Boyle temperatures have been calculated using the van der Waals, Redlich-Kwong, Soave and Peng-Robinson equations of state and compared to the values predicted from the McGlashan-Potter and Pitzer-Curl correlations for the second virial coefficient. The values calculated by the equations of state are systematically higher than those predicted from the correlations.

The $P-V-T$ surface for a real gas differs markedly from that of an ideal gas and hence cannot be described by the simple equation, $PV=RT$. It is customary to express the $P-V-T$ relationships of fluids by empirical equations designed to fit the experimental data. The complexity of such equations and the number of empirical constants required are dependent on the accuracy of experimental measurements, the precision required, and the experimental range of variables. Equations of state are useful for representation of the $P-V-T$ data, for data smoothing and interpolation and for calculating derived properties; they must satisfy a number of criteria developed from the experimental data on real gases.

(1) At sufficiently high temperatures or low pressures, ideal behaviour is observed and $PV=RT$. Nevertheless, the residual volume $\alpha$, defined as,

$$\alpha = \frac{RT}{P} - V \ldots (1)$$

does not go to zero when the pressure goes to zero.

(2) Existence of a critical point, identified by a nil value of the first and second derivatives of the pressure with respect to volume at the critical isotherm.

(3) Prediction of the Joule-Thomson inversion curve. This is considered one of the most severe tests for any equation of state.

(4) Behaviour of the product $PV$ with pressure at constant temperature is illustrated with the results of carbon dioxide as shown in Fig. 1. A portion of the critical isotherm has been drawn as a broken line. The departure from ideal gas behaviour is obvious since for an ideal gas all isotherms would be horizontal. It is seen that depending on the value of the temperature, the starting values of $PV$ at zero pressure, decrease or increase with increasing pressures. In other words, the equation of state must be able to satisfy the following mathematical conditions:

$$\left[ \frac{\partial PV}{\partial P} \right]_{T=0} \geq 0 \ldots (2)$$

Since the initial slope at zero pressure can be positive or negative the Boyle temperature ($T_B$) may be defined as

$$\lim_{P \to 0} \left[ \frac{\partial PV}{\partial P} \right]_{T_B} = 0 \ldots (3)$$

![Fig. 1—General $P-V$ behaviour of a real gas (CO$_2$)](image-url)
The pronounced minima in the isotherms become more marked as the temperature is lowered, and when the critical isotherm is reached \((T_c = 1)\), a vertical tangent occurs at the critical pressure. The critical isotherm is also tangent to the curve (dashed in Fig. 1) outlining the liquid-vapour domains. The minima fall on a smooth curve (dotted in Fig. 1) which would strike the \(P = 0\) axis at two points, one beyond the present data (see Fig. 2). The locus of all minima traces Boyle's curve that determines a pressure \(P_B\) for every temperature below the Boyle temperature. In the neighbourhood of that pressure, the product \(PV\) remains constant over a wider range of pressure since the minima are very shallow.

The virial equation can be used to obtain a simple estimate of the Boyle temperature, as follows. Differentiating the pressure form of the virial equation

\[
\frac{PV}{RT} = 1 + \frac{BP}{RT} + C' P^2 + \ldots
\]

with respect to \(P\) at constant temperature and taking the limit as \(P\) goes to zero we get

\[
\lim_{P \to 0} \left[ \frac{\partial PV}{\partial P} \right]_{T_B} = B(T_B) = 0 \quad (P \to 0)
\]

According to Eq. (5) the Boyle temperature may be identified as the temperature at which the second virial coefficient becomes equal to zero. At the Boyle temperature the \(PV\) product differs from \(RT\) only by the square terms in \(P\) and higher, and hence the ideal gas law will be satisfied with a higher degree of accuracy over an increased interval of pressure starting with \(P = 0\) than is otherwise the case.

It is a known fact that at sufficiently low temperatures the second virial coefficient \(B\) is negative, qualitatively this is attributed to the preponderance of long range attractive forces. As temperature increases, molecular collisions become more energetic, increasing the contribution of short-range repulsive forces and causing \(B\) to become less negative. At the Boyle temperature attractive and repulsive forces between pairs of molecules are approximately balanced and \(B\) becomes zero. For higher temperatures, repulsive forces dominate and \(B\) is positive, increasing slowly with temperature.

Eq. (4) can also be used to show that at \(P = 0\) and \(T = T_B\) the residual volume has the same numerical value but opposite sign as the second virial coefficient. Hence, from Eq. (4) it may be concluded that at \(T_B\) the specific volume of the gas is equal to that predicted by the ideal gas law.

Vetere\(^1\) has proposed two simple correlations for the Boyle temperature as a function of either the normal boiling point \(T_b\), or the critical temperature \(T_c\)

\[
T_B = 110.0 + 2 T_b \quad \ldots (6)
\]

for compounds having a boiling temperature below 120 K and

\[
T_B = 110.0 + 2 T_c \quad \ldots (7)
\]

for the other compounds.

**Results and Discussion**

The purpose of this study is to compare the ability of some common equations of state to predict the Boyle temperature using the values obtained from the virial equation for comparison purposes. To generalize the results, the equations have been transformed into reduced coordinates using \(X_r = X / X_c\).

**van der Waals equation**—Although the van der Waals equation is not a good predictor of the \(P-V-T\) behaviour of real gases is used to study qualitatively the behaviour of the Boyle curve.

In terms of reduced coordinates the equation reads

\[
\left( P_r + \frac{3}{V_r^2} \right) (3 V_r - 1) = 8 T_r
\]

Setting


\[ \left( \frac{\partial P_r V_r}{\partial P_r} \right)_{T_r} = 0 \]  

... (9)

we get

\[ T_r = \frac{27}{8} \left( 1 - \frac{1}{V_r} \right)^2 \]  

... (10)

and

\[ P_r V_r = 3 \left( 3 - \frac{2}{V_r} \right) \]  

... (11)

The relations between \( P_r, V_r \) and \( T_r \), and between \( T_r \) and \( P_r \), are plotted in Figs 2 and 3; they give the loci of all points, where the curves of \( PV \) vs \( P \) have a minimum value (Boyle's curve). Each point on the curve corresponds to a different temperature, the latter increasing as \( PV \) increases. Fig. 2 shows clearly the missing end in the loci described in Fig. 2 shows clearly the missing end in the loci described in Fig. 1. The following values are of interest:

<table>
<thead>
<tr>
<th>( T_r )</th>
<th>( P_r V_r )</th>
<th>( P_r )</th>
<th>( V_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.84375</td>
<td>0</td>
<td>0</td>
<td>0.667</td>
</tr>
<tr>
<td>1.90</td>
<td>4.5</td>
<td>3.375</td>
<td>1.333</td>
</tr>
<tr>
<td>3.375</td>
<td>9.0</td>
<td>0</td>
<td>( \infty )</td>
</tr>
</tbody>
</table>

Fig. 2 shows that there is not a substantial difference between the minima predicted by either the van der Waals or the Redlich-Kwong equations, the latter predicts slightly lower values for \( (P_r V_r)_{\text{min}} \). Nevertheless, both equations show substantial differences with respect to the temperature at which the minimum value occurs (Fig. 3), particularly at temperatures well above the critical \( (T_r = 1) \).

Soave equation—The Soave equation of state is a modification of the Redlich-Kwong equation where the constant in the second term in Eq. (12) is assumed to be a function of the temperature and the acentric factor \( \omega \):}

\[ P_r V_r = 3 T_r \frac{V_r}{V_r - 0.2599} \frac{3.8473 \alpha}{V_r + 0.2599} \]  

... (15)

with

\[ \alpha = \left[ 1 + (0.48508 + 1.55171 \omega - 0.15613 \omega^2) \times (1 - T_r^{0.5}) \right]^2 \]  

... (16)

Applying Eq. (9) we get the same expression for \( V_r \) as that given by Eq. (13) except that the expression of \( E \) becomes

\[ E = 4.93433 \alpha \]  

... (17)

Figs 4, 5 and 6 describe the variation of \( P_r V_r \)
Application of Eq. (9) yields

\[
\frac{T_r}{\alpha} = \frac{5.87764(0.064212 + V_r^2)}{V_r - 0.2534} \left[ \frac{V_r - 0.2534}{V_r^2 + 0.5068 V_r - 0.0642} \right]^2
\]

\[\ldots (21)\]

Figs 6 and 7 describe the variation of \(P_r, V_r, \) and \(T_r\) with \(P_r\), as a function of the acentric factor. The Boyle temperature is well correlated with the acentric factor with the following expression

\[
T_r = 5.87764 \left\{ \frac{0.064212 + V_r^2}{V_r - 0.2534} \right\} \left[ \frac{V_r - 0.2534}{V_r^2 + 0.5068 V_r - 0.0642} \right]^2
\]

\[\ldots (22)\]

with a coefficient of determination \(R^2 = 0.9999\).

The values of Boyle's temperature predicted by the different equations of state have been com-
pared with those obtained by making the second coefficient nil in the correlations of McGlashan and Potter and Pitzer and Curl. The results summarized in Table 1 indicate that all four equations predict values of $T_B$ substantially larger than those predicted from the second virial correlations.

The EOS used here are all particular forms of the general cubic equation of state. If they are written in virial form it will be seen that all of them keep the first term of the van der Waals EOS and attempt to improve the quality of the fitting by modifying the second van der Waals term. There is a certain "virial" logic to this procedure: The first term provides the "constant" in the expression of $B$ as a function of gas parameters, while the second term provides the required functionality in temperature. For example, the virial expansion of van der Waals predicts that only the second virial coefficient is a function of $T$ and that all higher coefficients are independent of $T$. This conclusion is obviously wrong. In addition, the predicted functionality in $T$ for the second virial coefficient is also wrong. If one or more of the EOS constants are made to depend on $T$ (Soave and Peng Robinson, for example), then the virial expansion will improve the fit for the second virial coefficient and will also introduce the required functionality on $T$ on every other virial term. The difference between the values of the Boyle temperature predicted by the two methods is probably another built-in limitation of a cubic equation of state.

It should be noticed that for all of the equations tested, the calculated Boyle curve ends at values below the critical temperature, it could well be that in some cases the curve will end at the vapour-liquid saturation envelope.

### Nomenclature

- $B$ = second virial coefficient
- $C$ = third virial coefficient, Eq. (4)
- $E$ = auxiliary function, Eqs (14) and (17)
- $P$ = pressure
- $P_c$ = critical pressure
- $P_r$ = reduced pressure, $P/P_c$
- $T$ = temperature
- $T_b$ = normal boiling point
- $T_B$ = Boyle's temperature
- $T_c$ = critical temperature
- $T_r$ = reduced temperature, $T/T_c$
- $V_r$ = reduced volume, $V/V_c$
- $V_c$ = critical volume
- $a$ = residual volume (Eq. 1) or parameter defined by Eqs (16) or (20)
- $\omega$ = acentric factor

### References