from 3.39% (7 633 points) to 1.70% (7 576 points) to produce a deviation comparable to that obtained from the Riedel method, 1.71% (7 633 points). The Thek-Stiel method (T-S) produced an overall average deviation of 2.28% (7 633 points). Again, if helium is

Table 4. Summary of Average Deviations According to Classes of Substances

			Average percent deviation								
			Present study					Methods available in literature			
	No. of substances	No. of points	Method A	Method B	Method C	Method D	Method E	Riedel	R-P-M	T-S	Z-T
Monatomic	5	459	0.52	0.42	0.38	0.48	0.68	1.17	28.79	6.05	1.62
Diatomic	8	608	1.55	1.84	1.50	1.60	2.27	1.57	1.70	3.39	1.61
Polyatomic	5	232	2.28	1.48	2.51	2.46	2.61	2.47	2.99	2.44	2.51
Polar	19	897	2.32	2.17	1.96	2.02	1.86	2.01	1.84	2.61	1.85
Hydrogen bonding	6	446	4.50	3.27	4.32	4.41	4.80	3.94	3.31	7.67	4.26
n-alkanes	20	1653	0.78	0.50	1.71	1.33	0.70	1.78	2.46	1.06	1.20
i-alkanes	31	1260	1.08	0.24	1.19	1.27	1.05	1.48	1.04	1.73	1.12
Monoölefins	11	567	0.68	0.34	0.72	0.82	0.62	0.95	0.58	0.41	0.67
Diolefins	8	289	2.39	1.72	2.29	2.39	2.14	2.43	1.61	1.13	2.13
Acetylenes	6	203	1.42	0.83	1.46	1.42	1.50	1.46	1.98	3.66	1.51
Naphthenes	10	421	1.32	0.82	1.10	1.12	1.08	1.16	1.47	1.24	1.19
Aromatics	9	598	0.99	1.01	0.89	0.94	0.80	1.02	0.99	0.83	0.86
Nonhydrocarbons	43	2642	2.19	1.91	2.03	2.10	2.31	2.13	6.84	4.22	2.22
Hydrocarbons	95	4991	1.03	0.59	1.34	1.26	0.94	1.49	1.56	1.25	1.14
Overall	138	7633	1.43	1.05	1.58	1.55	1.42	1.71	3.39	2.28	1.52

excluded from consideration, the average deviation for this method reduces to 1.96% (7 576 points).

In order to form an opinion on the capability of each of these methods to estimate vapor pressures for substances corresponding to their respective classification, the results included in Tables 1, 2, and 3 have been summarized into Table 4. This table presents the gross average deviations associated with different classes of compounds and thus assists in a broad sense to assess the capability of each method to estimate vapor pressures for each class of compounds.

A cursory review of the deviations presented in Table 4 indicates that the methods developed in this study and those available in the literature produce consistent trends, with the exception of the monatomic substances. For certain classes of compounds all methods yield low deviations, while for other classes all methods produce relatively higher deviations. For example, the hydrogen bonding substances produce the highest deviations for all methods developed in this study and all the literature methods considered in this comparison. This result could well be explained by the inherently different behavior of hydrogen bonding substances and possibly due to the fact that for some of them the existence of an inflection point is not apparent. Of the classes of compounds, the groups included within the classifications of polyatomic, polar, and diolefins also reflect relatively higher deviations, while the remaining groups exhibit lower deviations for all methods. In general, the methods developed in this study yield average deviations that range between 1.4 to 1.6%, while those already available in the literature produce average deviations that range between 1.5 to 2.0%.

NOTATION

a = van der Waals constant, $27R^2T_c^2/64P_c$
a, b, c = coefficients, Equation (4)
A = coefficient, Equation (1)
A, B, C = coefficients, Equation (2)
A, B, C, D = coefficients Equations (3), (5), (6), (8)
A, B, C, D, E, F = coefficients, Equation (7)
b = parameter, Equation (1)
m = exponent, Equation (9)
M = molecular weight
n = exponent, Equation (7)
P = vapor pressure, atm
P_c = critical pressure, atm
P_R = reduced pressure, P/P_c
R = gas constant
s = characterization parameter, $T_b \ln P_c/(T_c - T_b)$
T = absolute temperature, °K
T_b = normal boiling point, °K
T_c = critical temperature, °K
T_R = reduced temperature, T/T_c
T_{Ri} = reduced temperature of inflection point
v_c = critical molar volume, cm^3/mole
z_c = critical compressibility factor, P_cv_c/RT_c
α = Riedel parameter, $d \ln P_R/d \ln T_R$
α_c = Riedel parameter at critical point, $(d \ln P_R/d \ln T_R)_c$
α, β, γ = coefficient, Equation (9)
ω = Pitzer acentric factor, Equation (10)

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Gas Backmixing, Solids Movement, and Bubble Activities in Large Scale Fluidized Beds

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This paper illustrates the interrelation between bubbles, solids movement, and gas backmixing in large fluidized beds by presenting experimental data obtained with a 1.22 m square bed. The results demonstrate a close relationship between gas backmixing, solids movement, and bubble coalescence, with the behavior altering markedly as bubble coalescence patterns change.

SCOPE

Fluidization is attracting a high degree of interest, but detailed research into gas and solids mixing within the bed is lacking, particularly on a large scale.

Some progress, however, has been recently achieved with small scale equipment. In beds up to 30 cm in diameter, the phenomenon of gas backmixing has been experimentally studied in both reactive and nonreactive systems (Nguyen and Potter, 1974, 1975; Fryer and Potter, 1976). These studies reveal the important role that bubbles play in the overall gas and solid movement in the bed through their coalescence, size variation, and distribution. Experimental data showed that the countercurrent backmixing model provides an acceptable description of a fluidized bed. This model, incorporating the bubble wake, represents a significant forward step from other earlier one- or two-phase models which assume perfect mixing or plug flow in the dense phase.

Nevertheless, as reviewed by Potter (1971), information on systems of industrial size is sketchy and incomplete, uncomfortably so at this time when fluidization is assuming major importance in coal combustion and liquid fuel processes.

This paper reports experimental data on gas backmixing in a large fluidized bed operated at two fluidizing velocities. Together with information on solids circulation patterns and bubble distribution, these data provide a much more complete picture of the overall gas and solids movement within the bed than has hitherto been available.

CONCLUSIONS AND SIGNIFICANCE

Tracer studies in the large fluidized bed employed exhibit backmixing at about the level predicted by the countercurrent backmixing model. The downward movement of solids which is the dominant feature of the model certainly occurs and does so at about the expected order of magnitude.

The solids movement is shown to be clearly related to the bubble pattern and gas movement in the particulate phase related to the solids movement. Modeling of the bubble patterns, therefore, becomes considerably important. If the stable bubble pattern in the upper region of the bed is such as to leave a persistent central area rela-