A Simple Vapor Pressure Relationship for the Normal Paraffins

R. J. SMIALEK and GEORGE THODOS
Northwestern University, Evanston, Ill.

A single relationship has been developed which permits the rapid calculation of vapor pressures for the normal paraffins from their normal boiling points. This relationship produces reliable values for pressures from 5.0 p.s.i.a. to the critical point. Its reliability was tested with 10 normal paraffins. Altogether 72 vapor pressures for these normal paraffins were calculated and when compared with experimental values produced an average deviation of 1.81%. Vapor pressures calculated for other types of hydrocarbons indicate that the method outlined in this article may be used for other homologous series.

CONSIDERABLE INFORMATION concerning the vapor pressure behavior of pure substances has been reported in the literature. Attempts have been made to produce linear vapor pressure relationships that permit extrapolation beyond the range of available vapor pressure data. In 1923, Cox (*1*) devised a scheme in which the vapor pressure of a substance was plotted against the vapor pressure of a reference substance (both at the same temperature) using log-log coordinates. A temperature scale was developed from the corresponding vapor pressure of the reference substance in order to relate temperature with vapor pressure directly. This method of correlation produced essentially linear vapor pressure relationships which exhibited a common point of convergence for members of the same homologous series. This approach has been extended in application by Othmer (*4*). Myers and Fenske (*3*) relate the temperature of a hydrocarbon to a reference temperature to produce straight lines for each pressure for a wide range of hydrocarbons. Seglin (*5*) plotted the reciprocal of the reduced temperature of a substance against the reciprocal reduced temperature of a reference substance (both at the same reduced pressure) to develop a linear relationship for each substance.

A number of equations have also been presented which describe the vapor pressure behavior of substances. The Frost-Kalkwarf equation (*2*) enables accurate prediction of the vapor pressure of pure substances over the range between the triple point and the critical point. This equation is very precise, but requires that four constants be determined. Alternately, this equation can be written in reduced form; but the critical constants of the substance must be known.

The simplest vapor pressure relationship capable of producing moderately good values is:

$$\log P = A + B/T \tag{1}$$

Ordinarily, the constants A and B of Equation 1 are obtained from the known normal boiling point and critical point of the substance. Normally, the value of the boiling point is more accessible and is established more accurately than the corresponding value of the critical point. The regular behavior of the vapor pressure relationships of Equation 1 for the normal paraffins suggests that the vapor pressure behavior of these hydrocarbons can be established from a single vapor pressure value taken in this study to be the normal boiling point.

ESTABLISHMENT OF VAPOR PRESSURE RELATIONSHIP

From an enlarged plot of log P *vs.* $1/T$ for the normal paraffinic hydrocarbons ranging from methane through *n*-decane, values of $1/T$ at constant pressure were obtained and plotted against the corresponding reciprocal normal boiling point of each hydrocarbon. The resulting plot produced essentially linear relationships between $1/T$ and $1/T_b$ for each pressure investigated for the range of reciprocal temperatures, $1/T_b < 3.0000 \times 10^{-3}$. These lines have a common point of intersection at $1/T$, °R. $= 0.220 \times 10^{-3}$. In Figure 1 the normal boiling point at 14.7 p.s.i.a. is represented as a 45 degree line. For pressures greater than 14.7 p.s.i.a., the lines have slopes of less than unity while those at lower pressures had larger slopes. The pattern suggests that the equilibrium temperature for a specific vapor pressure can be established from the normal boiling point of the substance if the slope of the corresponding line were available. When the slope of each line of Figure 1 was plotted against the corresponding pressure on semilog coordinates, a linear relationship resulted as shown in Figure 2. This relationship can be expressed analytically as follows:

$$\log P = 5.113 - 3.951m \tag{2}$$

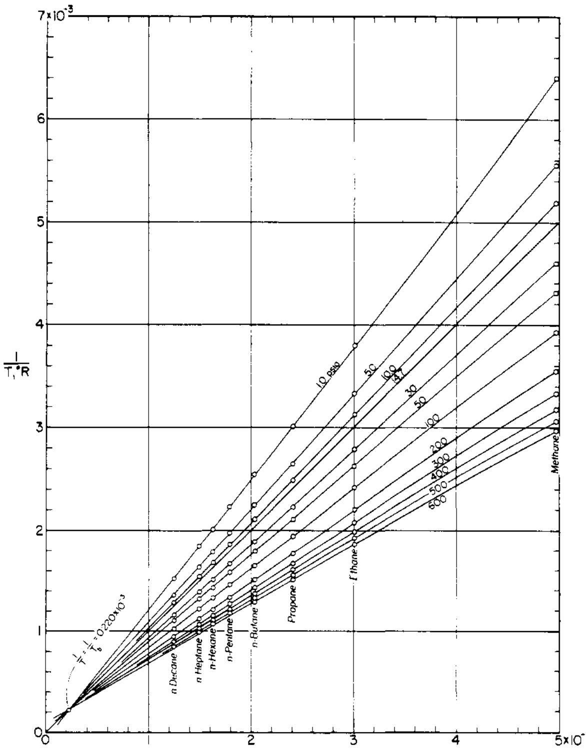

Figure 1. Relationships between $1/T$ and $1/T_b$ for the normal aliphatic hydrocarbons at constant pressures

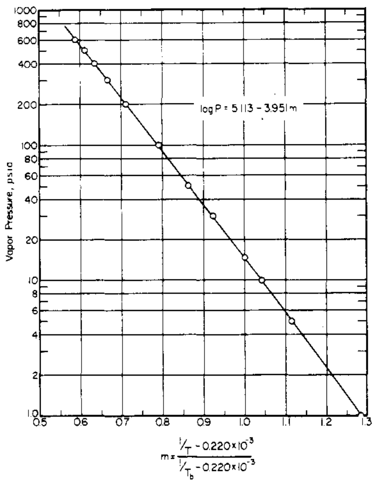

Figure 2. Relationship between vapor pressure and the slopes of the lines of Figure 1

where P is the vapor pressure in p.s.i.a. and m is the slope of each isobar presented in Figure 1. The straight line relationship of Equation 2 is applicable for pressures from 5.0 p.s.i.a. to about 600 p.s.i.a. A slight curvature exists below $P \approx 5.0$ p.s.i.a. Pressures greater than 600 p.s.i.a. are unrealistic since they represent conditions above the critical point of these normal paraffins.

As a result of the pattern of the straight lines of Figure 1, the slope m of Equation 2 can be expressed analytically as:

$$m = \frac{(1/T) - 0.0220 \times 10^{-3}}{(1/T_b) - 0.220 \times 10^{-3}} \tag{3}$$

where the temperature, T, and the normal boiling point, T_b, are in degrees Rankine. Therefore, Equations 2 and 3 represent a unified vapor pressure relationship for the normal paraffins which requires only that the normal boiling point of the substance be known. This method should be of considerable utility especially in the area of petroleum technology since it avoids lengthy calculations.

Equations 2 and 3 were used to calculate vapor pressures of the normal paraffins with the exception of methane whose reciprocal normal boiling point is $1/T_b$, °R. $> 3.000 \times 10^{-3}$. Calculated vapor pressures for *n*-pentane are compared with corresponding experimental values as follows:

n-Pentane

t, °F.	T, °R.	Vapor Pressure, P.S.I.A. Calculated	Vapor Pressure, P.S.I.A. Experimental	Deviation, %
55.9	515.6	6.34	6.29	0.79
75.9	535.6	9.63	9.68	−0.52
87.1	546.8	12.03	12.15	−0.99
96.9	556.6	14.52	14.70	−1.22
220.0	679.7	94.63	96.32	−1.75
280.0	739.7	188.5	185.6	1.54
340.0	799.7	346.4	329.2	5.20
386.0[a]	845.7	501.2	494.1	1.44
			Av. dev.	1.68

[a] Crit.

Similar comparisons were made with other light normal paraffins for which several vapor pressures were considered. The critical point was included when available. Comparisons produced the following deviations:

	No. of Points	Dev., %
Ethane	11	0.82
Propane	6	0.96
n-Butane	10	1.95
n-Pentane	8	1.68
n-Hexane	7	2.10
n-Heptane	8	1.96
n-Octane	6	1.75
n-Nonane	5	1.47
n-Decane	4	2.12
n-Dodecane	4	2.28
	Av. Dev.	1.81

Despite the fact that vapor pressure data for the normal paraffins were utilized to develop Equations 2 and 3, these relationships have been used to calculate vapor pressures for several branched chain and unsaturated aliphatic and cyclic hydrocarbons. Calculated vapor pressures were compared with experimental values to test the reliability of these equations for the prediction of vapor pressures of hydrocarbons other than normal paraffins. For all hydrocarbons examined, the following deviations were obtained:

	Hydrocarbons	Points	Av. Dev., %
Normal paraffins	10	72	1.81
Isoparaffins	7	34	3.61
Monoolefins	10	45	2.09
Diolefins	3	13	2.11
Naphthenes	2	8	6.22
Aromatics	7	31	3.12

At least four vapor pressure points were considered for each hydrocarbon when the available vapor pressures ranged from approximately 5 p.s.i.a. to the critical point. This was not the case for the monoolefins and diolefins since the majority of vapor pressures available for these substances did not extend beyond 30 p.s.i.a. In general, the equations developed from vapor pressure data for the normal paraffins were found to produce vapor pressures for other classes of hydrocarbons which were reasonable estimates of their true vapor pressures. Results indicate that the method applied to the normal paraffins can be extended to other individual homologous series to produce relationships of the type of Equations 2 and 3 with somewhat different constants.

LITERATURE CITED

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RECEIVED for review July 1, 1963. Accepted September 9, 1963.