Mathematical Analysis and Evaluation of the Law of Corresponding States for Real Gases

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MATHMATICAL ANALYSIS AND EVALUATION
OF THE LAW OF CORRESPONDING
STATES FOR REAL GASES

BY
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This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and acceptable as meeting the thesis requirements for this degree; but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Advisor

Head of the Major Department
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CHAPTER I

INTRODUCTION

The science of thermodynamics deals mainly with the eight thermodynamical properties of substances (usually in gas or vapor state). Among those eight thermodynamic properties, the pressure, volume and temperature can be physically measured, and, therefore, they are the basic measurable properties.

The relation of $P - v - T$ of a substance is usually represented by the equation of state which, in general, can be expressed in the form

$$f(P, v, T) = 0$$

Experience shows that the equations of state for real substances are extremely complicated and are different for different substances. Therefore, there are many equations of state of the form shown above developed in the different literatures.

When all those many equations of state for different substances can be reduced to a single equation, then this single equation rules the infinite variety of $P - v - T$ relations for all substances. On this basis, those substances are said to have the corresponding states. The law of corresponding states can be developed either empirically or theoretically. The empirical development should be based on thermodynamic experimental data while the theoretical development can be based on the classical mechanics, the quantum mechanics, or the

---

1They are: $P, v, T, U, H, S, G$ and $A$. 

transport theory of gases.

The practical application of the law of corresponding states is generally accomplished in two different ways, namely, the generalized compressibility charts and the generalized equations of state. The mathematical analysis of the law of corresponding states is to be treated in this study.

Statement of the Problem

If the law of corresponding states is exact, then:

1. There must be a generalized equation of state applicable to all substances.

2. All experimental data, when plotted on reduced coordinates, would have a same line or surface in the coordinates.

The first problem is a rather theoretical one while the second problem should be proved or verified by experiments. Since the exact equation of state is still not known, several more commonly used empirical equations of state are to be selected and generalized in this study. Those generalized equations of state are then compared with the experimental data.

Historical Review of the Problems

The problem of searching the P - v - T relations for substances is quite an old one. But the exact P - v - T relations of substances are extremely complicated and there are many mechanisms which govern the behaviour of a substance still unknown. However, the investigation of an individual equation of state for every newly produced substance in
the thermodynamic application will continue until the universal $P - \nu - T$ relation for substances is completely realized.

The search for the empirical equation of state attracted many known and unknown scientists\(^2\) since the time of van der Waals. Some of their contributions are still valuable today, while the rest of them have become the historical remarks of science. In a sense, the equation published by Beattie-Bridgeman\(^3\) in 1928 already implied that this equation is about the best for the empirical equations of state if both accuracy and practical application are considered equally important. For accuracy, more specific constants should be introduced. Benedict-Webb-Rubin\(^4\) (1940) involved eight specific constants in their equation, Martin-Hou\(^5\) (1955) used eleven specific constants while Hirschfelder\(^6\) (1958) used six specific constants.

The law of corresponding states was first proposed by van der Waals in 1881, therefore it had almost as long a history as the van der Waals equation had. Experience shows that the van der Waals law of corresponding states is merely a good approximation for substances. It is known


that this law works better at the region near the critical point than for the other regions. The modified law of corresponding states proposed by Kamerlingh Onnes, and modified by G. J. Su? applies fairly well as the pressure approaches zero, but the error is large near the critical point if the difference of $Z_0$ for substances is large.

Experience shows that the exact generalized equation of state must be very complicated; many universal constants should be involved just like many specific constants should be involved in an empirical equation of state. At the present time many scientists are performing research for more universal constants to bring theory and experiment on the law of corresponding states closer together, just like the period after van der Waals when many scientists were interested in establishing more and more specific constants.

Reason and Objective of Study

Thermodynamics is a science of the relation between heat and work. Since this relation can be only expressed in terms of the thermodynamic properties, especially the convenient terms of $P$, $V$, and $T$, therefore, the investigation of the equation of state for the real gases is an important part of thermodynamics.

Since both heat and work are path functions, the determination of the amount of heat and work crossing the boundaries of a system should be based on the change of state of the working substance, and

---

the known relation of thermodynamic properties defining the path through which the change of states takes place. For the evaluation of work, the term \( PdV \) is significant, because

\[
W = \int_{v_1}^{v_2} PdV \quad \text{for nonflow, and}
\]

\[
W = \int_{v_1}^{v_2} PdV - \Delta K.E. - \Delta P.E. - \Delta W_F \quad \text{for steady flow.}
\]

For the determination of heat crossing the boundaries either based on the First Law or Second Law of Thermodynamics, or other energy equations using specific heat, the \( P, V, \) and \( T \) data of the system should be known. Therefore, the properties \( P, V, \) and \( T \) are the independent variables of the thermodynamic equations not only for the work, and heat but also for the thermodynamic properties \( S, U, H, G, \) and \( A. \)

For the engineering applications a very complicated equation of state is not practical. Accuracy and ease of applications are equally important. Therefore, the investigation of complicated empirical equations of state loses its value, while the investigation of the law of corresponding states, either in the form of generalized compressibility charts or of the generalized equation of state, become more important. For accuracy and ease, the generalized compressibility chart is preferable, but the generalized equation of state enables the further thermodynamic developments based on mathematical calculations.

In this study, the mathematical analysis of the equation of state is used to investigate mathematically the possibility of reduced
equations. Several empirical equations of state are calculated to support the mathematical analysis and investigation, and those calculated results are compared graphically with the experimental data to evaluate the validity of the law of corresponding states.

Procedure

The procedure throughout this study will be analytical both thermodynamically and mathematically. Two important points emphasized are: (1) there is similarity in real gas behaviour (2) there are some coordinates in which all gas behaviours are ruled by a single equation.

In Chapter II, the background concepts will be discussed. It will be emphasized to show that all real gases behave similarity, or in other words, the \( P - v - T \) surfaces for different substances are qualitatively similar in shape. Both macroscopic and microscopic characteristics of gases will be discussed. In Chapter III, the determination of the specific constants will be discussed in detail, and removal of those constants by the transformation of coordinates will also be discussed. The mathematical calculation to find the generalized equations will be given in Chapter IV. Experimental data will be borrowed from different literature to compare with the calculated results graphically shown in Chapter V. Summary and discussion of this study will be given in Chapter VI.

Scope and Limitation of Study

There are many limitations of this study. First of all, the theoretical development of the law of corresponding states needs a sound
background in atomic physics, and makes use of the quantum mechanics and transport theory of gases. All these are beyond the scope of engineering thermodynamics. Secondly, the experimental data for reference in comparing with the calculated results are quite limited. For instance, the curve of Boyle points for different substances are seldom seen in the literature. The one used in this study is still a verified result from other diagrams. Thirdly, the explanations based on the molecular phenomena of substances, how the law of corresponding states exists, and why the critical properties are best suitable for the reducing parameter, are not known. Even the theoretical development of the law of corresponding states based on the quantum mechanics or the transport theory are not direct derivations of a generalized equation of state but merely a prediction of the existence of an equation involving only dimensionless terms.

\[\text{---}\]

\[8\text{The thermodynamical and mathematical reasons are discussed.}\]
CHAPTER II

SIMILAR BEHAVIOUR OF GASES

It has been mentioned previously in Chapter I that the P - v - T relations for different substances are all different. However, if we investigate the P - v - T surfaces for different substances, we can find that those surfaces are qualitatively similar in shape. All have the solid, liquid and vapor (or gas) states, and therefore each surface has the saturation line, triple point, critical point, etc. Further discussions regarding the similar behaviour of gases are given in this chapter.

Ideal Gas State

The perfect or the ideal gas was originally defined by scientists as one that could never be liquefied (the so-called permanent gas) and that its P - v - T relation was given by the equation

\[ P v = R T \]  \hspace{1cm} (1)

Unfortunately, it has been shown that no such hypothetical gas actually exists because: (1) different gases have been liquefied and (2) no real gas obeys the ideal gas equation for all range of pressures and temperatures.

A New Concept

Experience shows that there is an individual equation of the form

\[ f(P, v, T) = 0 \]  \hspace{1cm} (2)

existing for every substance, but the exact form of this equation is usually extremely complicated. Even though we cannot develop this exact
equation, we know that every substance follows the path predetermined by this unknown equation.

It is desirable to present this unknown equation graphically according to the experimental data available. The \( P = v = T \) surface is the most direct representation of Equation (2) but it is not a practical tool for solving the \( P = v = T \) relations. A much more useful diagram is the compressibility-pressure chart as shown in Figure 1. This diagram shows the deviation of a real gas from Equation (1). The following facts are observed from this chart:

1. All isotherms approach and meet at the point \((0, 1)\) when the pressure approaches zero.

2. For \( T \to \infty \), the isotherms approaches the line \( Z = 1 \).

\[ \frac{P_v}{RT} > 1.0 \]

\[ \frac{P_v}{RT} < 1.0 \]

\[ T_c = 1.1 \]

\[ T = 1.0 \]

\[ T = 2.5 \]

\[ T = 5.0 \]

\[ T = 10.0 \]

**Figure 1. The \( Z = P_v \) Chart**

Assume that there are different equations of state having the
form of Equation (2) for different substances. Then according to the facts concluded from Figure 1, the following relations exist,

$$\lim_{P \to 0} f_1(P, v, T) = \lim_{P \to 0} f_2(P, v, T) = \ldots = \frac{Pv}{RT} - 1$$  \hspace{1cm} (3)

regardless of the substance and its temperature. Two important ideas are introduced with this expression.

1. Any empirically or theoretically derived equation of state for a real gas should be able to be reduced to Equation (1) when the pressure approaches zero.

2. The problems of existence and the physical properties of the ideal gas become less important, while a new concept "thermodynamically ideal state of real gas" is more logical. In this state, different gases behave identically and ideally according to the following rules,

$$Pv = RT$$  \hspace{1cm} (1)

$$U \leq \text{K.E. of molecules} = f(T) \text{ only.}$$  \hspace{1cm} (4)

This new concept of defining the ideal gas as a "state" instead of "substance" not only gives better interpretation in the analysis and evaluation of the thermodynamic processes or cycles but also gives a basis for the law of corresponding states.

**Foundation**

The ideal gas equation can be either derived directly from Boyle's law and Charle's law, or indirectly from the kinetic theory of gases with some interpolations. The relation

\[ P = \frac{f(T)}{v} \text{ only.} \]
\[ K.E. = \frac{1}{2} m v^2 = \frac{3}{2} kT \quad (5) \]

is needed in order to bring the pressure directly derived
\[ P = \frac{1}{3} \frac{N}{v} m v^2 \quad (6) \]
up to have the form of ideal gas equation. Note that this relation
not only gives a molecular interpretation of the definition of absolute
temperature
\[ T = \frac{m v^2}{k} \quad (7) \]
but also implies the relation
\[ U = \sum K.E. = f(T) \text{ only.} \quad (4) \]

For reference in the discussion of real gas behaviour the molecular
type\textsuperscript{10} assumed in the kinetic theory of gases are listed as follows:

1. Molecules exert no force on each other except contact forces
at the instant of impact, thus \( \sum \text{P.E.} = 0 \) and therefore \( U = \sum K.E. \).  

2. Molecules are spherically symmetric.

3. Any finite volume of gas consists of a very large number of
molecules.

4. Molecules are negligibly small in size compared to the average
distance between molecules or the mean free path.

5. Molecules are in a state of continuous motion traveling in
straight lines except at the instant of collision with another molecule.

\textsuperscript{10} R. D. Present, \textit{Kinetic Theory of Gases}, PP. 2-5, McGraw-Hill:
and Statistical Mechanics}, PP. 208-218, Addison-Wesley: Reading,
Massachusetts, 1956.
or the wall.

6. All collisions of molecules as stated above are perfectly elastic.

7. Molecular distribution throughout the container is uniform in the absence of external forces.

8. Directional probabilities of molecular motion are equal.

9. Velocity distribution of molecules is unchanged during equilibrium.

**Real Gas Behaviour**

All real gases attain the same thermodynamic state; the ideal gas state, when their pressures approach to zero. It is not the aim here to propose a new equation of state, but to discuss briefly the qualitatively similar deviations of all real gases from the ideal state and the molecular mechanism governing them. However several typical empirical equations of state will be selected for further investigation in connection with the law of corresponding states.

**Deviation from the Ideal State—Macrosopic**

As has been stated before, Boyle's law and Charle's law are the foundations of the ideal gas state. Unfortunately, the departure of real gases from these laws is large, especially for high pressures and for low temperatures. Figure 2 shows the deviation of two samples of natural gas from Boyle's law. It is seen that when the pressure is high the deviation from the equation $Pv = C$ is large.
The deviation of real gases from Charle's law can be represented on either v - T or P - T diagram. Figure 3 shows the isobars of a real gas. For a large value of T, the isobars are given by $v = \frac{RT}{P}$ and are straight lines which, if produced, would pass through the origin. For medium values of T, the isobars are convex upward, and in the heterogeneous region there are three values of v for each value of T for the ideal isobars, while the real isobars are parallel to the v axis.

Figure 4 shows a P - T diagram for a real gas both in heterogeneous and homogenous state. The vapor-liquid line starts from the

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Figure 2. Deviation of Natural Gas from Boyle's Law. Data from T. W. Johnson, U. S. Bur. Mines Tech. Paper 539, 1932
Figure 3. The Isobars of a Real Gas

The triple point and end at the critical point. For high temperatures the isobars are straight lines and therefore, agree with the Charle's law. For medium temperatures they have a small curvature.

Figure 4. The Isochores of a Real Gas
The investigation of the \( PV - P \) experiment has been performed by many scientists. The typical \( PV - P \) isotherms are shown in Figure 5.

Figure 5. The \( PV - P \) Isotherms for Different Gases

Observing that in this diagram, there is one particular temperature for

---


which the $P_v - P$ isotherm has a horizontal tangent at $P = 0$. This particular temperature is called the Boyle temperature. The Boyle temperature for some gases are given in TABLE I.

**TABLE I. THE BOYLE TEMPERATURE FOR THE VARIOUS SUBSTANCES (IN °K)**

<table>
<thead>
<tr>
<th>Substance</th>
<th>$H_e$</th>
<th>$H_2$</th>
<th>$Ne$</th>
<th>$N_2$</th>
<th>$A$</th>
<th>$O_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °K</td>
<td>19</td>
<td>106</td>
<td>134</td>
<td>323</td>
<td>410</td>
<td>423</td>
</tr>
</tbody>
</table>

For the temperatures higher than Boyle temperature, the isotherms increase monotonically, while for the temperatures lower than the Boyle temperature each isotherm has a minimum at the point which is called the Boyle point.

Now, based on the nature of the $P_v - P$ isotherms, an equation of state can be expressed by means of a power series

$$P_v = A(1 + B'P + C'P^2 + \ldots) \quad (8)$$
or

$$P_v = A + BP + CP^2 + \ldots\ldots \quad (8a)$$

This is the general form of the equation of state and usually called the virial equation of state. Now referring back to the $Z - P_r$ chart shown in Figure 1, a general equation of state may be obtained in the following form

$$\frac{P_v}{RT} = 1 + \sum_{i=1}^{\infty} \alpha_1 p^i. \quad (9)$$

Equation (8) and (9) are of the same nature. Some other expressions for the virial equation of state are given below:

$$P_v = A + \frac{B}{v} + \frac{C}{v^2} + \ldots\ldots \quad (10)$$
\[
P_v = A(1 + \frac{B'}{v} + \frac{C'}{v^2} + \ldots) \quad (10a)
\]
\[
\frac{P_v}{RT} = 1 + \frac{B'}{v} + \frac{C'}{v^2} + \ldots \quad (11)
\]

Some statements regarding the nature of the virial equations of state that reflect the similar behaviour of real gases are given as follows:

1. The virial coefficients \(\alpha_i\) and \(A, B, C, \ldots\) or \(A', B', C' \ldots\) being a function of temperature only are different for different gases.

2. For very low pressure ranges\(^{13}\), the \(P_v - P\) isotherms are all nearly linear. In this case only the first two terms in the expansion of Equations (8), (9), (10), and (11) are significant.

3. For \(P \approx 0\), the first virial coefficient is a function of temperature only regardless of substance, and all the above virial equations of state reduce to the equation \(P_v = RT\) for the ideal state.

4. For higher pressure region, more virial coefficients are required in order to give better agreement with experimental data.

5. Referring to Figure 5, when the temperatures are below the Boyle temperature the second virial coefficient is negative, while for the temperatures above the Boyle temperature it is positive.

6. The virial equation can easily be solved for \(v\), where the volume "\(v\)" can not be easily measured, and therefore is usually

\(^{13}\)say \(0 \sim 40\) atm, refer to Figure 5.
treated as the dependent variable.

7. Virial coefficients can be determined either from experimental data or by calculation based on the assumed intermolecular forces.  

8. The more accurate the equation of state is, the greater will be the number of virial coefficients and specific constants that will be involved in the virial equation of state.

9. All behaviour of gases start from the common ideal state, then depart gradually one from another as governed by different virial coefficients. Therefore, if universal coefficients can be found instead of virial coefficients, then a single equation will apply to all substances.

**Deviation from Ideal State—Microscopic**

Nine assumptions regarding the molecular nature are assumed as the microscopic foundation of the ideal gas state. Every real gas deviates from its ideal state behaviour because some of those assumptions are not the actual case. The most important two are:

1. **Molecular size**: The molecules have finite size, so that each molecule prevents others from making use of a part of space determined by the container. This fact causes the volume of a gas to be larger than that calculated for ideal behaviour. Clausius in 1852 first introduced this correction and by use of the term "Equivalent collision" he deduced his equation

\[ P(v - b) = nRT \]  

(12)

\[ ^{14}Tbid. 10, P. 101. \]
where \( b = \frac{1}{3} N \cdot V_{\text{exclusion}} = \frac{1}{3} \pi \left( \frac{8}{3} (2 \rho)^3 \right) = \frac{16}{3} \pi \rho^3 \)

which is 4 times the total molecular volume. Therefore, \( b \propto \rho^3 \) is a constant, different for different molecules of gases.

2. Intermolecular forces: There are attraction or repulsion forces existing between molecules of a real gas. When two molecules are far apart, the attraction force is weak, while they come closer, the force becomes stronger and has a maximum at a certain distance. Further approach over this distance, the attraction force decreases and turns into a repulsion which increases rapidly when they come together. It is apparent that molecules of a gas in the outside layer exert inward or outward forces while those within the layer may be considered equally attracted or repelled in all directions. Therefore, the actual pressure exerted on a wall by a gas may be less than or greater than that calculated pressure based on the kinetic theory of gases. Therefore the Clausius equation may be modified as

\[
(P + \Delta P)(v - b) = RT
\]

where \( \Delta P \propto \left( \frac{\rho}{V} \right)^2 = \alpha \left( \frac{\rho}{V} \right)^2 \)

In 1873, van der Waals, a Dutch physicist, first derived his historically important equation of state

\[
\left( P + \frac{\Delta P}{\rho^2} \right)(v - b) = RT.
\]

**Nature of Specific Constants**

No attempt will be made to discuss the distinction and application

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\(^{15}\)Actually \( b = f(T) \).

\(^{16}\)Note that molecule is the smallest unit of substance having chemical properties.
of this qualitatively important equation of state, but the nature of the specific constants are of interest here. A more accurate investigation of intermolecular forces and collisions\textsuperscript{17} shows that both constants "a" and "b" are actually functions of temperature, but not simply constants of proportionality. These constants can also be found empirically by fitting the empirical equation of experimental data for a particular region. Therefore several sets of constants are needed. However, an approximate method can be used to calculate the constants from some special point. The most commonly used is the critical point. The reasons for using the critical point of a substance are given as follows:

1. Critical values of $P$ and $T$ for any gas are constant.

2. The critical point is a mathematically\textsuperscript{18} and thermodynamically significant point.

3. The compressibility factor $Z$ at critical point has very similar values for different substances. Therefore, it seems all substances behave similarly near the critical point.

4. The gaseous region is of great interest where the critical point occurs.

5. Experience shows that the results of using the critical point for calculating the constants in the equation of state is satisfactory for the engineering purposes.

\textsuperscript{17} This is beyond the scope of this study. For further reference, see R. D. Present, \textit{Kinetic Theory of Gases}, PP. 103-108, McGraw-Hill: New York, 1958.

\textsuperscript{18} Further mathematical analysis of the critical point is given in Chapter III of this thesis.
Empirical Equation of State

A very large number of equations of state\(^{19}\) have been proposed since van der Waals presented his famous equation of state in 1873. Different equations have been proposed based on the kinetic theory of gases, statistical mechanics and thermodynamic relations. Some of those equations were developed to describe the behaviour of certain groups of gases for a limited range. Others have been derived to cover the \(P \cdot v \cdot T\) relations of fluids covering the whole range of gas (or vapor) and liquid states.

For mathematical analysis and computations in connection with the law of corresponding states, three common equations of state are selected, as follows:

1. Mestel (1899)
\[
p = \frac{RT}{v - b} \cdot e^{-a/RTv}
\]

2. Berthelot (1903)
\[
p = \frac{RT}{v - b} - \frac{a}{Tv^2}
\]

3. Wohl (1914)
\[
p = \frac{RT}{v - b} - \frac{a}{Tv(v - b)} + \frac{C}{t^2v^3}
\]

\(^{19}\) J. Otto, op. cit.
CHAPTER III

MATHEMATICAL ANALYSIS

In this chapter, the mathematical analysis consists of two main parts. The first part will discuss the method of determining the values of specific constants of the empirical equation of state. The second part will discuss the method of reducing those specific constants out of the equation of state, so as to deduce to a universal equation of state applicable to all substances. Several thermodynamically significant points are discussed in detail their nature and mathematical expressions.

The Critical Point

It was discovered empirically by Caillet and Mathias\(^{20}\) that if the densities of a liquid and its saturated vapor are plotted against the temperature, the two saturated lines will join smoothly at a point and the entire curve is nearly parabolic in shape. This point is called the critical point. In other words, at the critical point the density of liquid is equal to the density of vapor.

There are two different mathematical expressions to define the critical point:

\[
\left( \frac{\partial P}{\partial v} \right)_T = 0, \quad \left( \frac{\partial^2 P}{\partial v^2} \right)_T = 0
\]

(13)

based on the characteristics of the isotherm at the critical point, and

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\(^{20}\)Caillet and Mathias, Compt. Rend. 102, 1202 (1886); 104, 1563 (1887); J. Phys., Vol. 5, 549 (1886).
\[(v - v_c)^n = 0 \quad (14)\]
based on the nature that n real roots of \(v\) are coincident at the point \(v = v_c\). These expressions mean that the isothermal compressibility is infinite at the critical point, and the properties of a substance are highly singular\(^{21}\) in the region near the critical point.

For most substances the pressure increases steadily with the temperature at constant volume, therefore

\[\left( \frac{\partial P}{\partial T} \right)_v > 0 \quad \text{at} \quad (v = v_c, \ T = T_c) \quad (15)\]

Now, from the relation\(^{22}\)

\[\left( \frac{\partial P}{\partial v} \right)_T \left( \frac{\partial v}{\partial T} \right)_P = - \left( \frac{\partial P}{\partial T} \right)_v \quad (16)\]

or

\[\left( \frac{\partial v}{\partial T} \right)_P = - \left( \frac{\partial P}{\partial v} \right)_T / \left( \frac{\partial P}{\partial T} \right)_v \quad (16a)\]

Substituting the first of Equation (13) in Equation (16a)

\[\left( \frac{\partial v}{\partial T} \right)_P = - \left( \frac{\partial P}{\partial v} \right)_v / 0 = \infty \quad \text{at} \quad (T = T_c, \ P = P_c) \ldots \ldots \quad (17)\]

Equation (17) means that at critical point, the volume of any gas increases infinitely with an infinitesimal increase of temperature when the pressure remains constant, or in other words, the volume expansivity\(^{23}\) at the critical point is infinite. This can be explained


\(^{23}\)Volume expansivity \(B = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P\).
in more physical meaning that the surface between the two phases is extremely diffuse in the neighborhood of the critical point regardless of substances.

Now, refer to the relation for the difference of specific heats \(^{24}\)

\[
C_P - C_v = T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V
\]

(18)

or

\[
C_P = C_v + T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V
\]

(18a)

In Equation (18a), \( C_v > 0 \), and \( (\frac{\partial V}{\partial T})_P = \infty \), therefore, we get

\[
C_P = \infty
\]

(19)

at critical point regardless of substances.

As far as the gas (and vapor) and liquid states are concerned, the boundary between the two phases is of primary interest. Since the critical point is the only special point on this boundary, it can be said that the location of the critical point in coordinates influences the \( P - v - T \) relation of a substance. The characteristics of the critical point is summarized as follows for further application:

1. The critical point can be defined mathematically by Equation (13) and (14).

2. The thermodynamical natures of the critical point for different substances are similar as expressed by Equation (17) and (18).

3. The critical point for any substance has a finite location in a \( P - v - T \) coordinates.

\(^{24}\) Zemansky, op. cit., P. 251.
Determination of the Specific Constants

It has been pointed out that the specific constants "a" and "b" in the van der Waals equation or constants in other equations of state are different for different substances, actually they are not constant for any substance but are functions of temperature. It is also mentioned that many different sets of constants may be obtained empirically, but the calculation based on the critical point is the most desirable.

Consider the equation of state in the form

\[ f(P, v, T) = 0 \]  \hspace{1cm} (2)

which may involve the specific constants \( \lambda_1, \lambda_2, \ldots, \lambda_4 \) as expressed by Equation (9). Now, in order to determine the values of \( \lambda_1, \lambda_2, \ldots, \lambda_4 \), we choose a characteristic or reference point \((P_q, v_q, T_q)\), such as the critical point of a substance. Then Equation (2) becomes

\[ f_1(P_q, v_q, T_q) = 0 \]  \hspace{1cm} (20)

This equation alone is not sufficient either to solve for \( P_q, v_q, \) and \( T_q \) in terms of \( \lambda_1, \lambda_2, \ldots, \lambda_4 \), or to solve \( \lambda_1, \lambda_2, \ldots, \lambda_4 \), in terms of \( P_q, v_q, \) and \( T_q \). In order to solve for \( P_q, v_q, \) and \( T_q \), two more independent equations are required. Similarly, in order to solve for \( \lambda_1, \lambda_2, \ldots, \lambda_4 \), additional \((4 - 1)\) independent equations are needed. All these additional equations to be set up such as Equation (13) must be substituted at the characteristic or reference point \((P_q, v_q, T_q)\).
Reference Point

The reference point must be able to be determined mathematically, physically and thermodynamically. It must have mathematical characteristics so as to set up additional independent equations. For physical significance the values of $P_q$, $v_q$, and $T_q$ must be constant for each substance. The reference point must also be similar thermodynamically to all substances, so that the equation of state can apply, in common, to all substances.

The thermodynamically similar points in the $P - v - T$ surface or any $P, v, T$, diagram\textsuperscript{25} are the triple point, the critical point, and the Boyle point at Boyle temperature. The critical point has appeared in Figures 1, 3, 4, etc. The triple point has been shown in Figure 4. Figure 6 shows both the critical point and triple point in a $T - P$ diagram. It must be noted that the triple point appears as a straight line in the $P - v$ diagram, as shown in Figure 7. The Boyle point at Boyle temperature had been defined in Chapter 2, and had been shown in Figure 5.

The triple point is a physically and thermodynamically significant point but it does not have mathematical characteristics to set up the additional independent equations, therefore this point is not qualified to be the reference point. Moreover, the equations of state were seldom developed for the region near the triple point.

The Boyle point at Boyle temperature has definite location in the

\textsuperscript{25}Such as $P - v$, $T - P$, $T - v$, $Pv - P$ ... etc.
PV - P coordinates is also a common point for all substances. This point has an important thermodynamical meaning but its physical significance is not apparent (It can not be observed in the P - v - T surface.) The mathematical conditions are

\[
(\frac{\partial^2 PV}{\partial P^2})_T = 0 \quad P = 0
\]  

(21)

Therefore, two additional equation are available from this point \( B(0, v_B, T_B) \) and the number of the specific constants up to 3 can be calculated. However, this point appears in a multi-variable coordinates \( PV = P \), at the condition \( \lim_{P \to 0} P_v \), the mathematical calculation would be very complicated. Furthermore, if the reduced properties are considered, this point loses its mathematical meaning immediately from the condition \( P_B = 0 \).
Finally, based on the mathematical, physical, and thermodynamical characteristics summarized before, the critical point is the most suitable reference point for determining the specific constants. This is the reason why many empirical equations of state were developed to describe the region near the critical point of the substance.

Critical Point as the Reference Point

If the critical point is used as the reference point and Equations (13) are used to obtain the additional independent equations, Equation (2) can be expressed in the form

\[ P = P(v, T) \]  \hspace{1cm} (22)

Fortunately, this is the most desirable form of the equation of state if the kinetic theory and statistical mechanics are used to calculate the pressure of a gas. The number of constants, say \( i \), involved in the equation of state such as Equation (9) must satisfy the condition below:

\[ i \leq 3 \]  \hspace{1cm} (23)

If the number of specific constants involved is greater than 3, say 4, 5, ..., Equation (14) should be used instead of Equations (13). In this case, Equation (2) should be rearranged in descending power of \( v \).

\[ v^n + a_1 v^{n-1} + a_2 v^{n-2} + \ldots + c = 0 \ldots \]  \hspace{1cm} (24)

---

\(^{26}\)The equations of state of van der Waals, Berthelot, Distriuci, Wohl, and Beattie-Bridgman, all can be expressed in this form.
Equation (14) may be expanded as
\[ v^n = a_1 v^{n-1} + a_2 v^{n-2} + \cdots + (-1)^n v^n = 0 \] (25)

In Equation (24) and (25), \( n + 1 \) terms are involved. Since these two
equations must be identical, therefore
\[ \begin{align*}
  a_1 &= a'_1 \\
  a_2 &= a'_2 \\
  a_3 &= a'_3 \\
  \vdots \\
  c &= (-1)^n v^n \\
\end{align*} \] (26)

Therefore, \( n \) equations can be set up to solve for the specific constants.
The number of specific constants involved is \( i \) which must satisfy the
following condition:
\[ i \leq n \] (27)

The condition of Equation (23) and (27) are checked with several equations
of state as follows:

1. The van der Waals, Dristici and Berthelot equation of state.
   \[ i = 2, \; n = 3, \; \therefore i < 3, \; i < n. \]
   Therefore, \( P_0, \; v_0 \) and \( T_0 \) can be mathematically determined in term of the
   specific constants \( a \) and \( b \). Conversely, \( a \) and \( b \) can be mathematically
determined in term of \( P_0, \; v_0 \) and \( T_0 \).

2. The Woal equation of state.
   \[ i = 3, \; n = 4, \; \therefore i < n \]
   Therefore, \( P_0, \; v_0 \) and \( T_0 \) can be also determined mathematically in terms
of the specific constants a, b and c and vice versa.

3. The Beattie-Bridgeman equation of state.

\[ i = 5, \quad n = 4 \quad \frac{i}{n} \]

In this case the required condition of Equation (27) is not satisfied. Therefore, no direct mathematical calculation is possible.

Transformation of Coordinates

It was discussed in the previous section that the specific constants involved in an equation of state can be determined mathematically in terms of \( P_0, V_0, \) and \( T_0 \) under certain condition. If those constants can be eliminated by the transformation of the coordinates, then the resulting equation in the new coordinates will be applicable to all substances. This is called the Law of Corresponding States in which the new variables are called the reduced variables, and the new coordinates may be called the reduced coordinates. Since the specific constants to be eliminated are in terms of \( P_0, V_0, \) and \( T_0 \), it is natural that the parameter to be used for the reduced coordinates must also be in terms of \( P_0, V_0, \) and \( T_0 \). There are several kinds of transformation of coordinates:

1. Linear transformation

Set \( v' = v + v_0, \quad P' = P + P_0, \quad T' = T + T_0 \quad \) where \( v', P' \) and \( T' \) are new variables

2. Uniform reduction transformation

Set \( v' = \frac{v}{k}, \quad P' = \frac{P}{k}, \quad T' = \frac{T}{k} \quad \) where \( k \) is a geometrical reduction constant which is different for different substances.
3. (Critical) reduced coordinates

Set \[ v_r = \frac{V}{V_c}, \quad P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c} \]

From the thermodynamic point of view, if the linear transformation is true, then all \( P - v - T \) surfaces must be same in size and shape but merely differently located. It is apparently not the actual case. If the uniform reduction transformation is true, it means that all \( P - v - T \) surfaces are symmetric with each other. This is not physically impossible. However, since \( k \) is a dimensionless constant, therefore, as far as the mathematical calculation is concerned, this kind of transformation is not applicable. Therefore, from the above, only the reduced coordinate is feasible.

The Reduced Equation of State

In Equation (2), let

\[ v_r = \frac{V}{V_c}, \quad P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}. \quad (28) \]

Then we obtain

\[ f(P_r, v_r, T_r) = 0 \quad (29) \]

In this equation, there is no specific constant, and the new variables are dimensionless. This kind of transformation can be explained as follows: Assume that there are two coordinates \( P - v - T \) and \( P_r - v_r - T_r \) to be correlated in such a manner that \[ \frac{V}{V_r} = v_r \]

\[ \frac{P}{P_r} = P_c, \quad \text{and} \quad \frac{T}{T_r} = T_c. \quad \text{We move all} \quad P - v - T \quad \text{surfaces and reduce accordingly to the} \quad P_r - v_r - T_r \quad \text{coordinates. Then set all critical} \]
points at the position \((1, 1, 1)\) of the coordinates, so that all surfaces coincide and the unique \(P_r - v_r - T_r\) relation exists.

The law of corresponding state may be stated as "All substances obey the same equation of state when the reduced variables are used." This statement can be supported either by experimental data plotted on reduced coordinates or by mathematical derivation of the generalized equations of state which are applicable to all substances. If the mathematical derivation is used, then the specific constants involved in the equation of state should be able to be expressed in terms of \(P_c, v_c, T_c\), and vice versa. For the reason given previously the Beattie-Bridgeman equation can not be generalized by mathematical computation.

The theoretical development of the law of corresponding states is usually complicated and needs making use of the advanced knowledges of modern physics. It can be done based on the classical mechanics, \(^{27,28}\) quantum mechanics, \(^{29}\) and transport theory of gases. \(^{30}\) Those are out of the scope of this study.

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\(^{29}\) Hirschfelder, *op. cit.* P. 424.

\(^{30}\) Hirschfelder, *op. cit.* P. 618.
CHAPTER IV

MATHEMATICAL CALCULATIONS OF THE GENERALIZED EQUATIONS

Mathematical treatment of several commonly used equations of state as mentioned in Chapter II will be given in this chapter. This is one of the method of attack to manifest the law of corresponding states for real gases. The calculations will emphasize the following items:

1. Specific constants (in terms of \( P_c \), \( v_c \), and \( T_c \)).
2. Compressibility factor at the critical point.
4. Generalized equation of the locus of Boyle points.
5. Generalized Boyle temperature.

The van der Waals Equation

The equation is given by (see Chapter II)

\[
(P + \frac{a}{v^2})(v - b) = RT
\]

or

\[
P = \frac{RT}{v - b} - \frac{a}{v^2}
\]

Specific Constants

Using the Equation (13) in Equation (30a), we have

\[
\left( \frac{\partial P}{\partial v} \right)_T = \frac{-RT}{(v - b)^2} + \frac{2a}{v^3} = 0
\]

at the critical point, the above equation becomes

\[
\frac{2a}{v_c^3} = \frac{RT_c}{(v_c - b)^2}
\]
Further

\[
\left( \frac{\partial^2 p}{\partial v^2} \right) T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0
\]

\[
\therefore \frac{3a}{v_c^4} = \frac{RT_c}{(v_c-b)^3}
\] (32)

Dividing Equation (31) by Equation (32), we get

\[
\frac{2}{3} \frac{v_c}{v_c-b} = v_c - b \quad \therefore \quad v_c = 3b
\] (33)

Substituting Equation (33) into Equation (31), it follows

\[
T_c = \frac{8a}{27bR}
\] (34)

Substitute Equation (33) and (34) into (30a) and simplifying, we have

\[
P_c = \frac{a}{27b^2}
\] (35)

Since the measurement of \( P_c \) and \( T_c \) is much easier than that of \( v_c \), solving Equation (34) and (35) for \( a \) and \( b \), it yields

\[
a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}
\] (36)

\[
b = \frac{1}{8} \frac{R T_c}{P_c}
\] (37)

**Compressibility Factor at C.P. (Critical Point)**

\[
Z_c = \frac{P_c v_c}{R T_c} = \frac{a}{27b^2} \frac{3b}{8a} = \frac{3}{8} = 0.375
\] (38)

**Generalised Equation of State**

Upon substitution of
\[ P = P_e P_r, \quad V = V_e V_r, \quad T = T_e T_r \]

In Equation (30), it follows
\[
\left[ P_e P_r + \frac{A}{(V_e V_r)^2} \right] (V_e V_r - b) = R T_e T_r
\]

Furthermore, substituting Equation (33), (34) and (35) in above equation and simplifying,
\[
(P_r + \frac{2}{V_r^2})(V_r - 1) = 8T_r
\]

This is the generalized van der Waals equation in the form
\[ f(P_r, V_r, T_r) = 0 \] which involves no specific constant and, therefore, applies to all substances.

**Boyle Points**

Let \( y = P_r V_r \), \( x = P_r \) in Equation (39)
\[
(x + \frac{3}{2} \frac{y}{x^2} ) (3 \frac{y}{x^2} - 1) = 8T_r
\]
\[
\therefore \quad 3x^3 - xy^2 + 9xy - 3x^2 = 8T_r y^2
\]

Since the slope of tangent at the Boyle point is zero
\[
(\frac{dy}{dx})_{T_r} = -y^2 + 9y - 6x = 0
\]
\[
y^2 - 9y + 6x = 0
\]

This equation is a parabola and represents the locus of the Boyle point.

Moreover, this equation should be universal to all substances.
Boyle Temperature

The Boyle temperature is the temperature where the Boyle point occur at \( x = 0, y = 0 \). Let \( x = 0 \) in Equation (41)

\[ y^2 - 9y = 0, \quad y(y - 9) = 0 \quad \therefore y = 9 \]

Substituting \( y = 9, x = 0 \) in Equation (40), one gets

\[ T_r = \frac{27}{8} = 3.375 \tag{42} \]

Therefore, the Boyle temperature is 3.375 \( T_c \). This value is close enough to the experimental values as will be shown in Figure 11.

Berthelot Equation

\[ p = \frac{RT}{v - b} - \frac{8}{Tv^2} \tag{43} \]

Specific Constants

\[ (\frac{dp}{dv})_T = \frac{-RT}{(v - b)^2} + \frac{2a}{Tv^3} = 0 \]

\[ \therefore \frac{2a}{Tv^3} = \frac{RT_c}{(v_c - b)^2} \tag{44} \]

\[ (\frac{d^2p}{dv^2})_T = \frac{2RT}{(v - b)^3} - \frac{6a}{Tv^4} = 0 \]

\[ \therefore \frac{6a}{Tv_c^4} = \frac{2RT_c}{(v_c - b)^3} \tag{45} \]

Dividing Equation (44) by Equation (45), we have

\[ \frac{v_c}{3} = \frac{v_c - b}{2} \quad v_c = 3b \tag{46} \]
Substituting Equation (46) into Equation (44), it gives

\[ RT_c^2 = \frac{8a}{27b} \quad \therefore \quad T_c = \sqrt{\frac{8a}{27bR}} \quad (47) \]

Upon substitution of Equations (46) and (47) in Equation (43), one gets

\[ P_c = \frac{RT_c^2}{2b} - \frac{a}{9T_c b^2} \quad (48) \]

or

\[ P_c = \sqrt{\frac{aR}{216b^3}} \quad (48a) \]

Solving Equations (47) and (48) for \( a \) and \( b \), we get

\[ a = \frac{27}{64} \frac{R^2 T_c^3}{P_c} \quad (49) \]

\[ b = \frac{1}{8} \frac{RT_c}{P_c} \quad (50) \]

**Compressibility Factor at C.P.**

\[ z_c = \frac{P_c V_c}{R T_c} = \frac{27R^2 T_c^3}{64a} \frac{3b}{R T_c} = \frac{3}{8} = 0.375 \ldots \ldots \quad (51) \]

This is the same as that obtained in the van der Waals equation.

**Generalized Equation of State**

Substituting the reduced properties in Equation (43), we get

\[(P_c p_R + \frac{8}{T_c T_R (v_c v_R)^2})(v_c v_R - b) = R T_c T_R \]

Substituting again the values of \( a \) and \( b \) from Equations (49) and (50)
in the above equation and referring to the procedures used before, one has

\[ (P_r + \frac{2}{T_r T_r^\prime}) (3y_r - 1) = 8T_r \]  

(52)

This generalised Berthelot equation is very similar to the generalised van der Waals equation.

**Boyle Points**

In Equation (52), let \( P_r y_r = y, \ P_r = x \), we get

\[ 3y - x + \frac{2y}{T_r y} - \frac{y^2}{T_r y^2} = 8T_r \]

Multiplying this by \( y^2 \), one gets

\[ 3y^3 - xy^2 + \frac{2xy}{T_r} - \frac{y^2}{T_r} = 8T_r y^2 \]

(53)

Since \( \left( \frac{\partial y}{\partial x} \right)_{T_r} = 0 \)

\[ - y^2 + \frac{2y}{T_r} - \frac{6x}{T_r} = 0 \]

or

\[ T_r y^2 - 9y + 6x = 0 \]

(54)

\( T_r \) is calculated\(^{32} \) from Equations (53) and (54) and equals to 1.84.

Therefore Equation (54) becomes

\[ 1.84y^2 - 9y + 6x = 0 \]

(54a)

This is the generalised equation for the locus of Boyle points.

\(^{32}\)Refer to the calculation of Boyle temperature.
Boyle Temperature

Let \( x = 0 \) in the Equation (53), which yields
\[
3y^3 = 8T_{v}y^2 \quad \text{or} \quad T_{r} = \frac{3y}{8} \tag{55}
\]

In addition, let \( x = 0 \) in Equation (54), we get
\[
T_{v}y^2 = 9y \quad \text{or} \quad T_{r} = \frac{2}{y} \tag{56}
\]

Solving Equations (55) and (56) for \( T_{r} \), we have
\[
\frac{3y}{8} = \frac{2}{y} \quad \quad 3y^2 = 72 \quad \quad y = \sqrt{24} = 4.9
\]
\[
\therefore \quad T_{r} = \frac{2}{4.9} = 1.84 \tag{57}
\]

Dioteric Equation
\[
P = \frac{RT}{v - b} \exp \left( -\frac{a}{RTv} \right) \tag{58}
\]

Specific Constants
\[
\left( \frac{d^2P}{dv^2} \right)_T = \frac{RT}{v - b} \exp \left( -\frac{a}{RTv} \right) \frac{a}{RTv^2}
\]
\[
+ \exp \left( -\frac{a}{RTv} \right) \cdot \frac{-RT}{(v - b)^2}
\]
\[
= \frac{RT}{v - b} \exp \left( -\frac{a}{RTv} \right) \left( \frac{a}{RTv^2} - \frac{1}{v - b} \right)
\]
\[
= \left[ P \right] \left( \frac{a}{RTv^2} - \frac{1}{v - b} \right) = 0 \tag{59}
\]
\[
\left( \frac{d^2P}{dv^2} \right)_T = \left[ P \right] = -\frac{2a}{RT^2} + \frac{a}{RTv^2} \frac{dP}{dv}
\]
\[
- \left[ \frac{\partial}{\partial v} \right]\frac{\partial}{\partial (v-b)^2} \left\{ \frac{a}{RTv^3} \right\} - \frac{1}{v-b} \left( \frac{a}{RTv^2} - \frac{1}{v-b} \right) \frac{\partial}{\partial v}
\]

\[
= \left( \frac{\partial}{\partial v} \right) \left\{ \frac{a}{RTv^3} + \left( \frac{a}{RTv^2} \right)^2 - \frac{a}{RTv^2(v-b)} \right\}
\]

\[
+ \frac{1}{(v-b)^2} - \frac{a}{RTv^2(v-b)} + \frac{1}{(v-b)^2}
\]

\[
= \left( \frac{\partial}{\partial v} \right) \left\{ \left( \frac{a}{RTv^2} \right)^2 - \frac{2a}{RTv^3} - \frac{2a}{RTv^2(v-b)} + \frac{2}{(v-b)^2} \right\} = 0 \quad (60)
\]

In Equation (59), \( P \neq 0 \)

\[
\frac{a}{RTv^2} - \frac{1}{v-b} = 0 \quad \text{or} \quad \frac{1}{v-b} = \frac{a}{RTv^2} \quad (61)
\]

In Equation (60), \( P \neq 0 \), the terms in the second bracket must be zero.

Substituting Equation (61) in this bracket, we get

\[
\frac{1}{(v-b)^2} - \frac{2}{(v-b)v} - \frac{2}{(v-b)^2} + \frac{2}{(v-b)^2} = 0
\]

Solving above equation for \( v \), and substituting for the C.P., we get

\[
v_c = 2b \quad (62)
\]

Substituting Equation (62) in Equation (61), one gets

\[
T_C = \frac{a}{4\pi Rb} \quad (63)
\]
\[ P_c = \frac{A}{4b^2} e^{-2} = \frac{A}{29.56b^2} \]  

(64)

The "a" and "b" are solved from Equations (63) and (64). Hence

\[ a = \frac{4R^2T_T^2}{P_c e^2} \]  

(65)

\[ b = \frac{RT_T}{P_c e^2} \]  

(66)

**Compressibility Factor at C.P.**

\[ z_c = \frac{P_c v_c}{RT_c} = 2e^{-2} = 0.2706 \]  

(67)

This value is in better agreement with the experimental data than the value \( \frac{3}{8} \) obtained in the van der Waals and Berthelot equations.

**Generalized Equation of State**

Let \( P = P_c P_T \), \( v = v_c v_T \) and \( T = T_c T_T \) in Equation (58), we get

\[ P_c P_T (v_c v_T - b) = RT_c T_T \exp \left( -\frac{A}{RT_c T_T v_c v_T} \right) \]

Substituting the values of \( P_c, v_c, \) and \( T_c \) in this equation, it yields

\[ \frac{A}{4b^2} e^{-2} P_T (2bv_T - b) = \frac{A}{4b} T_T \exp \left( -\frac{A}{4b} T_T 2bv_T \right) \]

\[ e^{-2} P_T (2v_T - 1) = T_T \exp \left( -\frac{2}{T_T v_T} \right) \]

\[ \text{or} \quad P_T (2v_T - 1) = T_T \exp \left( 2 - \frac{2}{T_T v_T} \right) \]

(68)
Boyle Points

Let \( P_x y = y \), and \( P_x = x \) in Equation (68), then

\[
2y - x = T_x \exp \left( 2 - \frac{2x}{T_x y} \right)
\]

(69)

Partial differentiation with respect to \( x \) for constant \( T_x \) above equation becomes

\[
2\left( \frac{d V}{d x} \right) - 1 = T_x \exp \left( 2 - \frac{2x}{T_x y} \right) \left[ \frac{2}{T_x} \frac{d}{d x} \left( \frac{x}{y} \right) \right]
\]

\[
= -2 \exp \left( 2 - \frac{2x}{T_x y} \right) \left( \frac{y - x \frac{d V}{d x}}{y^2} \right)
\]

Since \( \left( \frac{d V}{d x} \right)_{T_x} = 0 \), therefore, above equation becomes

\[
-1 = -2 \exp \left( 2 - \frac{2x}{T_x y} \right) \left( \frac{1}{y} \right)
\]

or

\[
y = 2 \exp \left( 2 - \frac{2x}{T_x y} \right)
\]

(70)

This equation represents the Boyle points at temperature \( T_y \). The locus of the Boyle points is obtained by eliminating \( T_y \) between Equations (69) and (70). Equation (69) over Equation (70), we get

\[
\frac{2y - x}{y} = \frac{T_x}{2} \quad \therefore \quad T_x = \frac{2(2y - x)}{y}
\]

(71)

Substitute Equation (71) in Equation (70)

\[
y = 2 \exp \left( 2 - \frac{2x}{2(2y - x)} \frac{y}{y} \right)
\]
\[ y = 2 \exp \left( 2 - \frac{x}{2y - x} \right) \]

(72)

**Boyle Temperature**

In Equation (71), let \( x = 0 \)

\[ T_p = \frac{2(2y - 0)}{y} = 4 \]  

(73)

This is even further from truth than that of \( \frac{27}{8} \) given by van der Waals equation.

**Wohl Equation of State**

\[ P = \frac{RT}{v - b} - \frac{a}{Tv(v - b)} + \frac{c}{T^2v^3} \]  

(74)

**Specific Constant**

There are three specific constants involved in Equation (74).

Using Equation (14) to solve for these constants, we rearrange Equation (74) as

\[ v^\prime (b + \frac{RT}{P})v^3 + \frac{a}{Pl} v^2 - \frac{c}{P^2l} v + \frac{be}{P} = 0 \]  

(74a)

The expanded form of Equation (14) for \( n = 4 \) is

\[ v^4 - 4v_c v^3 + 6v_c^2 v^2 - 4v_c^3 v + v_c^4 = 0 \]  

(14a)

By comparing the corresponding coefficients in Equation (74a) and (14a), we get

\[ 4v_c = b + \frac{RT}{P} \]  

(75)
\[ 6v_0^2 = \frac{a}{P_0 T_0} \quad (76) \]
\[ 4v_0^3 = \frac{a}{P_0 T_0^2} \quad (77) \]
\[ v_0^4 = \frac{b}{P_0 T_0^3} \quad (78) \]

There are four equations available. Therefore, both the critical properties and the specific constants can be determined. Dividing Equation (78) by Equation (77), it gives
\[ v_0 = 4b. \quad (79) \]

From Equation (76)
\[ a = 6v_0^2 P_0 T_0. \quad (80) \]

From Equation (75) and (79)
\[ b = \frac{v_0}{4} = \frac{m_e}{15 P_0}. \quad (81) \]

From Equation (77)
\[ c = 4v_0^3 P_0 T_0^2. \quad (82) \]

In order to eliminate \( v_0 \), which is very difficult to measure, from Equations (80) and (81), we get
\[ a = \frac{26}{(15)^2} \frac{R T_0^3}{P_0} \quad (80a) \]

from Equations (81) and (82)
\[ c = \frac{256}{(15)^3} \frac{R T_0^3}{P_0^2} \quad (82a) \]
The critical properties are found as

\[ v_c = 4b \]  \hspace{1cm} (79) \\
\[ T_c = \sqrt{\frac{15a}{96bR}} \]  \hspace{1cm} (83) \\
\[ P_c = \frac{aR}{1440b^3} \]  \hspace{1cm} (84)

**Compressibility Factor at CIP**

From Equation (81)

\[ \frac{P_c v_c}{R T_c} = \frac{4}{15} = 0.266 \]  \hspace{1cm} (85)

This value is very close to the result obtained from the Disterici equation \( z_g = 0.2706 \), and both values agree very well with the experimental data.

**Generalized Equation**

Substituting \( P = P_c P_r \), \( v = v_c v_r \), \( T = T_c T_r \) in Equation (74), one has

\[ P_c P_r = \frac{R T_c T_r}{v_c v_r^{15}} - \frac{a}{T_c T_r v_c v_r (v_c v_r - b)} + \frac{c}{(T_c T_r)^2 (v_c v_r)^3} \]

then, substituting Equation (80), (81) and (82) into above Equation, the simplified result is obtained

\[ P_r = \frac{15T_r}{4v_r} - \frac{6}{T_r v_r (v_r - \frac{b}{c})} + \frac{4}{T_r^2 v_r^3} \]  \hspace{1cm} (86)

**Boyle Points and the Boyle Temperature**

The generalized equation for the locus of the Boyle points and the reduced Boyle temperature are too complicated to be given here.
CHAPTER V

ANALYSIS ON THE GRAPHICAL REPRESENTATION

The thermodynamically significant points, lines, and surfaces calculated in the previous chapter, expressed in the reduced coordinates are to be compared graphically with those expressed in an ordinary coordinate. These points, lines, and surfaces for different substances having different location in the ordinary coordinate are seemed to coincide when they are reduced to move into the reduced coordinates. This is called the law of corresponding states of gases. It is the aim of this chapter to show graphically and evaluate thermodynamically the existence of the corresponding states of real gases.

Compressibility Factor

The compressibility factor $Z$ is defined as

$$Z = \frac{Pv}{RT}$$

Furthermore,

$$Z = \frac{Pv}{RT} = \left( \frac{Pcv_c}{R T_c} \right) \left( \frac{Pv_r}{Tr} \right) = Z_c \frac{Pv_r}{Tr}$$

where $Z_c = \frac{Pcv_c}{R T_c}$ is the compressibility factor at the critical point.

If the law of corresponding states is perfectly satisfactory, the term $Z_c = \frac{Pcv_c}{R T_c}$ must be a universal constant for all substances.
Values of \( Z_c \) from Experiments

The critical compressibility factor for different substances calculated from the experimental data of \( P_c, v_c \) and \( T_c \) varies widely from 0.18 to 0.31 as shown in Table II. In this table, the substances are divided into three groups according to their molecular characteristics. For the simple non-polar molecules, the values of \( Z_c \) are ranged from 0.267 to 0.304, with an average of 0.294. Since those values are very close, therefore those substances seem to have a single reduced equation of state. For the hydrocarbons, the values are ranged from 0.257 to 0.291 with an average value of 0.27. Therefore, for the hydrocarbons, apparently there is another reduced equation of state. The values of \( Z_c \) for those polar gases vary widely from 0.181 to 0.269 with an average value of 0.231.

The values of \( Z_c \) shown in Table II are plotted in Figure 8. It is observed that the non-polar substances and the hydrocarbons have rather close values in two groups, while for the polar substances, the values of \( Z_c \) spread quite broadly. Therefore, it is apparent that a single law of corresponding states is applicable only in a rough approximation to all substances. For accuracy, substances may be divided into several groups based on the values of \( Z_c \), and may be satisfied by different reduced equation of state. For instance, in Figure 10, the curves\(^{31} (1) \) and (2) are to be applied to non-polar substances and hydrocarbons respectively. It is seen, however, that

\(^{31}\)Not in scale.
<table>
<thead>
<tr>
<th>Simple Non-polar Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2 0.300</td>
</tr>
<tr>
<td>H_2 0.304</td>
</tr>
<tr>
<td>N_2 0.296</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane 0.267</td>
</tr>
<tr>
<td>Propane 0.270</td>
</tr>
<tr>
<td>Isobutane 0.276</td>
</tr>
<tr>
<td>n-butyine 0.257</td>
</tr>
<tr>
<td>Isopentane 0.266</td>
</tr>
<tr>
<td>n-Pentane 0.266</td>
</tr>
<tr>
<td>n-Hexane 0.260</td>
</tr>
<tr>
<td>n-Heptane 0.253</td>
</tr>
<tr>
<td>n-Octane 0.253</td>
</tr>
<tr>
<td>Bensene 0.265</td>
</tr>
<tr>
<td>Cyclohexane 0.276</td>
</tr>
<tr>
<td>Diisopropyl 0.266</td>
</tr>
<tr>
<td>Diisobutyl 0.262</td>
</tr>
<tr>
<td>Ethyl ether 0.262</td>
</tr>
<tr>
<td>Ethylene 0.291</td>
</tr>
<tr>
<td>Propylene 0.273</td>
</tr>
<tr>
<td>Acetylene 0.275</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polar Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_3CN 0.181</td>
</tr>
<tr>
<td>H_2O 0.224</td>
</tr>
<tr>
<td>NH_3 0.238</td>
</tr>
<tr>
<td>CH_3OH 0.220</td>
</tr>
<tr>
<td>CH_3Cl 0.258</td>
</tr>
<tr>
<td>C_2H_5Cl 0.269</td>
</tr>
</tbody>
</table>

Figure 8. The Values of $Z_c$ for Different Substances
hydrogen and helium are not agreeable to the group.

**Values of Zc as Calculated from the Equations of State**

The calculated compressibility factor at the critical point for different equations of state are as follows:

- van der Waals: 0.375
- Berthelot: 0.375
- Dieterici: 0.2706
- Wohl: 0.266

These values are also shown in Figure 8 to compare with the experimental data. It is observed that the results obtained from the Dieterici and Wohl equations give good agreement with the experimental data, and especially good for the hydrocarbons.

**The Boyle Isotherms**

**Experimental Values**

The Boyle temperature for various substances are quite different. For instance, it is as low as 19 oK for helium and as high as 423 oK for oxygen. Therefore the range is quite wide. The Boyle temperature for several substances are given already in Table I. Those temperatures when divided by their critical temperatures should be an universal value as we would expect from the law of corresponding states. Unfortunately, this is not quite true. The Boyle temperature, the reduced Boyle temperature and the critical temperatures for several substances are shown in Figure 9.
Figure 9. The Boyle Temperature and the Critical Temperature for Several Substances

Referring to the Figure 3, the values of $Z_0$ for the seven gases shown in Figure 9 are ranged from 0.29 for oxygen and xenon to 0.304 for hydrogen. This means that the range of variation in percentage of the average value of $Z_0$ is

$$\frac{Z_{\text{max}} - Z_{\text{min}}}{Z_{\text{av}}} \times 100 = \frac{0.304 - 0.29}{0.296} \times 100 = 4.74\%$$

at $T_F = 1$.

The range of variation of the reduced Boyle isotherm in percentage of the average value is

$$\frac{3.65 - 2.5}{2.96} \times 100 = 39\%$$

at $T_F$ around 3.

Although these two variations are not based on the same reduced temperature,
it is realized that the deviation from the law of corresponding state is small at or near the critical point compared to that at the other regions.

*Calculated Values.*

The reduced Boyle isotherms as calculated theoretically from the equations of state are

<table>
<thead>
<tr>
<th>Equation of State</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>3.375</td>
</tr>
<tr>
<td>Berthelot</td>
<td>1.84</td>
</tr>
<tr>
<td>Dieterici</td>
<td>4.0</td>
</tr>
</tbody>
</table>

These are also shown in Figure 9 for the purpose of comparison with the experimental values. Those values show the defects of the original equations of state rather than the deviation from the law of corresponding states.

In Figure 9, it is also shown that the Boyle isotherms of the Berthelot and Dieterici equations are quite off from the experimental values while the Boyle isotherm of the van der Waals equation is between the experimental values. Therefore, for this point the generalised van der Waals equation of state is superior to the others when the reduced temperature \( T_r \) is around three.

*Generalized Equations of the Boyle Points*

The generalised equations for the locus of the Boyle point have been derived in Chapter IV. Here, they are

\[
\begin{align*}
    y^2 - 9y + 6x &= 0 & \text{van der Waals} \\
    1.34y^2 - 9y + 6x &= 0 & \text{Berthelot}
\end{align*}
\]

(87)
\[ y = 2 \exp \left( \frac{4y - 3x}{2y - x} \right) \quad \text{Disterici} \quad (87) \]

Tabulation of Equation

From the above three equations, the numerical values for the Boyle points are calculated and tabulated in Table III, IV and V.

**TABLE III. THE VAN DER WAALS EQUATION, \( P_{f}V_{f} = P_{f} \) BOYLE POINTS**

<table>
<thead>
<tr>
<th>( y = P_{f}V_{f} )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = P_{f} )</td>
<td>1.33</td>
<td>2.34</td>
<td>3</td>
<td>3.34</td>
<td>3.34</td>
<td>3</td>
<td>2.34</td>
<td>1.33</td>
<td>0</td>
</tr>
</tbody>
</table>

**TABLE IV. THE BERTHELOT EQUATION, \( P_{f}V_{f} = P_{f} \) BOYLE POINTS**

<table>
<thead>
<tr>
<th>( y = P_{f}V_{f} )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = P_{f} )</td>
<td>1.19</td>
<td>1.77</td>
<td>1.74</td>
<td>1.11</td>
<td>-0.166</td>
</tr>
</tbody>
</table>

**TABLE V. THE DISTERICI EQUATION, \( P_{f}V_{f} = P_{f} \) BOYLE POINTS**

<table>
<thead>
<tr>
<th>( y = P_{f}V_{f} )</th>
<th>2.2</th>
<th>2.4</th>
<th>2.6</th>
<th>2.8</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = P_{f} )</td>
<td>2.89</td>
<td>3.1</td>
<td>3.3</td>
<td>3.5</td>
<td>3.69</td>
<td>4.53</td>
</tr>
<tr>
<td>( y = P_{f}V_{f} )</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>( x = P_{f} )</td>
<td>5.2</td>
<td>5.68</td>
<td>6</td>
<td>6.12</td>
<td>6</td>
<td>5.61</td>
</tr>
</tbody>
</table>

Locus of the Boyle Points—Experimental

The experimental data for the locus of the Boyle point are seldom
A set of the data was obtained by varying the $P_v - P$ isotherms for nitrogen.\textsuperscript{33} The values of $P_v^0$ and $P_v$ used\textsuperscript{34} in the calculation are

$$P_v^0 = 3.015 \quad P_v = 33.5$$

The calculated data are tabulated in Table VI.

**Table VI. Locus of Boyle Points for Nitrogen**

<table>
<thead>
<tr>
<th>$P_v$</th>
<th>6.4</th>
<th>10.25</th>
<th>13.8</th>
<th>19.7</th>
<th>22</th>
<th>24.4</th>
<th>26.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_v^0$</td>
<td>2.12</td>
<td>3.40</td>
<td>4.58</td>
<td>6.54</td>
<td>7.3</td>
<td>8.1</td>
<td>8.78</td>
</tr>
<tr>
<td>$P_v$</td>
<td>93</td>
<td>112</td>
<td>118</td>
<td>100</td>
<td>75</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>$P_v^0$</td>
<td>2.78</td>
<td>3.34</td>
<td>3.54</td>
<td>2.99</td>
<td>2.24</td>
<td>1.2</td>
<td>0</td>
</tr>
</tbody>
</table>

$P_v^0 - P_v$ Diagram of the Boyle Points

In Figure 9, it was shown that the reduced Boyle isotherms calculated from several empirical equations of state do not agree very well with one another. Since the Boyle isotherm is a particular temperature corresponding to the Boyle point at $p = 0$, it can be predicted that the loci of the Boyle points calculated from the empirical equation of state must also differ from each other. The calculated values of the Boyle points given in Table III, IV and V are plotted in Figure 10. It is observed that all those curves intersect the ordinate $P_v^0$ or $y$ at

\textsuperscript{33} A. S. Friedman, op. cit.

\textsuperscript{34} Weber, *Thermodynamics for Chemical Engineers*, p. 110, John Wiley Co., 1939.
Figure 10. The locus of the Boyle points.
two points, one at \((0, 0)\) and another one at \((0, y)\). If the law of corresponding states is perfect, the values of \(y\) should be universally constant, \(^{35}\) and all curves should coincide to a single one. The values of \(y\) obtained from Equations (87) are given below:

\[
\begin{align*}
\text{van der Waals equation} & \quad y = 0 & y = 9 \\
\text{Berthelot equation} & \quad y = 0 & y = 4.89 \\
\text{Disterici equation} & \quad y = 0 & y = 2c^2 = 14.8 \\
\text{nitrogen by experiments} & \quad y = 0 & y = 3.78
\end{align*}
\]

Since the values of \(y \neq 0\) vary widely, so that the three curves are fairly apart from one another. These mean that the empirical equations of state themselves deviate extensively. If the curve of the Boyle points for nitrogen can be considered as a single curve for all substances, a rough comparison of the generalized Boyle-point curves is possible. It is observed that for higher \(T_r\), the van der Waals equation gives better agreement with the experimental data, while for lower \(T_r\) near the critical temperature, the Disterici equation is superior.

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\(^{35}\)In another words, the reduced Boyle temperature must be a universal constant.
show that how different gases behaving differently can be brought together by a single reduced equation of state. For the reduced isotherms, both the experimental and the reduced equation of state are used at \( T_r = 1 \). For evaluating the validity of the reduced equation of state at different \( T_r \), Obert\(^36\) has given the outlines in his work.

### Z - P and Z - \( P_r \) Isotherms—Experimental

Experimental data are used to plot the \( Z = P \)\(^37\) and \( Z = P_r \)\(^38\) isotherms as shown in Figure 11. If the law of corresponding state is perfect, then all reduced isotherms should coincide to a single curve. The reduced isotherms for nitrogen, ethylene, and carbon dioxide show that they are close enough but not exactly concordant. However, the important point is that the ordinary isotherms for the four gases at 273 K are quite apart while the four reduced isotherms at \( T_r = 1 \) coincide roughly. Therefore, the law of corresponding states is satisfactory for a good approximation in the engineering practice.

### Z - P and Z - \( P_r \) Isotherms—Empirical

The \( Z = P \) isotherms at 273 K for four selected gases are calculated and plotted in Figure 12, 13, and 14 for the van der Waals,

---


Figure 11. The Experimental $Z - P$ and $Z - P_r$ Isotherms
Berthelot, and Dieterici equations of state respectively. The reduced isotherms at \( T_r = 1 \) calculated from the generalised equations of state, given in Chapter IV, are also plotted in these figures accordingly for comparison. The experimental reduced isotherm at \( T_r = 1 \) is also drawn in each of these three figures. It is seen that the four 273 °K isotherms in each figure are quite apart from one another although nitrogen and oxygen, ethylene and carbon dioxide behave closely with each other. This is due to the fact that their critical temperatures are close to each other. As mentioned previously in Chapter II, all isotherms in the \( Z - P_r \) chart meet at the point \((0, 1)\), that is the point of ideal state. Therefore, if the law of corresponding states exists perfectly, same isotherms for different substances must coincide to one. This can be verified best by experiments.\(^{39}\) There are still some other kinds of experiments and diagrams for evaluating the law of corresponding state, such as \( P_r - T_r \) reduced isometrics,\(^{40}\) \( Z - v_r \) reduced isotherms,\(^{41}\) \( P_r v_T - P_r \) reduced isotherms, \( P_r - f_r \) reduced isotherms,\(^{42}\) etc. If mathematical method is used, the critical point and the Boyle points can be checked, as had been done in the previous section of this chapter.

\(^{39}\)Ibid., Su, op. cit.


Figure 12. \( Z - P \) and \( Z - P_r \) Isotherms for the van der Waals Equation of State

\[ \text{Figure 12. } \text{\textit{Z - P and Z - P}_r \text{ Isotherms for the van der Waals Equation of State}} \]
Figure 13. The $Z - P$ and $Z - P_r$ Isotherms for the Berthelot Equation of State
Figure 14. The $Z - P$ and $Z - P_r$ Isotherms for the Dieterici Equation of State
It has been demonstrated in Chapter IV that several equations of state with two or three constants can be reduced to a generalised equation of state respectively for all gases. Therefore, logically speaking, if any of those generalised equation of state is exact, then the law of corresponding state must be exact too. However, since they are not, therefore those generalised equation should not be exact, and the law of corresponding state is a good approximation for practical purposes.

**Deviation from the Law of Corresponding States**

The law of corresponding states discussed so far is usually called the van der Waals law of corresponding states because he first proposed this law in 1881. This law may be expressed by the Equation

\[ f(P_r, v_r, T_r) = 0 \]  \quad or \quad \[ v_r = f(P_r, T_r) \]  \quad \text{(88)}

The deviation is that the compressibility factor at the critical point \( Z_c \) for different substances is not a universal constant. Since

\[ Z = Z_c \frac{P_{r}v_{r}}{T_r} \]  \quad \text{(89)}

where the factor \( \frac{P_{r}v_{r}}{T_r} \) is determined by Equation (88). Therefore the variation of \( Z_c \) means that the law is not exact. However, at the critical point, all \( T_r, P_r \) and \( v_r \) are unity, therefore, the factor \( \frac{P_{r}v_{r}}{T_r} \) is also unity and Equation (89) becomes

\[ Z = Z_c \quad \text{at critical point} \]  \quad \text{(90)}

Equation (90) indicates that the van der Waals law of corresponding states is exact only at the critical point.
It was shown in Figure 1 that when the pressure approaches zero, the compressibility factor for all isotherms is unity. But in Equation (89), the factor \( \frac{P_{r}^{v_{r}T}}{T_{r}} \) has a constant value\(^{43}\) for \( P_{r} \approx 0 \) and \( T_{r} \) constant, while the value of \( Z_{c} \) differs from different substances. It is apparent that Equation (89) does not hold well at low pressure. Therefore, the van der Waals law of corresponding states is discrepant for the low pressures.

The difficulty of the van der Waals law of corresponding states in its practical application is that the value for the critical volume, \( V_{c} \), is extremely difficult to measure, and experimental data of \( V_{c} \) for many substances are lacking. This difficulty limits the application of this law. For this reason \(^{44}\) had proposed the modified law of corresponding states by introducing the ideal reduced volume \( V_{ri} \)

\[
V_{ri} = \frac{V_{ci}}{Z_{c}} = Z_{c} V_{r} = Z \frac{T_{r}}{P_{r}} \tag{91}
\]

and

\[
V_{ci} = \frac{RT_{c}}{P_{c}} \tag{92}
\]

Note that this modified law of the corresponding states is then exact only at \( P \approx 0 \), and deviates badly at the critical point.

\(^{43}\)Because \( V_{r} = f(P_{r}, T_{r}) \).

CHAPTER VI

SUMMARY AND DISCUSSION

The law of corresponding states can be proved in different ways, namely, theoretical, empirical, and experimental methods. The theoretical method gives a sound background for the law. Experimental data enable us to make practical applications of the law with ease. In this study, the mathematical treatment was emphasized in analyzing and evaluating the law of corresponding states, and the results were compared with the experimental data.

The important parts of this study are given as follows:

1. Defining the ideal gas as the common state of all real gases, which gives better correlation for the law of corresponding states of real gases.

2. Discussing in general, the similar behaviors of real gases.

3. Analyzing the mathematical and thermodynamic characteristics of several thermodynamically similar points, and deducing the conditions for the mathematical calculation of the specific constants involved in the empirical equation of state. These conditions, in turn, are the necessary conditions for the generalization of an equation of state.

4. Investigating the law of corresponding states based on the transformation of coordinates.

5. Calculating the following terms (1) the specific constants (2) the compressibility factor at the critical point (3) the generalized
equation of state (4) the generalized equation for the loci of the Boyle points (5) the generalized Boyle temperature, from the van der Waals, Dieterici, Berthelot and Wohl equations of state.

6. The calculation as mentioned above seems to be one of the most complete calculations of this kind. Some terms involved in the calculation, say terms (4) and (5), seldom appear in the literature.

7. All calculated result of the above five terms were expressed graphically for the comparison each other, and with the experimental data available. Each one of those diagram has the important meaning in showing the existence of the law of corresponding states.

8. Evaluation of the generalized equations of state calculated, and the validity of the law of corresponding states were done based on those graphical expressions.

Mathematical calculations of the specific constants involved in the empirical equations of state were discussed. The expressions of these specific constants in terms of the critical data were thought as the simple way to attack the problem from the mathematical characteristics and thermodynamical nature of the critical point. As aforementioned, this kind of calculation is not applicable to all existing equations of state. The condition required for the calculation was discussed on the basis of the theory of equations. The van der Waals, Berthelot, Dieterici and Wohl equations of state were checked. The Beattie-Bridgeman equation was checked to be no direct calculation for the specific constants possible.

Mathematical meaning of the transformation of coordinates to
generalize an equation of state was discussed and referred to the actual P - v - T surfaces. It was predicted that a kind of transformation is possible by reducing the coordinates with certain parameters. The reducing parameters were discussed and the critical data were selected because of both mathematical and thermodynamical reasons. It must be pointed out here that there is no absolute reason that only the critical data can be used as the reducing parameters. The mathematical condition for the complete generalization (no universal constant) was mentioned.

The van der Waals, Berthelot, Disterici and Wohl equations of state were mathematically treated. Their generalized equations were all calculated involving no universal constant. Other calculations done are (1) specific constants in terms of the critical data (or $P_c$ and $T_c$) and vice versa, (2) compressibility factor at the critical point, (3) generalized equation for the locus of the Boyle points, (4) the reduced Boyle temperature. The calculated result was shown graphically for further investigation.

It was mentioned before that, if the law of corresponding states is exact, the compressibility factor at the critical point must be a universal constant. The calculated values from the generalized equations of state are not quite in agreement. However, the result of Disterici and Wohl equations are close enough to the experimental values. Therefore, it is realized that these two generalized equations of state apply very well at the critical point. By observing the experimental data of $Z_c$, the nine none-polar substances and seventeen hydrocarbons
have very close values of $Z_c$ in each group. Therefore individual application of the law of corresponding states for every individual group of substances seems fairly accurate.

The calculated reduced isotherms for different generalized equations of state are quite different. The results from the Disterici and Berthelot reduced equations of state are far off from the experimental values, while the result of the van der Waals equation is between the experimental values. This means that the van der Waals generalized equation of state fits better in the neighborhood of the reduced Boyle isotherms, say $T_R = 2.5 \sim 3.5$.

The generalized equations for the loci of the Boyle points were plotted in a $P_{R^2} - P_R$ diagram, Figure 10. Observation of the curves shows that at the critical temperature, the Disterici's result is in good agreement with the experimental data, while for higher $T_R$, the van der Waals result is superior (for $T_R$ up to the reduced Boyle isotherms). This agrees well with that observed from the compressibility factor and the Boyle isotherms.

The generalized equations of state were plotted in the $Z - P_R$ diagram, Figure 12, 13, and 14. Those diagrams emphasize the effectiveness of the reduced coordinates in bringing the isotherms for different substances to better agreement, but give no evaluation of the accuracy of the generalized equations of state except for $T_R = 1$. At $T_R = 1$, the Disterici generalized equation is in good agreement with the experimental data. Generally speaking, at $T_R = 1$, the Disterici reduced equation is the best for both low pressure (say $P_R = 1 \sim 4$) and high pressure.
(say $P_r > 4$). For $T_r = 1 \sim 1.3$, the van der Waals equation may be used for moderate pressure, while the Disterici reduced equation of state may be used for high pressures. For $T_r > 1.3$, the van der Waals equation is superior through all range of pressures.

Based on the previous calculations and analysis, the van der Waals law of corresponding states are summarized as follows:

1. It is applicable to all substances in a good approximation for practical purposes.

2. The law is exact at the critical point.

3. At very low pressure, the law loses its validity.

4. The deviation from the exact value is small near the critical point and large for the region far from the critical point.

5. For practical use, the generalized $Z - P_r$ chart is convenient, while for thermodynamical calculation the generalized empirical equation of state should be used.

6. In constructing the generalized $Z - P_r$ chart, average values should be used for drawing the isotherms. If different charts are designed for different groups of substances having similar compressibility factor, the deviation may be greatly decreased.

7. Because of the difficulty in measuring the critical volume, the modified law of corresponding states is recommended for the region of low pressures.
LITERATURE CITED


