# A New Reduced Vapor Pressure Equation

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The determination of the vapor pressure of pure substances is essential for many important practical and theoretical applications. Because only fragmentary or inconsistent experimental data are available for most substances over the complete range from the triple point to the critical point, it is necessary to have available a relationship sufficiently general to enable the calculation of this property for wide ranges of substances and conditions.

The most accurate reduced vapor pressure equations which have been proposed were developed by the integration of the reduced Clapeyron equation:

$$\frac{d \ln P_R}{dT_R} = \frac{\Delta H}{RT_c\, T_R^2\, \Delta z} \qquad (1)$$

Riedel (*16*, *18*) assumed that $\Delta z$ is unity and that $\Delta H$ varies linearly with temperature for the low reduced temperature region, and included a term proportional to the reduced temperature to the sixth power to correct these assumptions for the high temperature region. From experimental vapor pressure data Riedel found that at the critical point $\alpha = d \ln P_R / d \ln T_R$ was a characteristic constant $\alpha_c$ for each substance and that the slope $\left.\frac{d\alpha}{dT_R}\right|_{T_R=1.0}$ is equal to zero. Riedel used these conditions and applied the equation at the critical point to produce the following reduced vapor pressure relationship:

$$\ln P_R = \alpha_c \ln T_R - 0.0838\,(\alpha_c - 3.75) \left(\frac{36}{T_R} - 35 - T_R^6 + 42 \ln T_R\right) \qquad (2)$$

The constant $\alpha_c$ can be obtained by applying Equation (2) at the normal boiling point.

Frost and Kalkwarf (*5*) integrated Equation (1) with the use of the linear approximation for the temperature variation of the latent heat and the assumption that the volumes of the saturated liquid and gas can be calculated from Van der Waal's equation of state. Thodos and coworkers (*7*, *19*, *20*) expressed the Frost-Kalkwarf equation in reduced form and combined several constants to obtain the following relationship:

$$\log P_R = (5/9\,\beta - 40/27) \left(\frac{1}{T_R} - 1\right) + \beta \log T_R + 0.1832 \left(\frac{P_R}{T_R^2} - 1\right) \qquad (3)$$

Miller (*10*) obtained a similar equation involving $\alpha_c$ by the application of the Riedel conditions to the Frost-Kalkwarf equation.

The assumption that the latent heat of vaporization varies linearly with temperature is only approximately correct at low and moderate temperatures (*2*) and is incorrect at high temperatures. For a wide range of temperatures the following equation suggested originally by Watson (*25*) is a better representation of the temperature variation of the latent heat:

$$\Delta H = \Delta H_b \left[\frac{(1 - T_R)}{(1 - T_{Rb})}\right]^q \qquad (4)$$

where $q$ is between 0.3 and 0.4 Narsimhan (*13*) has presented a semitheoretical justification of the form of this equation with the exponent $q$ equal to 0.375. Miller (*11*) used Equation (4) with $q = 0.38$ in conjunction with the Haggenmacher equation for $\Delta z$ (*6*) and numerically integrated the resulting form of the reduced Clapeyron equation to obtain the following equations:

$$\ln P_{\text{atm}} = A\left[0.60706\, T_R^2 - 1.44779\, T_R - I_b - \frac{3.87603}{T_R}\right] \qquad (5)$$

where

$$I_b = -1.44779 \left(T_{Rb} - \frac{1}{T_{Rb}}\right) + 0.60706 \left(T_{Rb}^2 - \frac{4}{T_{Rb}}\right) \qquad (6)$$

Miller (*12*) also obtained the following equation by assuming the form of Equations (5) and (6) and by applying the conditions used by Riedel in the development of Equation (2):

$$\log P_R = -\frac{G}{T_R}\,[1 - T_R^2 + g\,(1 - T_R)^3] \qquad (7)$$

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where $g$ is obtained by fitting the equation at the normal boiling point and

$$G = 0.2421 + 0.19654a \qquad (8)$$

Othmer (*15*) has developed a reduced vapor pressure equation of a different type by writing Equation (1) for a compound and for water at the same reduced temperature. The ratio of the resulting equations $m_R$ is essentially constant; therefore the following reduced equation results from integration:

$$\log P_R = m_R \log P_R' \qquad (9)$$

None of the reduced vapor pressure equations proposed previously give results of high accuracy for a wide range of substances and conditions. Large errors result from the use of the Riedel and Frost-Kalkwarf equations at low temperatures for high molecular weight substances (2) because of the assumption made in the development of these equations that the latent heat of vaporization varies linearly with temperature (constant heat capacity difference). In addition, both the Riedel and Frost-Kalkwarf equations contain an insufficient number of parameters to be suitable for polar substances. Reid and Sherwood (*17*) suggest that the Riedel equation not be used for polar substances for reduced temperatures below $T_R = 0.65$. The Frost-Kalkwarf equation also has the disadvantage that is requires an iterative procedure for the calculation of every vapor pressure point.

Miller (*11*) made a detailed comparison of his equations with the Frost-Kalkwarf and Riedel relationships. He found that Equations (5) and (6) are the most accurate relationships for the low pressure region but that very poor results are obtained from their use for the high pressure region. Equation (7) was found to produce better results than Equations (5) and (6) in the high pressure region but to give results similar to the Frost-Kalkwarf and Riedel equations for the low pressure regions.

Equation (9) has been found to produce large errors at low reduced temperatures for several substances, particularly polar compounds, if $m_R$ is established by fitting the equation at the normal boiling point of the substance. Alternate procedures are available for the calculation of $m_R$, and some caution must be used in the selection of the proper method for a particular substance.

## DEVELOPMENT OF REDUCED VAPOR PRESSURE EQUATION

The goal of the present study was to develop a single reduced vapor pressure equation with an accuracy comparable to that of Equations (5) and (6) for low reduced temperatures and to that of Equations (2) and (3) for high reduced temperatures. Since the use of Equation (4) for the temperature variation of tthe latent heat has lead to the best previous results for the low reduced temperature region, this equation with $q = 0.375$ was chosen as the starting point in the present investigation. In order to integrate Equation (1), Equation (4) was expanded as follows:

$$\frac{\Delta H}{RT_c} = A\left[\begin{array}{l} 1 - 0.375\,T_R - 0.11719\,T_R^2 - 0.063477\,T_R^3 \\ \quad - 0.041656\,T_R^4 + \cdots \end{array}\right] \qquad (10)$$

where

$$A = \Delta H_b/RT_c\,(1 - T_{Rb})^{0.375}$$

Equation (10) truncated after the fourth ($T_R^3$) term is virtually an exact representation of Equation (4) with $q = 0.375$ for reduced temperatures below $T_R = 0.50$. In addition, for this temperature range the compressibility factor difference $\Delta z$ is essentially unity for all substances. For higher reduced temperatures additional terms in the series of Equation (10) and a relationship for the temperature dependence of $\Delta z$ are required for the integration of Equation (1). The Haggenmacher equation for $\Delta z$ (*6*) is probably the best analytical expression; however, its use in Equation (1) results in a form which cannot be integrated directly. Also, the inclusion of additional terms in Equation (10) would result in a vapor pressure equation containing an inordinate number of terms. Therefore, these substitutions were not made into Equation (1); instead a correction term was added to Equation (10) truncated after the fourth term to account for the combined effects of $\Delta z$ and the higher terms in the series. Thus, the following equation was obtained:

$$\frac{\Delta H}{RT_c\Delta z} = A\,[1 - 0.375\,T_R - 0.11719\,T_R^2 - 0.6347\,T_R^3] + f \qquad (11)$$

where the correction term $f$ should vanish at $T_R = 0.5$

Kordes (*8*) previously used the series expansion of Equation (10) truncated after the fifth term with no correction for $\Delta z$. Thomas (*22*) expanded Equation (4) with $q = 0.40$ into a series truncated after the seventh term and used a relationship for $\Delta z$ which is valid for the region below the normal boiling point. The approach used in the present study is similar to that utilized in the development of the Frost-Kalkwarf and the Riedel equations in that the resulting vapor pressure equation will contain terms obtained from the integration of the proposed form of the variation of $\Delta H$ in the low reduced temperature region, and terms to correct for the high reduced temperature region.

The correction term $f$ should be of such a form that it vanishes at low reduced temperatures and that Equation (11) should exhibit a minimum at approximately $T_R = 0.8$ and its slope approach $\alpha_c$ at $T_R = 1.0$ (*24*). In order to establish the appropriate form for the correction term, values of $f$ resulting from the use of actual data for $\Delta H$ and $\Delta z$ for several substances were plotted against the reduced temperature on log-log coordinates. The resulting relationships were slightly curved but the following linear form was indicated.

$$f = c\,(T_R^n - k) \qquad (12)$$

where $k$ is a small constant for each substance. Equation (12) was combined with Equation (11) and the resulting relationship integrated according to Equation (1) to produce the following reduced vapor pressure equation:

$$\ln P_R = A\left(1.16286 - \frac{1}{T_R} - 0.11719\,T_R - 0.03178\,T_R^2 - 0.375 \ln T_R\right) + c\left[\frac{T_R^{n-1} - 1}{n-1} + k\left(\frac{1}{T_R} - 1\right)\right] \qquad (13)$$

The following relationships for the constants $c$ and $n$ resulted from the application of the two Riedel conditions for $\alpha_c$ to Equation (13):

$$c = \frac{\alpha_c - 0.44433A}{1 - k} \qquad (14)$$

$$n = \frac{\alpha_c - 0.79980A}{c} \qquad (15)$$

## RESULTS AND CONCLUSIONS

In order to evaluate the constants $\alpha_c$ and $k$ of Equations (13), (14), and (15), experimental vapor pressure data were utilized. For the region between 10 and 1,500 mm.

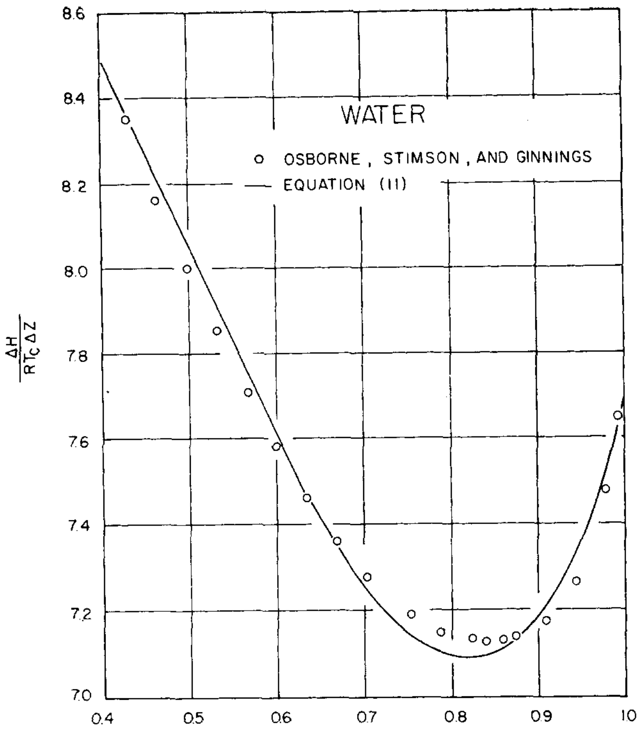

Fig. 1. $\Delta H/RT_c\Delta z$ vs. $T_R$ for water.

Hg, the data were obtained from Manufacturer's Chemist Association reports (9) for thirty-seven inorganic and polar organic substances and from API project 44 (*1*) for thirty-two hydrocarbons. For the high pressure region the data were obtained from Edwards (*4*) for twenty-two inorganic substances and from Stull (*21*) for ten hydrocarbons. The data were similar to those used by Miller (*11*). In general, approximately thirty experimental vapor pressures were used for each substance investigated for the low pressure region and approximately ten points for the high pressure region.

Although $k$ is a characteristic parameter for each substance, it can be considered to be a constant, since it must have a small value to enable $f$ to be essentially zero for low temperatures. Therefore, values of $k$ from 0 to 0.05 were used in the reduced vapor pressure equation, and the corresponding values of $\alpha_c$ were calculated by the application of Equations (13), (14), and (15) at the normal boiling point through a Newton-Raphson iterative procedure on an IBM 7074 computer. For both the low and high pressure regions minimum overall percent errors were obtained for $k = 0.040$, and therefore this value was accepted for use. Similar calculations were also performed with one additional term in the series of Equation (10) but no overall improvement in the results was obtained.

In Figure 1 a comparison is presented between values of $(\Delta H/RT_c\Delta z)$ resulting from experimental data for water (*14*) and values calculated from Equations (11), (12), (14), and (15) with $k = 0.04$ and $\alpha_c$ obtained by fitting the equations at the normal boiling point. It can be seen that the proposed form of the variation of $(\Delta H/RT_c\Delta z)$ is accurate over the entire range of reduced temperatures.

In order to eliminate the iterative procedure required for the calculation of $\alpha_c$ through the application of Equations (13), (14), and (15), values of $n$ resulting for the sixty-nine substances investigated for the low pressure region were correlated by a least squares procedure with $A$ and $a$ as follows:

$$n = 6.2691 + 2.0753A - 3.1738a \qquad (16)$$

The resulting reduced vapor pressure equation is

$$\ln P_R = A\left(1.16286 - \frac{1}{T_R} - 0.11719\,T_R - 0.03178\,T_R^2 - 0.375\ln T_R\right) + (1.042\,\alpha_c - 0.46284A)\left[\frac{T_R^{5.2691+2.0753A-3.1738a} - 1}{5.2691 + 2.0753A - 3.1738a} + 0.040\left(\frac{1}{T_R} - 1\right)\right] \qquad (17)$$

Values of $\alpha_c$ were calculated by the application of Equation (17) at the normal boiling point for the substances investigated, and calculated vapor pressures for the complete reduced temperature range were compared with the corresponding experimental values. The maximum percent errors and average percent errors between experimental vapor pressures and values calculated from Equation (17) for the substances investigated are presented in Tables 1, 2, and 3.*

A comparison between the results obtained with Equation (17) and the maximum and average percent errors resulting from the use of other reduced vapor pressure equations is presented in Table 4. It can be seen that very good results were obtained with Equation (17) for both the low and high pressure regions. Equation (17) produced the best overall average errors for the complete range of temperature reduced temperatures, 0.68% for 2,050 data points.

For many substances the maximum error in the low reduced temperature region occurred at the lowest point investigated, corresponding to a pressure of 10 mm. Hg. For several substances for which vapor pressure data were available for very low pressures (23), Equation (17) was found to reproduce experimental vapor pressures to 0.5 mm. with an average of the maximum percent errors of approximately 5%. The higher error for these low pressures cannot be attributed to the slight persistence of $k$ in Equations (11) and (12), indicating that Equation (4) with $q = 0.375$ is not generally completely accurate for this region. The other reduced vapor pressure equations produced poorer results than Equation (17) for this region, with the exception of Equations (5) and (6) which gave comparable results. In Figure 2 a comparison is presented between experimental vapor pressures for hexane (*1*, *3*) at low temperatures and those calculated from Equation (17).

TABLE 4. COMPARISON OF RESULTS FOR REDUCED VAPOR PRESSURE EQUATIONS

| Equation | Low pressure percent error Maximum | Low pressure percent error Average | High pressure percent error Maximum | High pressure percent error Average | Overall average percent error |
|---|---|---|---|---|---|
| (*17*) | 2.91 | 0.62 | 1.42 | 0.73 | 0.66 |
| (*5*) and (*6*) | 2.69 | 0.75 | 13.35 | 7.86 | 3.01 |
| (*7*) | 4.83 | 1.09 | 1.62 | 0.84 | 1.01 |
| (*2*) | 4.86 | 1.21 | 1.50 | 0.74 | 1.11 |
| (*3*) | 4.60 | 1.06 | 1.38 | 0.68 | 0.94 |

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* Tabular material has been deposited as Document 8796 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

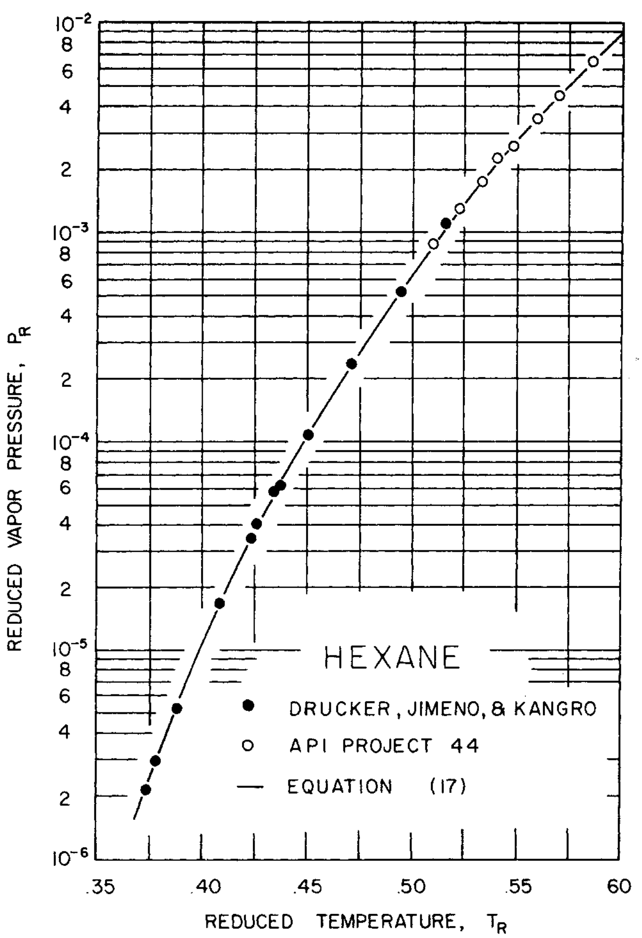

**Fig. 2. Reduced vapor pressure vs. reduced temperature for hexane.**

The major improvement of Equation (17) and Equations (5) and (6) over the Riedel and reduced Frost-Kalkwarf equations for the low reduced temperature region is obtained for polar, hydrogen-bonding substances. The improvement for polar substances resulting from these equations can be attributed to the more accurate form for the temperature variation of the latent heat of vaporization used in their development, and to the fact that through the use of Equation (4) both of these equations require the value of the latent heat of vaporization at the normal boiling point. The group $A$ is effectively an additional parameter accounting for polarity effects. Equation (17) produces better results than Equations (5) and (6) for the high pressure region, because the former equation requires additionally the critical pressure of the substance. It appears that the information required by the reduced vapor pressure equation developed in the study (the critical temperature, critical pressure, normal boiling point, and normal latent heat of vaporization) is the minimum needed for a reduced vapor pressure equation to be of sufficient accuracy for a wide range of substances and conditions.

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## NOTATION

$a$ = characteristic parameter, $-T_{Rb} \ln P_c/(T_{Rb}-1)$
$A$ = coefficient in Equations (5) and (10), $\dfrac{\Delta H_b}{RT_c(1-T_{Rb})^{0.375}}$
$c$ = coefficient in Equation (12)
$f$ = correction term in Equation (11)
$g$ = coefficient in Equation (7)
$G$ = coefficient in Equation (7)
$\Delta H$ = latent heat of vaporization, cal./g.-mole
$\Delta H_b$ = latent heat of vaporization at the normal boiling point, cal./g.-mole
$I_b$ = term in Equation (5)
$k$ = coefficient in Equation (12)
$m_R$ = ratio of Equation (1) to that for water at the same reduced temperature
$n$ = parameter in Equation (12)
$P$ = pressure, atm.
$P_c$ = critical pressure, atm.
$P_R$ = reduced pressure, $P/P_c$
$P_R'$ = reduced vapor pressure of water
$q$ = exponent in Equation (4)
$R$ = gas constant, 1.9865 cal./g.-mole
$T$ = absolute temperature, °K.
$T_c$ = critical temperature, °K.
$T_R$ = reduced temperature, $T/T_c$
$T_{Rb}$ = reduced temperature at the normal boiling point
$\Delta z$ = difference between compressibility factors for saturated vapor and liquid

### Greek Letters

$\alpha$ = slope, $d \ln P_R/d \ln T_R$
$\alpha_c$ = slope $\alpha$ at the critical point
$\beta$ = coefficient in Equation (3)

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