A Reduced State Vapor-Pressure Relationship and its Application to Hydrocarbons

ENRIQUE G. REYNES and GEORGE THODOS

The Technological Institute, Northwestern University, Evanston, Illinois

The Frost-Kalkwarf vapor-pressure equation has been modified to include as variables the reduced temperature and pressure of the substance. The resulting relationship was found to contain a universal constant $\delta = 0.1832$ and three other constants α, β, and γ, which are characteristic of the substance. Relationships between α, β, and γ were found to exist, and thus a vapor-pressure equation was produced which contains only one characteristic constant β and which is capable of predicting vapor pressures of pure substances up to the critical point.

This vapor-pressure relationship has been applied to hydrocarbons of all types, including normal paraffins, isoparaffins, olefins, diolefins, acetylenes, naphthenes, and aromatics. In these calculations values of β were estimated from the molecular structure of the hydrocarbons. For hydrocarbons the approach developed in this study was found to reproduce experimental vapor pressures with an average deviation of 2.7% for 456 experimental points representing fifty four hydrocarbons.

This study indicates that if reliable vapor-pressure data, however meager, are available for a hydrocarbon, these data can be used to obtain constants which enable the prediction of the critical temperature and the critical pressure of the substance.

The Frost-Kalkwarf equation (2) has been found to be of considerable utility for the calculation of vapor pressures of individual substances. This equation can be expressed as

$$\log P = A + \frac{B}{T} + C \log T + D \frac{P}{T^2} \quad (1)$$

The constants A, B, and C result from the use of the Clausius-Clapeyron equation, in which the van der Waals' term $(a)/(V^2)$ has been introduced to define the constant D as $a/2.303\ R^2$.

Sondak and Thodos (7) have used vapor-pressure data, which include a reference point (P_b, T_b), to determine the constants A, B, and C for the saturated aliphatic hydrocarbons. They showed that the constant B is the slope, and the constant C the intercept, of the line

$$Y = BX + C \quad (2)$$

where

$$Y = \left\{\log \frac{P}{P_b} - D\left[\frac{P}{T^2} - \frac{P_b}{T_b^{\,2}}\right]\right\} \Bigg/ \log \frac{T}{T_b} \text{ and } X = \left\{\frac{1}{T} - \frac{1}{T_b}\right\} \Bigg/ \log \frac{T}{T_b}$$

This approach has also been applied to the unsaturated aliphatic hydrocarbons (6), the naphthenes (4), and the aromatics (1). In these investigations the constant B was also shown to be related to the molecular structure of the hydrocarbon. Although Equation (2) is useful for establishing exacting values of B and C for the calculation of vapor pressures for these substances, it would be desirable to employ an approach which utilizes observed relationships between these coefficients to produce a vapor-pressure expression requiring less characteristic constants.

REDUCED VAPOR-PRESSURE EQUATION

Equation (1) can be expressed in the alternate form containing reduced variables:

$$\log P_R = \alpha + \frac{\beta}{T_R} + \gamma \log T_R + \delta \frac{P_R}{T_R^{\,2}} \quad (3)$$

where $\alpha = A - \log P_c + C \log T_c$, $\beta = B/T_c$, $\gamma = C$, and $\delta = D \frac{P_c}{T_c^{\,2}} = 0.1832$. At the critical point Equation (3) reduces to

$$\alpha + \beta + 0.1832 = 0 \quad (4)$$

Thus a unique linear relationship exists between α and β for all substances.

If vapor-pressure data are available, values of both B and C can be determined from Equation (2). From these values and the critical temperature of the substance, β and γ can be obtained. However if no vapor-pressure data are available for a hydrocarbon, values of β, but not γ, can be estimated from the methods available (*1, 3, 4, 6, 7, 8, 9, 10, 11*) for the prediction of B and T_c from the molecular structure of the substance. Therefore it would be advantageous to relate β and γ so that vapor pressures can be calculated for substances for which no experimental data are reported.

The values of β obtained from experimental vapor-pressure data for fifty-four hydrocarbons were plotted vs the corresponding values of γ to produce the linear relationship presented in Figure 1. This relationship, applicable to all hydrocarbons, can be expressed as follows:

$$\beta = \frac{5}{9}\left[\gamma - \frac{8}{3}\right] \quad (5)$$

When one combines Equations (3), (4), and (5), the following expression containing only one characteristic constant results:

$$\log P_R = \beta\left[\frac{1}{T_R} - 1\right] + \left[\frac{9}{5}\beta + \frac{8}{3}\right] \log T_R + 0.1832\left[\frac{P_R}{T_R^{\,2}} - 1\right] \quad (6)$$

Equation (6) was used to calculate vapor pressures for the fifty-four hydrocarbons. For each substance values of B and T_c were estimated from the molecular structure (*1, 4, 6, 7, 8, 9, 10, 11*) to produce values of β for use in Equation (6). This procedure is illustrated by the following example.

Example 1

Calculate the vapor pressures of *n*-heptane at 273.2°, 298.9°, 345.1°, 371.6°, 423.2°, 463.2°, and 523.2°K. from its molecular structure and Equation (6).

The van der Waals' constants for *n*-heptane have been estimated by Thodos (8) from its molecular structure to be $a = 30.696 \times 10^6$ (cc./g.-mole)^2 atm., and $b = 205.27$ cc./g. mole. Therefore

$$T_c = \frac{8a}{27Rb} = \frac{8(30.696 \times 10^6)}{27(82.055)(205.27)} = 540.0\text{°K.}$$

$$P_c = \frac{a}{27b^2} = \frac{30.696 \times 10^6}{27(205.27)^2} = 26.98 \text{ atm.}$$

Also from the molecular structure the constant B for this substance can be estimated to be $B = -2764.97$ with the method of Sondak and Thodos (7) Therefore

$$\beta = \frac{B}{T_c} = \frac{-2{,}764.97}{540.0} = -5.1203$$

For $T = 371.6$°K., $T_R = 371.6/540.0 = 0.688$, and therefore from Equation (6)

$$\log P_R = -5.1203\left[\frac{1}{0.688} - 1\right] +$$

$$\left[\frac{9}{5}(-5.1203)+\frac{8}{3}\right]\log 0.688+$$

$$0.1832\left[\frac{P_R}{(0.688)^2}-1\right]$$

$$\log P_R=-1.4515+0.3871\,P_R$$

which by trial-and-error produces a value of $P_R = 0.03653$ or $P = 749$ mm. Hg. This value is to be compared with the value of 760 mm. Hg at 371.6°K. reported by Rossini et al. (5). A comparison between the calculated and experimental values for the seven temperatures is presented below:

T, °K.	Vapor pressure, mm. Hg P_{calc}	P_{exptl}	% deviation
273.2	11.67	11.45	1.66
298.9	48.17	47.66	1.07
345.1	329.3	325.0	1.34
371.6	749	760	1.45
423.2	2,815	2,784	1.10
463.2	6,178	6,095	1.37
523.2	16,124	15,980	0.90

The approach outlined above was found to reproduce experimental vapor pressures for all types of hydrocarbons with an average deviation of 2.73% for 456 experimental points obtained from references listed previously (*1, 4, 6, 7*). A maximum deviation of 7.72% resulted from vapor pressures for 1-methyl-4-ethylbenzene ranging from 10 to 1,500 mm. If substances for which the deviations are excessive are eliminated from the comparison, an average deviation of 1.9% results for 350 experimental points representing thirty-nine different hydrocarbons. If more accurate vapor pressures are desired for hydrocarbons for which some vapor-pressure data are available, β for Equation (6) can be calculated from Equations (2) and (5), since $C = \gamma$. This avoids the empirical estimations inherent in the calculations of B and T_c from the molecular structure of the substance.

CRITICAL CONSTANTS FROM VAPOR-PRESSURE DATA

Equation (5) can be expressed in the alternate form

$$\frac{B}{T_c}=\frac{5}{9}\left(C-\frac{8}{3}\right)$$

or

$$T_c=\frac{27B}{5(3C-8)} \qquad (7)$$

Thus the critical temperatures of those substances for which some reliable vapor-pressure data are available can be obtained from Equation (7).

Since $\beta = B/T_c$, Equation (6) can then be used to calculate the reduced vapor pressure corresponding to a given reduced temperature. From the available vapor-pressure data the critical pressure of the substance can finally be established. This approach for the calculation of critical constants from vapor-pressure data is demonstrated in Example 2.

Example 2

Calculate the critical temperature and pressure of *n*-heptane from the vapor-pressure data presented in Example 1.

When one follows the procedure outlined by Sondak and Thodos (7), Equation (2) can be used with the vapor-pressure data to determine constants $B = -2{,}753.17$ and $C = 6.46159$. Substituting these values into Equation (7) one gets

$$T_c=\frac{27\,(-2{,}753.17)}{5[3(-6.46159)-8]}=542.9^\circ\text{K.}$$

This value should be compared with the value of $T_c = 540.2$°K. reported in the literature.

From this information $\beta = -2{,}753.17/542.9 = -5.0712$. Thus at $T = 371.6$°K., or $T_R = 371.6/542.9 = 0.684$, Equation (6) gives

$$\log P_R=-5.0712\left[\frac{1}{0.684}-1\right]+$$

$$\left[\frac{9}{5}(-5.0712)+\frac{8}{3}\right]\log 0.684+$$

$$0.1832\left[\frac{P_R}{(0.684)^2}-1\right]$$

$$\log P_R=-1.4603+0.3915\,P_R$$

which by trial-and-error produces a value of $P_R = 0.03578$. When one uses the reported vapor pressure at this temperature, $P_c = 760/0.03578 = 21{,}240$ mm. Hg. Thus the seven vapor-pressure points of *n*-heptane considered in this illustration produce the following critical pressures:

T, °K.	P, mm.	P_c, mm.
273.2	11.45	20,980
298.9	47.66	21,160
345.1	325	21,050
371.6	760	21,240
423.2	2,784	21,070
463.2	6,075	21,010
523.2	19,980	21,050
		21,080 (27.73 atm.)

The calculated critical pressures resulting for each reported vapor pressure are essentially constant with an average value of $P_c = 27.73$ atm., which compares well with the value $P_c = 27.00$ atm. reported in the literature.

NOTATION

a = pressure van der Waals' constant, (cc./g.-mole)^2 atm.
b = volume van der Waals' constant, cc./g.-mole
A,B,C,D = constants for Equation (1)
$\alpha,\beta,\gamma,\delta$ = constants for Equation (3)

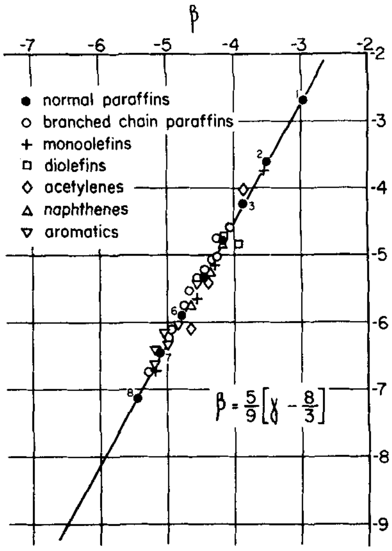

Fig. 1. Relationship of β and γ for hydrocarbons of all types.

P = vapor pressure
P_b = reference vapor pressure
P_c = critical pressure
P_R = reduced vapor pressure, P/P_c
R = gas constant
T = absolute temperature, °K.
T_b = reference temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v = molar volume, cc./g.-mole
X = temperature modulus, $\left[\frac{1}{T}-\frac{1}{T_b}\right]\Big/\log\frac{T}{T_b}$
Y = vapor-pressure modulus, $\left[\log\frac{P}{P_b}-D\left(\frac{P}{T^2}-\frac{P_b}{T_b^2}\right)\right]\Big/\log\frac{T}{T_b}$

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