

Generalized equation predicts vapor pressure of hydrocarbons

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One of the most important physical properties of hydrocarbons needed by practicing engineers in the oil and gas industries is vapor pressure.¹⁻⁵ But until now, no reliable equation could predict hydrocarbon vapor pressures accurately, with only one set of generalized parameters.

A new equation addresses this critical industry need. The accuracy of this generalized equation for predicting 1,106 vapor pressure data points for 94 different fluids has been successfully tested.

This testing has demon-

strated that the simple equation performs better than the other vapor pressure equations for all data points tested.

The equation also requires only critical pressure, critical temperature, and acentric factor.

It should be noted that several equations for vapor pressures exist in the literature.⁶⁻⁹

The Antoine equation (Equation 1) is the oldest and simplest of such equations (see Equations and Nomenclature).¹⁰

Equation 1 contains the

constants A, B, and C, which must be obtained by fitting the equation to the experimental vapor pressure data of every hydrocarbon separately. As a result, the use of this equation for all hydrocarbons requires a large data bank for the equation coefficients.

On the other hand, an equation developed by Wagner is a bit more generalized (Equation 2).¹¹ In Wagner's equation, a, b, c, and d are characteristic constants for the fluid under study, and P^s is the vapor (saturation) pressure. If parameters a, b, c, and d are available for a

pure hydrocarbon, the equation predicts vapor pressures within the acceptable accuracy down to a reduced temperature (see Nomenclature) of 0.5.

The simple generalized equation presented here accurately estimates vapor pressure of hydrocarbons, nonhydrocarbons, and polar fluids, using only the critical properties (P_c and T_c) and acentric factor (ω).

The equation has been successfully tested for a variety of fluids and can be readily used in the oil and gas industry.

EQUATIONS

$$\ln P^s = A - B/(T + C) \quad (1)$$

$$\ln P_r^s = (a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6)(1 - \tau)^{-1} \quad (2)$$

$$\ln P_r^s = [a(\omega)\tau + b(\omega)\tau^{1.5} + c(\omega)\tau^3 + d(\omega)\tau^6] (1 - \tau)^{-1} \quad (3)$$

$$\omega = (-\text{Log}P_r^s)_{T_r=0.7} - 1 \quad (4)$$

$$a(\omega) = -6.1559 - 4.0855 \omega \quad (5)$$

$$b(\omega) = 1.5737 - 1.0540\omega - 4.4365 \times 10^{-3} d(\omega) \quad (6)$$

$$c(\omega) = -0.8747 - 7.8874\omega \quad (7)$$

$$d(\omega) = (-0.4893 - 0.9912\omega + 3.1551\omega^2)^{-1} \quad (8)$$

NOMENCLATURE

- a,b,c,d = Parameters in the Wagner equation
- A,B,C = Parameters in the Antoine equation
- ln = Natural logarithm
- P = Pressure
- P_c = Critical pressure
- P_r = Reduced temperature (= P/P_c)
- P^s = Vapor temperature
- P_r^s = Reduced vapor temperature (= P^s/P_c)
- T = Absolute temperature
- T_c = Critical temperature
- T_r = Reduced temperature (= T/T_c)
- τ = 1 - T_r
- ω = Acentric factor

Table 1

COMPARISON OF VAPOR PRESSURE EQUATIONS

No. of data points	No. of compounds	Average error, %		
		LK eq.	AP eq.	Eq. 3
n-Alkanes and alkenes 177	16	6.41	6.13	5.53
Aromatics 85	7	2.66	8.47	2.40
Nonhydrocarbons 96	7	9.82	11.97	8.63
Halogens 49	3	2.98	13.69	2.49
Noble gases 25	2	2.08	2.08	1.65
Alcohols 140	11	6.19	20.37	14.73
94 compounds* 1,106	94	6.87	11.63	6.06

*Including the above families (see Reference 15).

Generalized equation

To develop a generalized vapor pressure equation with a simple form, applicable to wide ranges of temperature and a variety of fluids, the authors propose the use of Equation 2, but with its parameters defined as functions of ω .

The result of this is Equation 3.

Based on coefficient data of Equation 2—available for 73 compounds—and applying a regression method by considering Pitzer's definition of acentric factor (Equation 4), the parameters of Equation 3 can be defined by Equations 5-8.¹²

Equation 3, together with Equations 5-8, constitute the new generalized, accurate correlation for vapor pressure.

The applicability of this equation has been tested for a variety of fluids.

Equation comparability

The results of calculations indicate that Equations 3, 5, 6, 7, and 8 can predict vapor pressures of hydrocarbons, nonhydrocarbons, and polar fluids more accurately than the other vapor pressure equations available in the literature without the need for information about any additional parameters.

Table 1 compares vapor pressures of pure liquids, as predicted by the Ambrose and Patel (AP) equation, the Lee-Kessler (LK) equation, and Equation 3.^{13,14}

The new equation predicts

vapor pressure more accurately than the AP interpolative method. The prediction of the new equation is also superior to the LK equation for all hydrocarbons and other substances, excluding alcohols.

Also reported in Table 1 are the overall average percentage errors of the present and other equations for all 94 substances, tested with a total of 1,106 vapor pressure data points.¹⁵

This comparison shows that, overall, the new equation predicts vapor pressure more accurately than the other equations.

It should be pointed out that the application of the other vapor pressure equations requires knowledge of the coefficients of those equations for every individual substance. The new equation, however, does not require such knowledge, and is accurate and suitable for engineering design calculations.

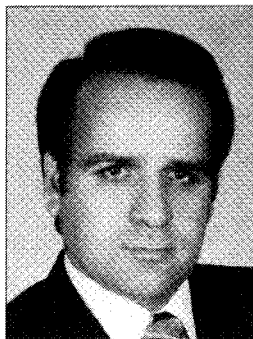
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BOOK

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