

**APPLIED  
HYDROCARBON  
THERMODYNAMICS**

**WAYNE C. EDMISTER**

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# ***Applied Hydrocarbon Thermodynamics***

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by

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## DEDICATION

—to my colleagues and students in past studies  
and applications of thermodynamics.

## ACKNOWLEDGEMENTS

The author is indebted to W. S. Hanna for his help in preparing the enthalpy and volume charts for the hydrocarbons and to K. K. Okmoto for his able assistance in developing the equilibrium flash vaporization correlations; to M. Ludwig for the advice and help he gave in developing the compressible fluids flow material in Chapter 11 and H. D. Eddy for his assistance in developing the generalized fugacity correlations and vapor-liquid K-value charts.

## APPLIED HYDROCARBON THERMODYNAMICS

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## ***Preface***

Although there are many books available on theoretical thermodynamics, there has been a shortage of material dealing with the practical application of these theoretical principles. There has been an even greater lack of converting the theoretical equations into working equations so the working process engineer can use them. Thus, there has developed over the years an ever increasing need for a single volume or two which would put this practical information into the hands of the working engineer—a volume which would be understandable yet one which would be consistent with theoretical meaning.

This book, *Applied Hydrocarbon Thermodynamics* by Professor Wayne C. Edmister, has at last filled this great void in our technical knowledge. As an example of how well this has been done, note the expertness with which the author has related fugacity and activity coefficients into the language of equilibrium ratio constants. He then presents these constants in terms of simplified equations and working nomographs for accurate and rapid usage by young and veteran engineers throughout the process design world.

It was no coincidence that Wayne C. Edmister was picked to prepare this book—for who else has a better background to prepare such a wealth of material for the design engineer? Professor Edmister was a natural choice because of his tremendous background in developing engineering design methods, data correlations, and other translations of theoretical literature into working information. As a reader, you will recognize immediately that the author draws heavily on his talents in the fields of engineering design, research and teaching in presenting his compilations with crystal clarity.

This volume includes working information on: (1) equations of state and other correlations of PVT data, (2) Mollier charts for pure hydrocarbons, (3) compression and expansion charts for gases, (4) flow calculations for compressible fluids, (5) flash vaporization correlations for petroleum, (6) integral technique for petroleum distillation calculations, (7) fundamentals of vapor-liquid phase equilibria, (8) generalized vapor-liquid K correlations, (9) convergence pressure correlations, (10) fugacity and activity coefficients correlations.

Individuals and organizations alike will for many years be grateful to Professor Edmister for making available "*Applied Hydrocarbon Thermodynamics*."

JOHN J. MCKETTA  
Chairman, Editorial Committee  
*Hydrocarbon Processing and Petroleum Refiner*

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## Chapter

# 1

## A Review of Fundamentals

Thermodynamic tools for solving process engineering problems are the objectives of this book. Sufficient theory and mathematical derivations will be included to show the basis for and preparation of these tools.

No attempt is made to make this a comprehensive treatise of thermodynamics. For a discussion of fundamental laws, proofs of theorems, and rigorous development of equations, the reader is referred to the many fine text books that are available. For convenience, many of these texts are listed at the end of this chapter.

This discussion of fundamentals is restricted to simple but real systems. The thermodynamics for systems with more than one phase present or with chemical reactions taking place have not been covered.

Heats of vaporization, fusion, and solution will be covered later. So will fugacities and activity coefficients and the reaction equilibrium constants. This and other additional theory and equations will be developed as they are needed.

For the present purposes, compactness in presenting thermodynamics fundamentals is more important than thoroughness.

**Scope.** Thermodynamics has been defined as "Science of Heat and Work."

Thermodynamics can *predict*: (a) Behavior of substances with minimum experimental data; and (b) performance limitations of processes, e.g., possible extent and maximum work, thus providing efficiency standards.

An *advantage* of thermodynamics is that conclusions reached by it are independent of molecular or kinetic hypothesis.

*Limitations* of thermodynamics are: (a) It cannot predict rates or actual performance (only standards of perfection); and (b) it applies only to a large number of molecules (not to individual molecules).

**Definitions.** A thermodynamic *system* is the portion of universe arbitrarily chosen for study, while *surroundings* refer to portion of universe excluded from system.

Thermodynamic *properties* are variables depending only on the state of a substance. Properties are functions of the state and in no way dependent on its history. As will be shown later, heat and work are not functions of the state and, therefore, are not properties.

It follows that a change in a property is dependent only on the initial and final states and in no way dependent upon the method or path followed in going from one state to another.

*Intensive* properties are not dependent upon the mass of the substance, as illustrated by: temperature, pressure, fugacity, etc.

*Extensive* properties are dependent upon the mass of the substance, as illustrated by: volume, enthalpy, entropy, etc.

*Temperature* is the potential or driving force for flow of heat. It is an intensive variable or parameter of the system. *Thermometry* is the measurement of temperature, by changes in gas volume or e.m.f.

*Pressure* is a force per unit area. *Vapor pressure* is an equilibrium property of a substance. *System pressure* is a defining parameter or an intensive variable of a system.

Any change (reaction, vaporization, condensation, expansion, compression, etc.) of a system is a thermodynamic *process*.

A process may take place under conditions defined as:

Adiabatic:	no heat added to or removed from system
Isothermal:	constant temperature
Isometric:	constant volume
Isobaric:	constant pressure
Isentropic:	constant entropy
Isenthalpic:	constant enthalpy

Experiments have shown that changes in a system eventually stop; and unless conditions are altered, no further change will take place. An *equilibrium* state then exists.

**Phase Rule.** When the *state* or *phase* condition of a system is defined by fixing the required number of properties, all other properties are fixed. The *Phase Rule* gives the number of independent variables, or degrees of freedom for a system, as follows:

$$F + \phi = N + 2 \quad (1.1)$$

where  $F$  = number of degrees of freedom or independent variables  
 $N$  = number of components  
 $\phi$  = number of phases

The independent variables referred to in Equation 1.1 include pressure, temperature, and mole fractions of components.

**Reversibility.** A *reversible* process is a series of equilibrium states with the criteria:

1. Allow process to go forward along selected path and measure forward work.†
2. Return process along same path and measure backward work.†
3. If sum of forward and backward work† equals zero, the process is reversible.

**Heat and Work.** By definition:

$Q$  = heat added to system  
 $W$  = work done by system

*Heat,  $Q$ ,* is the agent postulated to account for temperature differences. In other words: Heat is the type of energy which responds to temperature only as a potential. Heat is energy in motion, and the unit of heat is the amount necessary to effect a standard temperature change in a standard substance at a standard condition. Heat is measured by a calorimeter.

*Work,  $W$ ,* is also energy in transit. Work includes all forms of energy which are completely interconvertible to heat (by friction) but not vice versa. Experiments show that heat and work accompanying a process depends on details of process and cannot be determined by end points alone. Work is defined as force times distance in direction of force.

*Reversible Work* equation is found by expressing Work (= force times distance) differentially:

$$d^*W = Fdx = PA \frac{dV}{A} = PdV, \quad (1.2)$$

from which  $W = \int PdV$  for a reversible process.

If the process is not reversible, the actual work will be numerically greater than  $\int PdV$  for compression and less

than  $\int PdV$  for expansion. If an expanding piston works against a force that is significantly less than the  $P \cdot A$  product, the work will be less than  $\int PdV$ . This term,  $\int PdV$ , is the *batch* or *total work* for a nonflow process.

*Shaft work* is the energy available to turn the shaft of an expansion engine or a turbine. For actual processes it is less than reversible work because of friction.

The shaft work for a reversible *batch* or *nonflow process* is equal to  $\int PdV$ . For a *flow process*, an amount of energy equal to  $\Delta(PV)$  is required to keep the fluid flowing through the system when changes in kinetic and potential energies are negligible. The shaft work for a reversible flow process is  $-\int VdP$ . A relationship between *batch*, *shaft*, and *flow* works for complete reversibility is obtained by differentiating the  $PV$  product, as follows:

$$d(PV) = PdV + VdP \quad (1.3)$$

Integrating

$$P_2V_2 - P_1V_1 = \int_1^2 PdV + \int_1^2 VdP \quad (1.4)$$

From Equation 1.4

$$-\int_1^2 VdP = \int_1^2 PdV - \Delta(PV) \quad (1.5)$$

For reversible process

$$-\int_1^2 VdP = \text{shaft work}$$

$$\int_1^2 PdV = \text{batch work}$$

$$\Delta(PV) = \text{flow work}$$

$$W_s = W - \Delta(PV) \quad (1.6)$$

(As mentioned above, work terms refer to work done by the fluid system.)

### First and Second Laws

The *first law* of thermodynamics is a *conservation of energy* statement

$$E_2 - E_1 = \Delta E = Q - W \quad (1.7)$$

where:  $E_2 - E_1$  = the change in energy of the system  
 $Q$  and  $W$  are as defined above

In differential form for an infinitesimal change

$$dE = d^*Q - d^*W \quad (1.8)$$

Equation 1.7 is the preferred form of the mathematical definition of the first law. Equation 1.8 is included for convenience in deriving thermodynamic functions.

The *second law* of thermodynamics deals with *energy degradation* and introduces an abstract quantity called entropy,  $S$ , which is defined for a reversible process by the following

$$d^*Q = TdS \quad (1.9)$$

Where:  $d^*Q$  and  $d^*W$  are inexact differentials and depend upon the path followed.

† Refers to all work terms.



Combining Equations 1.2, 1.8, and 1.9 gives the following important relationship:

$$\boxed{dE = TdS - PdV} \quad (1.10)$$

Equation 1.10 will serve as the basis for developing equations for other thermodynamic functions.

**Other Functions.** By definition the *enthalpy* is

$$H = E + PV \quad (1.11)$$

Differentiating

$$dH = dE + PdV + VdP \quad (1.12)$$

Combining Equations 1.10 and 1.12

$$\boxed{dH = TdS + VdP} \quad (1.13)$$

Another term, *net work*, is defined as

$$A = E - TS \quad (1.14)$$

Differentiating

$$dA = dE - TdS - SdT \quad (1.15)$$

Combining Equations 1.10 and 1.15

$$\boxed{dA = -SdT - PdV} \quad (1.16)$$

*Free energy* is defined as

$$F = H - TS \quad (1.17)$$

Differentiating

$$dF = dH - TdS - SdT \quad (1.18)$$

Combining Equations 1.13 and 1.18

$$\boxed{dF = -SdT + VdP} \quad (1.19)$$

Equations 1.10, 1.13, 1.16, and 1.19 are the basic differential equations for the four thermodynamic potentials *energy, enthalpy, net work, and free energy*. For more convenient application, they will be converted to other independent variables. This requires the Maxwell Relations for transformation of variables.

**Maxwell Relations.** The *Maxwell Relations* relate pressure, volume, temperature, and entropy to each other. This makes them most useful in deriving thermodynamic formulations.

There are four Maxwell Relations, each obtained from one of the above four basic differential equations; i.e., 1.10, 1.13, 1.16, and 1.19, by using Green's Theorem. If

$$dZ = MdX + NdY \quad (1.20)$$

is exact it can be shown that

$$\left(\frac{\partial N}{\partial X}\right)_Y = \left(\frac{\partial M}{\partial Y}\right)_X \quad (1.21)$$

Equation 1.21 is obtained by defining *Z* as a function of

*X* and *Y* which leads to the following total differential which is Equation 1.20.

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY$$

let  $M = \left(\frac{\partial Z}{\partial X}\right)_Y$  and  $N = \left(\frac{\partial Z}{\partial Y}\right)_X$

This is the same as Equation 1.20. Since the order of differentiation is unimportant with two or more variables, when the function is continuous as it is in thermodynamics the first derivative of *M* with respect to *Y* is equal to the first derivative of *N* with respect to *X*, i.e.,

$$\frac{\partial^2 Z}{\partial Y \partial X} = \frac{\partial^2 Z}{\partial X \partial Y} = \left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y$$

This is Green's theorem given by Equation 1.21.

Using Green's theorem the four Maxwell Relations are written by inspection from the reference equations, as follows:

From Equation 1.10

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \quad (1.22)$$

From Equation 1.13

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad (1.23)$$

From Equation 1.16

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad (1.24)$$

From Equation 1.19

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P} \quad (1.25)$$

These four Maxwell Relations are used with the four basic equations to obtain convenient formulations.

Expressions for the isothermal effect of volume on energy and of pressure on enthalpy are the most frequently used in engineering applications of thermodynamics.

Dividing Equation 1.10 by *dV*, keeping *T* constant, and combining with Equation 1.24 gives the isothermal effect of volume on energy.

$$\left(\frac{\partial E}{\partial V}\right)_T = \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] \quad (1.26)$$

Dividing Equation 1.13 by  $dP$ , keeping  $T$  constant, and combining with Equation 1.25 gives the isothermal effect of pressure on enthalpy.

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[ V - T \left(\frac{\partial V}{\partial T}\right)_P \right] \quad (1.27)$$

Equations 1.26 and 1.27 will be used in formulations that follow.

**Heat Capacities.** The heat capacity at constant pressure is defined as

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P \quad (1.28)$$

At constant pressure

$$dQ = TdS = dH = C_p dT \quad (1.29)$$

Rearranging

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} = \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P \quad (1.30)$$

Differentiating with respect to pressure, temperature constant

$$\left(\frac{\partial^2 S}{\partial T \partial P}\right) = \frac{1}{T} \left(\frac{\partial C_p}{\partial P}\right)_T = \frac{1}{T} \left(\frac{\partial^2 H}{\partial T \partial P}\right) \quad (1.31)$$

Differentiating Equation 1.25 with respect to  $T$ , keeping  $P$  constant

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = - \left(\frac{\partial^2 S}{\partial P \partial T}\right) \quad (1.32)$$

Combining Equations 1.31 and 1.32

$$\left(\frac{\partial C_p}{\partial P}\right)_T = - T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad (1.33)$$

The heat capacity at constant volume is defined as

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V \quad (1.34)$$

At constant volume

$$dQ = TdS = dE = C_v dT \quad (1.35)$$

Rearranging

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V \quad (1.36)$$

Differentiating with respect to volume, temperature constant

$$\left(\frac{\partial^2 S}{\partial T \partial V}\right) = \frac{1}{T} \left(\frac{\partial C_v}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial^2 E}{\partial T \partial V}\right) \quad (1.37)$$

Differentiating Equation 1.24 with respect to  $T$ , keeping  $V$  constant

$$\left(\frac{\partial^2 P}{\partial T^2}\right) = \left(\frac{\partial^2 S}{\partial V \partial T}\right) \quad (1.38)$$

Combining Equations 1.37 and 1.38

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad (1.39)$$

**Heat Capacity Differences.** The development of an expression for  $C_p - C_v$  is started by differentiating Equation 1.11 with respect to  $T$ , keeping  $V$  constant

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial T}\right)_V \quad (1.40)$$

Next,  $H$  is expressed as a function of  $P$  and  $T$  in differential form

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (1.41)$$

Divide Equation 1.41 by  $dT$ , keeping  $V$  constant

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \quad (1.42)$$

Combining Equations 1.40 and 1.42 with the definitions of  $C_p$  and  $C_v$  (Equations 1.28 and 1.34) and Equation 1.27 and rearranging

$$C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \quad (1.43)$$

Equation 1.43 can be put in another form by a transformation of variables. Defining  $V$  as function of  $T$  and  $P$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (1.44)$$

Divide by  $dT$ , keeping  $V$  constant and rearranging

$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \quad (1.45)$$

Combining Equations 1.43 and 1.45

$$C_p - C_v = - T \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \quad (1.46)$$

**Energy.** Defining energy as a function of  $T$  and  $V$  and writing the total differential

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad (1.47)$$

Combining Equations 1.26, 1.34, and 1.47 gives the following expression for the effects of temperatures and volume on the energy

$$dE = C_v dT + \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad (1.48)$$

**Enthalpy.** A similar equation is derived for enthalpy by defining  $H$  as a function of  $T$  and  $P$  and writing the total differential

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (1.49)$$

Combining Equations 1.27, 1.28, and 1.49 gives the following expression for the effects of temperature and pressure on the enthalpy

$$dH = C_p dT + \left[ v - T \left(\frac{\partial v}{\partial T}\right)_P \right] dP \quad (1.50)$$

**Entropy.** Defining entropy as a function of  $T$  and  $V$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (1.51)$$

Combining Equations 1.24, 1.35, and 1.51 gives

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \quad (1.52)$$

An expression for entropy as a function of  $T$  and  $P$  is derived similarly

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (1.53)$$

Combining Equations 1.25, 1.29, and 1.53 gives

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP \quad (1.54)$$

**Joule-Thomson Coefficient.** By definition, the Joule-Thomson coefficient is

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \quad (1.55)$$

An expression for  $\mu$  may be obtained by expressing  $H$  as a function of  $T$  and  $P$ , i.e., Equation 1.41; dividing this

expression by  $dP$ , keeping  $H$  constant and rearranging gives:

$$\left(\frac{\partial T}{\partial P}\right)_H = - \frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \quad (1.56)$$

Combining Equations 1.27, 1.28, and 1.56 gives:

$$\mu = \left[ \frac{T \left(\frac{\partial v}{\partial T}\right)_P - v}{C_p} \right] \quad (1.57)$$

The above equations are basic and apply to single and multi-component systems. Generally their application is limited to single phase systems with no change in chemical form. Changes in phase and chemical form will be taken up later.

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## Chapter

## 2

# A Review of P-V-T Data Correlations

Many of the applications of thermodynamics to hydrocarbon systems that are of interest to process engineers require P-V-T (pressure-volume-temperature) data or correlations. Typical of these are calculating: (1) densities of compressible fluids, (2) the isothermal effects of pressure on enthalpy, entropy, and heat capacity, (3) the fugacity coefficients of the components of mixtures, and (4) partial volumes and partial enthalpies.

The basic equations used in calculating the effects of pressure on thermodynamic properties from P-V-T data were given in the previous chapter. These equations apply to pure components and mixtures, V being volume per unit mass of fluid (pure or mixture). These equations do not apply to the components in the mixtures, however. Fugacity coefficients and partial properties for components of mixtures require P-V-T-C (pressure-volume-temperature-composition) data for computation by thermodynamic methods.

P-V-T data are usually correlated by compressibility factor charts or by equations of state. For many years process engineers have regarded equations of state as chart development tools only and not very practical for problem solving. With the increasing use of computers in engineering work, equations of state become more practical.

The compressibility factor charts use reduced temperature and pressure parameters. Generalized charts of PV/RT versus  $P_r$  and  $T_r$  are widely used in estimating fluid densities.

Reduced temperature and pressure parameters are also used in some equations of state. When this general form is used, the constants in the equations are found from the critical properties of the fluid. Usually actual temperature and pressure units are used in equations of state, however. In this case separate empirical constants are used for each substance.

Empirical constants or coefficients for equations of state are obtained by fitting curves to experimental

P-V-T data. Various forms of equations are used, depending upon the desired application. A simpler equation may be used for vapor phase calculations than for the liquid phase calculations.

One of the least exacting equation of state applications is defining the P-V-T behavior of the so-called permanent gases, such as air, in compression and flow calculations. Perfect gas law assumption is usually adequate. One of the most exacting equation-of-state applications is in the computation of vapor-liquid equilibria. This involves representing the P-V-T-C data for mixtures. These are the two equations of state examples that are of interest.

**Equation-of-State Forms.** The form of an equation of state, for a given application, is first set by the nature of the application and theoretical considerations. Then the coefficients of the equation are found empirically to give the best fit to the P-V-T data. A few general remarks are of interest before looking at the details of the equations.

Following are a few characterizing terms that apply to equations of state:

The virial equation of state is a converging power series of the forms:

$$P = \frac{C_1}{V} + \frac{C_2}{V^2} + \frac{C_3}{V^3} + \frac{C_4}{V^4} + \dots \quad (2.1)$$

or

$$V = \frac{C_1}{P} + \frac{C'_2}{P^2} + \frac{C'_3}{P^3} + \frac{C'_4}{P^4} + \dots \quad (2.2)$$

where:  $C_1 = RT$  = first virial coefficient  
 $C_2$  and  $C'_2$  = second virial coefficient  
 $C_3$  and  $C'_3$  = third virial coefficient  
 $C_4$  and  $C'_4$  = fourth virial coefficient

All the virial coefficients are functions of temperature. Successive terms generally become progressively less important.

Equation 2.1 is explicit in pressure, while Equation 2.2 is explicit in volume. The pressure-explicit equation is

more accurate than an volume-explicit equation of the same number of terms.

The density ( $d = 1/V$ ) is sometimes used in place of volume as an equation-of-state variable. Changing from  $V$  to  $1/d$  in Equation 2.1 gives

$$P = C_1 d + C_2 d^2 + C_3 d^3 + C_4 d^4 + \quad (2.3)$$

In this form the equation of state looks simple. As density approaches zero, so does the pressure. The relations for the virial coefficients are complicated functions of temperature, however.

Modifications to the virial form equation of state have been used. One such modification is to replace  $V$  with  $(V-b)$ , where  $b$  is a different constant for each substance. Another modification is an exponential temperature term in one of the virial coefficients. The virial form is not altered by the use of this exponential temperature term. An exponential density term is another modification of interest.

**Perfect Gas.** In 1662, Boyle found that the volume of a simple gas at constant temperature was inversely proportional to the pressure; and in 1801, Charles discovered that the volume of a simple gas at constant pressure was directly proportional to its absolute temperature. Combining these proportionalities for one mole of this same simple gas, gives the so-called "perfect gas" equation,  $PV = RT$ , where  $R$  is the gas constant in the same units as  $P$ ,  $V$ , and  $T$ .

Although there are no truly perfect gases, real gases approach the P-V-T behavior defined by this equation under some conditions. This phenomenon is utilized in some methods used in plotting and correlating P-V-T data. The  $PV$  product and the ratio  $PV/RT$  are plotted against pressure in two correlation techniques. As pressure is decreased toward zero,  $PV$  approaches  $RT$ , while  $PV/RT$  approaches unity.

The perfect gas P-V-T equation may be approached in another way. When all virial coefficients higher than the first are equal to zero, the general equation of state Equation 2.1 reduces to the P-V-T relationship for a perfect gas, i.e.,

$$PV = RT \quad (2.4)^*$$

On  $P$  versus  $V$  coordinates, Equation 2.4 defines a family of hyperbolas that exhibit no two phase border curves at the critical point. For this reason, Equation 2.4 should only be applied at temperatures well above the critical and at low pressures.

From Equation 2.4, it can be shown that pressure has no effect on the enthalpy of a perfect gas. From Equation 2.4

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad (2.5)^*$$

Combining with Equation 1.27 gives

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[V - T \frac{R}{P}\right] = 0 \quad (2.6)^*$$

Combining Equation 2.5 with Equation 1.25 gives the following for entropy

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{R}{P} \quad (2.7)^*$$

Equations 2.6 and 2.7 plus a few other similar expressions define an "ideal gas" state, which is of utility in preparing compilations of thermodynamic properties.

**Compressibility Factor.** Deviations from the perfect gas law, i.e., from Equation 2.4, are frequently expressed in terms of a compressibility factor,  $z$ , which is the ratio of the actual gas volume,  $V$ , to the perfect gas volume,  $RT/P$ . In other words

$$z = \frac{V}{RT/P} = \frac{PV}{RT} \quad (2.8)$$

The compressibility factor,  $z$ , is a function of  $T$  and  $P$  for each compound. This makes the first temperature derivative at constant pressure (differentiating the product of two variables),

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \left[ z + T \left(\frac{\partial z}{\partial T}\right)_P \right] \quad (2.9)$$

When the compressibility factor is constant at unity, Equation 2.9 reduces to Equation 2.5.

Combining with Equations 1.27 and 1.25 gives the following relations for the isothermal effect of pressure on enthalpy and entropy

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{RT^2}{P} \left(\frac{\partial z}{\partial T}\right)_P \quad (2.10)$$

and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{R}{P} \left[ z + T \left(\frac{\partial z}{\partial T}\right)_P \right] \quad (2.11)$$

With precise  $z$  factor correlations, pressure effects on thermodynamic properties may be computed by relationships similar to Equations 2.10 and 2.11.  $z$  factor correlations are usually graphical so this involves getting graphical derivatives. These calculations are usually generalized by using correlations of  $z$  with  $T_r$  and  $P_r$ , the reduced values of temperature and pressure. Figure 2.1 is a generalized compressibility factor chart. This chart was prepared from hydrocarbon P-V-T data by plotting  $PV/RT$  versus  $P_r$  for lines of constant  $T_r$ . Points for different hydrocarbons fall approximately but not exactly on the same curves.

Because of imperfections in the generalized compressibility factor correlations, such as Figure 2.1, their main utility is in computing fluid densities. They are used occasionally in thermodynamic property derivations but are not the preferred type of P-V-T correlation for this more fundamental application.

\* Equations identified thus apply only to perfect gases.

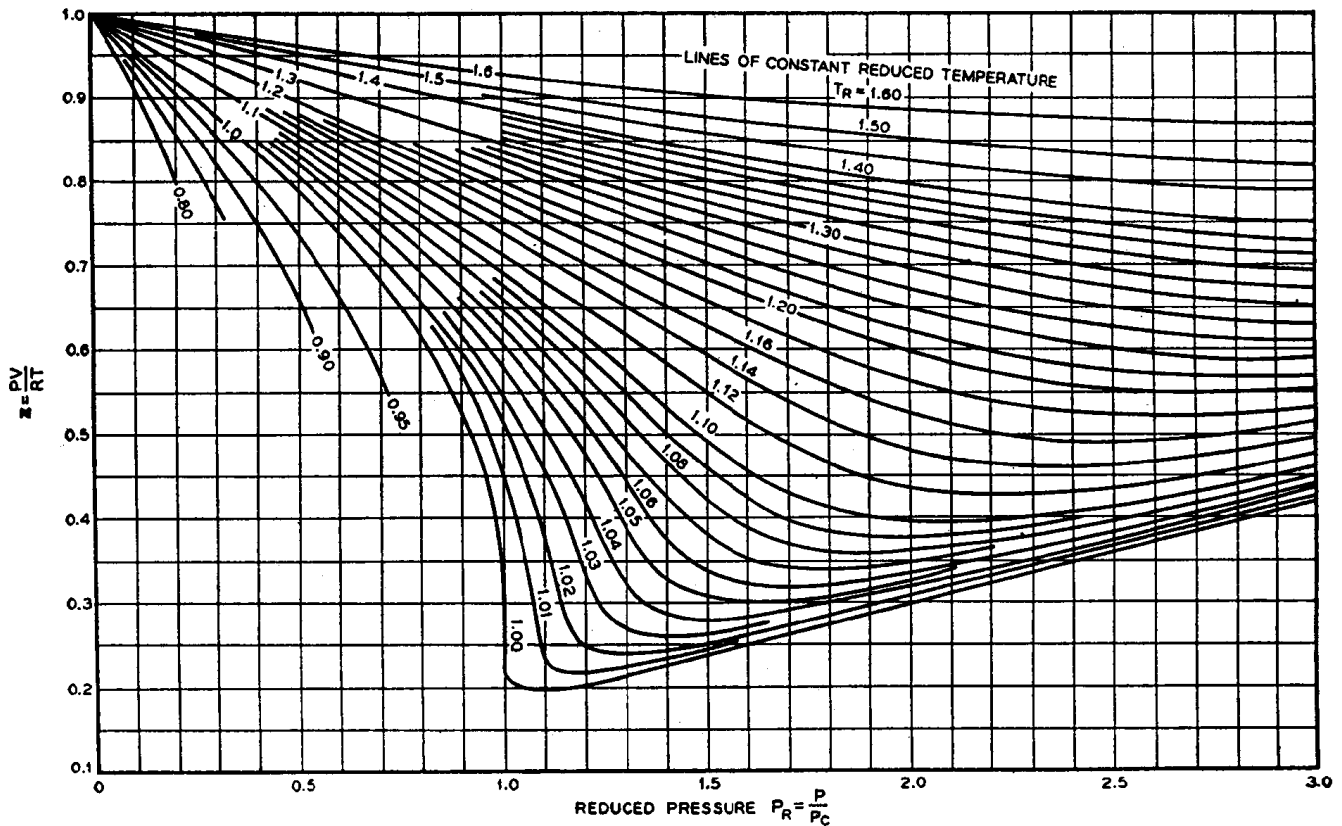


FIGURE 2.1—Generalized compressibility factor chart.

Most compressibility factor charts are limited to the vapor phase and do not include the liquid phase or the two phase regions. These regions cannot be covered accurately on a generalized correlation without a molecular characterizing parameter. This will be brought out later by reference to other charts.

**P-V-T Plots.** The P-V-T data correlation problem for single and multicomponent mixtures is more clearly evident from the P-V, P-T, and V-T plots in Figure 2.2.

All of these diagrams cover both liquid and vapor phases, as well as the two phase (vapor-liquid) region. The parameter in each case is the remainder of the P-V-T variables. The plots show important differences between single and multicomponent systems. Isobaric vaporization and condensation take place isothermally for pure components. For multicomponent systems, isobaric vaporization takes place with an increase in temperature, while isobaric condensation takes place with a temperature decrease. Likewise, the isothermal vaporization (or condensation) of a multicomponent system takes place with a decrease (or an increase) in pressure.

The general trends in the P-V-T relations in the subcooled liquid and superheated vapor regions are indicated most clearly on the P-V plots. The isochors on the P-T plots are nearly straight lines. The isobars on the

V-T plots are curved to a much lesser degree than the isotherms on the P-V plots.

As can be seen by the diagrams in Figure 2.2, the effects of pressure and temperature are more pronounced on gas densities than on liquid densities. For this reason, most correlations are concerned with the vapor phase and analytical correlations (i.e. Equations of State) have been developed from observations made on the volumetric behavior of the gas phase.

**Boyle Temperature.** For ordinary gases and conditions  $PV < RT$  and  $(PV/RT) < 1.0$ ; i.e.,  $z$  has a value of less than unity. At sufficiently high temperatures these magnitudes reverse, and the temperature at which this reversal occurs is called the Boyle Temperature,  $T_{Boyle}$ .

Figure 2.3 illustrates the PV versus P plot for three cases,  $T > T_{Boyle}$ ,  $T = T_{Boyle}$ , and  $T < T_{Boyle}$ . At the Boyle point temperature, which is believed to occur for all real gases, the product PV is equal to or greater than the RT product at all pressures. At lower temperatures the effect of pressure shown in Figure 2.3 is observed; i.e., the PV product decreases with increasing pressure, goes through a minimum, then increases in value until it crosses the  $PV = RT$  line at some high pressure. This is the behavior followed for hydrocarbon and most gases

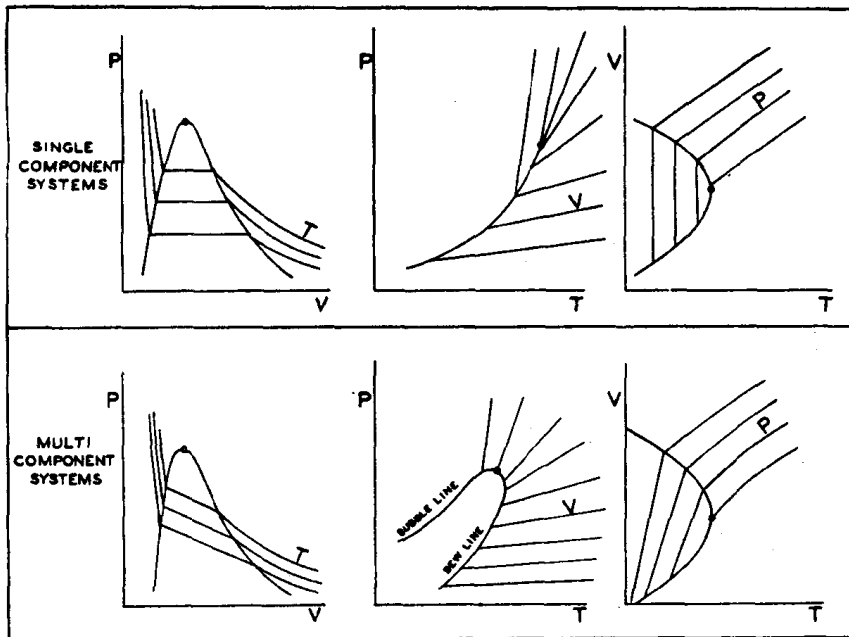


FIGURE 2.2—Types of P-V-T plots for single component and multicomponent systems.

at the temperatures encountered in most industrial operations.

At higher temperatures (the Boyle point is well above atmospheric temperature except for hydrogen and helium, where  $T > T_{Boyle}$ ), the PV product increases with increase in pressure. The Boyle point is of more than theoretical interest because the location relative to  $T_{Boyle}$  determines the temperature change upon throttling.

The absolute value of the Boyle temperature is between 3 and 4 times the critical temperature. This is beyond the range of Figure 2.1 and most industrial applications of the generalized compressibility factor chart.

**Mixture P-V-T.** Densities of mixtures may be estimated in either of two ways: (a) partial volumes (or densities) and (b) equivalent single component compressibility factor. Partial volumes are functions of pressure, temperature, and composition for each component. The compressibility factor for mixtures may be found from the z plots by using the pseudo-reduced temperature and pressure of the mixture.

Before partial volume data and the pseudo-reduced concept became available, it was customary to use two simple laws in computing densities of vapor mixtures. These are: "Dalton's Law of Additive Pressures" and "Amagat's Law of Additive Volumes."

Dalton's Law states that the partial pressure of each component of a mixture is equal to the pressure that component would exert if it alone occupied the entire volume. The total pressure is then the sum of these partial pressures. In terms of compressibility factor, z

$$P = \bar{P}_A + \bar{P}_B + \dots = \frac{z_A N_A RT}{V} + \frac{z_B N_B RT}{V} + \dots = \frac{z_{mix} N_{total} RT}{V} \quad (2.12)$$

From this equation it follows for Dalton's Law of additive pressures that:

$$z_{mix} = x_A z_A + x_B z_B + \dots = \sum x_i z_i$$

Where  $z_A, z_B$ , etc. are evaluated at the values T and V for the system.

Amagat's Law states that the total volume occupied by a gaseous mixture is equal to the sum of volumes that each component would occupy at the temperature and pressure of the system. In terms of compressibility factor, z:

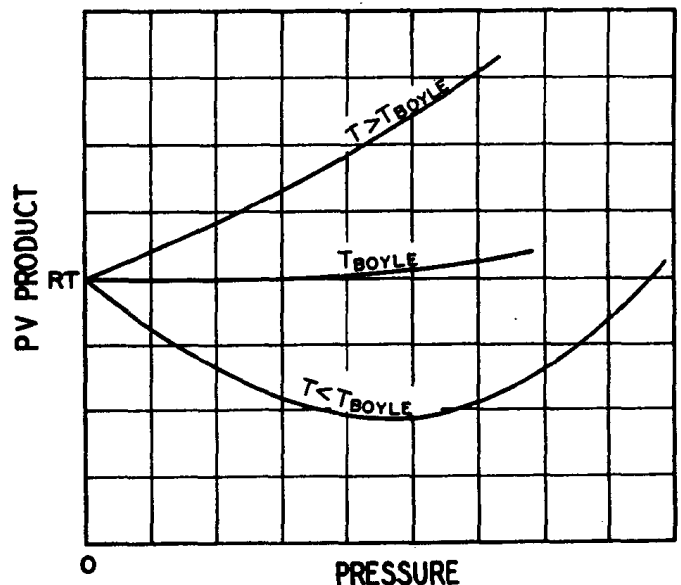


FIGURE 2.3—The relation of temperature and Boyle temperature.

$$V = x_A V_A + x_B V_B + \dots = \frac{x_A z_A RT}{P} + \frac{x_B z_B RT}{P} + \dots = \frac{z_{m1} RT}{P} \quad (2.13)$$

From the above it follows for Amagat's Law of additive volumes that:

$$z_{m1} = x_A z_A + x_B z_B + \dots = \sum x_i z_i$$

Where  $z_A$ ,  $z_B$ , etc. are evaluated at the values of  $T$  and  $P$  for the system.

A widely accepted method for predicting mixture P-V-T data is to apply the generalized compressibility factor chart, such as Figure 2.1, to mixtures by the pseudo-reduced conditions, defined as follows:

$$T_{pr} = \frac{T}{T_{pc}} = \frac{T}{\sum x_i T_{ci}} \quad (2.14)$$

$$P_{pr} = \frac{P}{P_{pc}} = \frac{P}{\sum x_i P_{ci}} \quad (2.15)$$

where  $x_i$  = mole fraction of  $i$ th component.

The pseudo-critical conditions, which were proposed by W. B. Kay in 1936, are defined as the molar average of the critical properties of the mixture components. This concept was described in a previous article.<sup>1</sup> Reference to this earlier discussion for more details about the pseudo-critical is recommended.

The density of a gas mixture may be calculated from the following equation, using a compressibility factor found from Figure 2.1 by the pseudo-reduced conditions.

$$\rho_m = \frac{PM_m}{z_m RT} \quad (2.16)$$

where  $\rho_m$  = mixture density, lb/cu ft  
 $P$  = pressure, psia  
 $M_m$  = average molecular weight of mixture  
 $z_m$  = compressibility factor for mixture  
 $R$  = 10.73 (psia) (cu ft/lb mole)/(°F)  
 $T$  = temperature, °R

The compressibility factor is evaluated in the same way as for pure components, except the pseudo-reduced temperature and pressure of the mixture are used. For gas mixtures containing hydrogen and/or nitrogen, adjusted values of  $T_c$  and  $P_c$  should be used for the  $H_2$  and  $N_2$  in computing the pseudo-critical constants. Adding 8° C. to the critical temperatures and 8 atmospheres to the critical pressures of these two gases had been recommended previously for the application of the generalized compressibility factor chart to these two gases. A similar correction is suggested in computing the pseudo-criticals for mixtures containing these two gases.

**Partial Volumes.** For imperfect gases and nonideal solutions, particularly those involving highly polar compounds, deviations from the above simple additivity laws can be quite serious; and direct density measurement or partial molar volume data should be obtained.

The partial molar volume for a component is defined as:

$$\bar{V}_i = \left( \frac{\partial V}{\partial N_i} \right)_{P, T, N_j} \quad (2.17)$$

where  $\bar{V}_i$  = partial molar volume of component, i.e., cu ft/lb mole  
 $V$  = volume of mixture, cu ft/lb moles  
 $N_i$  = moles of component  $i$ , lb moles

Thus, the partial molar volume is a function of the temperature, pressure, and concentration.

The volume of the mixture in terms of the partial molar volume is then:

$$V = \sum N_i \bar{V}_i \quad (2.18)$$

or for one mole of mixture

$$V = \sum x_i \bar{V}_i \quad (2.19)$$

Partial molar volumes correlations are more trouble than the equivalent component method and need not be used except where the simpler method gives questionable results. Partial molar volumes for mixture components may be evaluated by applying Equation 2.17 with an equation of state that represents the P-V-T-C data for the mixture. This calculation will be covered in a later chapter.

**Equations of State.** At this point it is of interest to review some of the equations of state that are used in correlating P-V-T data and calculating thermodynamic properties.

Three equations of state use two constants. These are the van der Waals, the Berthelot, and the Redlich-Kwong equations.

**van der Waals Equation.** Because of the shape of  $P$  versus  $V$  isotherm curves illustrated on Figure 2.2, the best fit to experimental data is obtained by the explicit-in-pressure form of equation. The van der Waals equation of state is the simplest and best known of this type and is:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (2.20)$$

Other forms of van der Waals equation are:

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \quad (2.21)$$

$$PV/RT = z = 1 + \frac{b}{V-b} - \frac{a}{RTV} \quad (2.22)$$

where

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \text{ and } b = \frac{RT_c}{8P_c}$$

For mixtures:  $\sqrt{a} = \sum x_i \sqrt{a_i}$  and  $b = \sum x_i b_i$ .

In generalized units:

$$\left( P_r + \frac{3}{V_r^2} \right) \left( 3V_r - 1 \right) = 8 T_r \quad (2.23)$$

A more convenient generalized form is obtained in terms of the ideal reduced volume,  $V_r' = V / \frac{RT_c}{P_c}$ , thus:

$$\left( P_r + \frac{27/64}{(V_r')^2} \right) \left( V_r' - \frac{1}{8} \right) = T_r \quad (2.24)$$



In Equations 2.23 and 2.24, the constants are fixed, while in Equations 2.20, 2.21, and 2.22, the constants have different numerical values for each component. The van der Waals equation of state is of limited accuracy because the two constants do not permit fitting P-V-T data very accurately. More complex equations are required for precise work.

**Berthelot Equation.** The Berthelot equation of state is also a two constant equation of state similar to the van der Waals, the only difference being in the last term, which is  $a/TV^2$  instead of  $a/V^2$ , as in Equation 2.20.

Following is the Berthelot counterpart of Equation 2.22

$$PV/RT = z = 1 + \frac{b}{V-b} - \frac{a}{RT^2V} \quad (2.25)$$

The original  $a$  and  $b$  constants were  $a = 27 R^2 T_c^3 / 64 P_c$  and  $b = RT_c / 8 P_c$ . An improvement is made by using  $b = \frac{9RT_c}{128P_c}$ . Combining these values of  $a$  and  $b$  with Equation 2.25 and making two simplifying assumptions that are acceptable at higher volumes gives the following convenient equation:

$$z = 1 + \frac{9P_r}{128T_r} \left( 1 - \frac{6}{T_r^2} \right) \quad (2.26)$$

The necessary assumptions in deriving Equation 2.26 are that

$$\frac{9}{128} \frac{RT_c}{P_c} \ll \ll V$$

and

$$\frac{RT_c}{P_c V} \approx \frac{P_r}{T_r}$$

Equation 2.26 is a convenient approximation equation for the compressibility factor. Being explicit in  $z$  makes it much easier to use than the form of Equation 2.25 but not as accurate.

**Redlich-Kwong Equation.** This is another similar two-constant equation of state that is of interest. It is similar in form to the previous two equations of state. An important similarity is that the constants for both equations are computed from the critical temperature and pressure values. The following Redlich-Kwong<sup>3</sup> equation is more accurate, however.

$$P = \frac{RT}{(V-b)} - \frac{a}{T^{0.5}V(V+b)} \quad (2.27)$$

The two constants  $a$  and  $b$  are related to the critical temperature and pressure, i.e.

$$a = \frac{0.4278 R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.0867 RT_c}{P_c}$$

For mixtures

$$\sqrt{a} = \sum x_i \sqrt{a_i}$$

or

$$b = \sum x_i b_i$$

The generalized form of Equation 2.27 is

$$P_r = \frac{T_r}{V_r' - 0.0867} - \frac{0.4278}{T_r^{0.5} V_r' (V_r' + 0.0867)} \quad (2.28)$$

where:  $V_r' = \frac{V}{RT_c/P_c}$  = ideal reduced volume

Redlich and Kwong<sup>3</sup> put the equation in another form, which they recommended for application, i.e.,

$$\frac{PV}{PT} = z = \frac{1}{1-h} - \left( \frac{A^2}{B} \right) \frac{h}{1+h} \quad (2.29)$$

$$A^2 = \frac{a}{R^2 T^{2.5}} = \frac{0.4278}{P_c T_r^{2.5}} \quad (2.30)$$

$$B = \frac{b}{RT} = \frac{0.0867}{P_c T_r} \quad (2.31)$$

$$h = \frac{BP}{Z} = \frac{b}{V} \quad (2.32)$$

For mixtures

$$A = \sum x_i A_i$$

$$B = \sum x_i B_i$$

The numerical solution of the Redlich-Kwong equation involves the simultaneous solution of Equations 2.29 through 2.32. These equations have been applied to vapor phase fugacity coefficients.<sup>4</sup>

**Wohl Equation.** This equation of state has three constants which are also obtained from the critical constants. Its application to hydrocarbons has been discussed.<sup>2</sup> Following is the form that is comparable to Equations 2.20 and 2.27:

$$P = \frac{RT}{V-b} - \frac{a}{TV(V-b)} + \frac{c}{T^2 V^2} \quad (2.33)$$

where

$$a = 6 P_c T_c V_c^2$$

$$b = V_c / 4$$

$$c = 4 P_c T_c^2 V_c^3$$

$$\frac{RT_c}{P_c V_c} = \frac{15}{4}$$

In reduced form the Wohl equation is

$$P_r = \frac{15 T_r}{4 V_r - 1} - \frac{24}{T_r V_r (4 V_r - 1)} + \frac{4}{T_r^2 V_r^2} \quad (2.34)$$

It would appear that the Wohl equation should be superior to the two-constant equations. According to a comparison made by Redlich and Kwong,<sup>4</sup> their equation gives a better fit to experimental P-V-T data than the other two and three constant equations of state.

**Other Graphical P-V-T Correlations.** Figure 2.4 shows a reduced isochor plot. On this plot reduced pressure ( $P_r = P/P_c$ ) is plotted against reduced temperature ( $T_r = T/T_c$ ) for lines of constant reduced volume