

Chapter 2

Properties of Pure Substances

2.1 Introduction

A pure substance is a material with a constant chemical composition throughout its entire mass. A pure substance can exist in one or more physical phases such as a solid, liquid or vapor. Each phase will have homogeneous physical characteristics, but all three phases could be different physical forms of the same pure substance. The temperature and pressure boundaries between phases are well defined and it usually requires an input or extraction of thermal energy to change from one phase to another. Most pure substances have a well defined Triple Point where all three phases exist in equilibrium.

In general matter can be classified into two broad categories:

1. **Pure-Substances.**
2. **Mixture.**

Each of these categories can be described as.

1. **Pure substance:** A pure substance is defined as a substance having a constant and uniform chemical composition. Typically, it can be divided in two groups as:
 1. **Elements**—all the same type of atom.
 2. **Compounds**—substances made from two or more different kinds of atoms.
2. **Mixture:** The thermodynamic properties of a mixture of substances can be determined in the same way as for a single substance. The most common example of this is dry air, which is a mixture of oxygen, nitrogen, a small percentage of argon, and traces of other gases. The properties of air are well determined and it is often considered as a single substance. Mixtures can be categorized as two general types:

This chapter deals with the relationship between pressure, specific volume, and temperature for a pure substance.

1. **Homogeneous**—A substance that has uniform thermodynamic properties throughout is said to be homogeneous. The characteristics of a homogeneous mixture are;
 - a. Mixtures, which are the same throughout with identical properties everywhere in the mixture.
 - b. Not easily separated.
 - c. This type of mixture is called a solution. A good example would be sugar dissolved in water or some type of metal alloy like the CROMium-MOLYbdenum steel used in many bike frames.
2. **Heterogeneous**—A heterogeneous mixture is a type of mixture in which the composition can easily be identified. Often there is two or more phases present. Each substance retains its own identifying properties (e.g., granite) and it includes.
 - a. Mixtures, which have different properties when sampled from different areas. An example of this would be sand mixed with water.
 - b. A mixture in which the individual components can be seen with the naked eye.
 - c. A mixture that can be easily separated.

Air is a homogeneous mixture of the gases nitrogen, oxygen, and other minor gases. Here are some other examples of homogeneous mixtures

- Salt water
- Brewed tea or coffee
- Soapy water
- A dilute solution of hydrochloric acid
- Hard alcohol
- Wine

Here are some examples of heterogeneous mixtures

- Sandy water.
- Cake mix and cookie dough.
- Salad.
- Trail mix.
- Granite.
- Sodium chloride (table salt) stirred up with iron filings.
- Sugar and salt mixed in a bowl.
- Carbonated beverage or beer (the CO_2 gas is mixed with the liquid).
- Orange juice with pulp in it
- Water with ice cubes in it.
- Chicken noodle soup.

A pure substance normally requires only two independent properties to specify its state. If pressure and specific volume, for example, are fixed, then all the other properties become fixed. The equation relating pressure, volume, and temperature to each other is called an *Equation of State*. However, a more fundamental

Classification of Matter

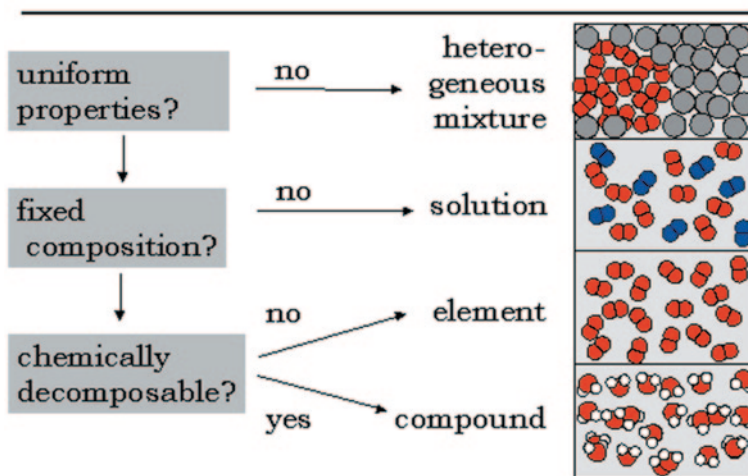


Fig. 2.1 Classification of matter. (Courtesy of NASA)

equation is required to specify all thermodynamic variables as a function of only two properties. These fundamental equations will be called Thermodynamic Potentials (Fig. 2.1).

An example of a simple equation of state which is satisfactory for most dilute gases is the Ideal Gas Law— $pV=nRT$.

2.2 Properties of Pure Substances—Phase Changes

Now consider how a pure substance changes phases. the most common pure substance that is available around the world is water in its three phases—ice, liquid water and steam.

Start with a solid body like ice and add heat. At first the temperature of the body increases proportional to the amount of heat that is added. However, at some point continued addition of heat will cause the body to start to melt. Once it starts to melt the temperature stops increasing and remains constant while the solid is melting. The amount of heat that is added to complete the melting is called the *Heat of Fusion* and is normally expressed on per unit mass or per unit mole basis. Once the entire solid is melted the temperature increases again in proportion to the amount of heat input. Note that the increase in temperature per unit heat input for the solid and liquid are not usually equal. As the substance continues to heat up, at some point the liquid will start to vaporize. Once it starts to vaporize, the temperature remains constant until all of the liquid is vaporized. The heat input per unit mass or unit mole required to change the substance from a liquid to a vapor is called the *Heat of Vaporization*. Once all of the liquid is vaporized, the temperature of the substance starts to increase again propor-

tional to the heat input. This sequence of events is illustrated in Fig. 2.2 below, which is called Temperature-Specific Volume or T - v Diagram.

A three dimensional view of these processes is presented in the Fig. 2.3. Note that the surface has the following regions; Solid, Liquid, Vapor, Solid-Liquid,

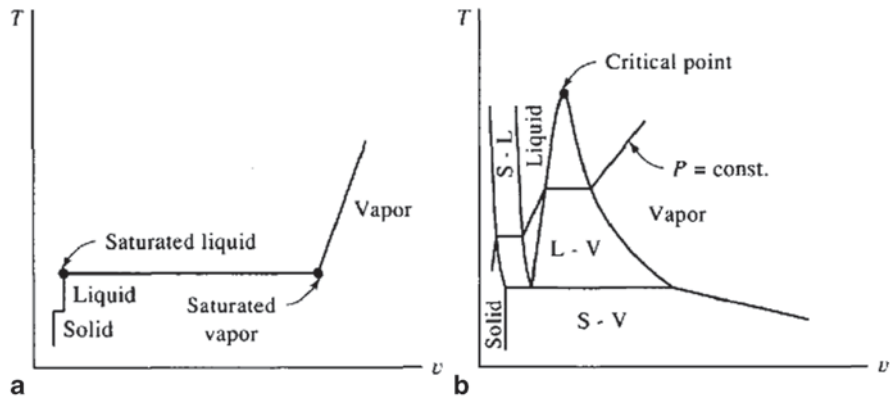


Fig. 2.2 The T - v diagram

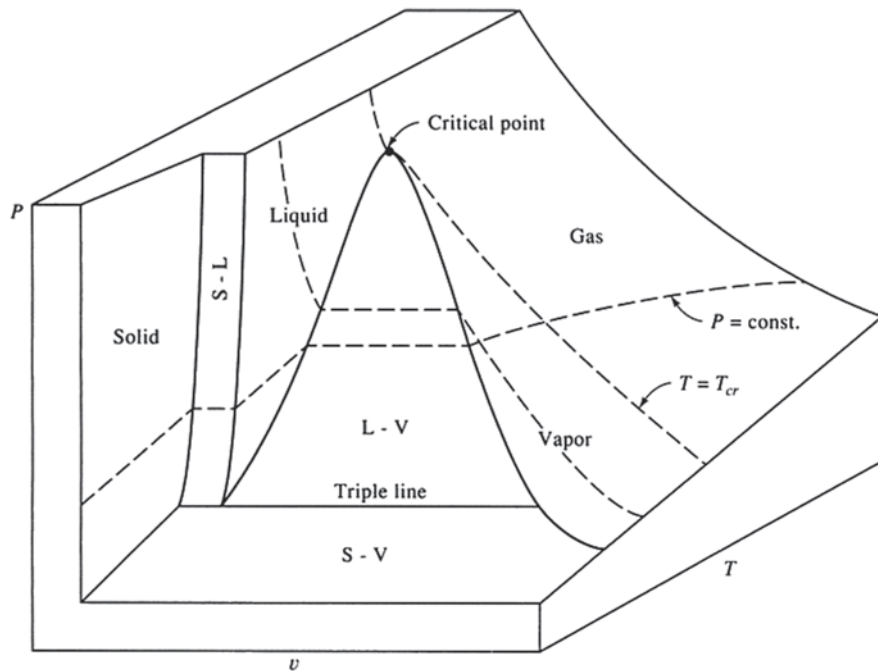


Fig. 2.3 The P - v - T rendering of a substance that contract on freezing

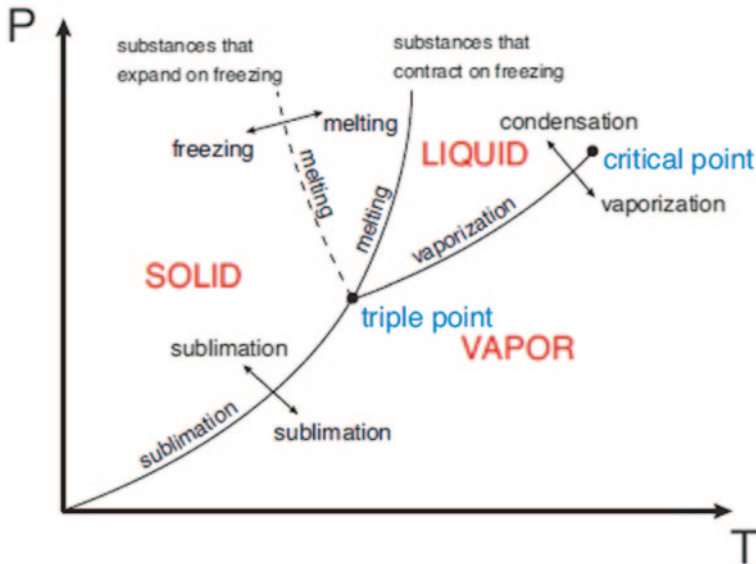


Fig. 2.4 Illustration of phase diagram

Solid-Vapor, and Liquid-Vapor. It also has a line where all three phases can coexist called the *Triple Line* with an interest point that called Triple Point and depicted in Fig. 2.4 as well. At the top of the Liquid-Vapor region, a point exists called the *critical point*. Above the Critical Point, in either pressure or temperature, the fluid cannot be identified as either Liquid or Vapor. In the Liquid-Vapor region called the *Vapor Dome*, the following definition in Sect. 2.2.1 (next section) applies.

2.2.1 Phases of Pure Substances

A pure substance may exist in different phases, where a phase is considered to be a physically uniform form of the substance. The three principle phases are as solid, liquid and gas.

Figure 2.4 shows the typical behavior of pure substances. It is called a “*phase diagram*” because three lines separate all three phases from each other.

2.2.2 Equations of State

Consider a *closed system*, in a vessel so equipped that the pressure, volume, and temperature may be easily measured. If the volume is set at some arbitrary value and the temperature is maintained at a specific value, then the pressure will be fixed at a definite value. Once the V and T are chosen, then the value of P at equilibrium

is fixed. That is, of the three thermodynamic coordinates P , V , and T , only two are independent variables. There exists an equation of equilibrium which connects the thermodynamic coordinates and which robs one of them of its independence. Such an equation, called an equation of state, is a mathematical function relating the appropriate thermodynamic coordinates of a system in equilibrium. Every thermodynamic system has its own equation of state, although in some cases the relation may be so complicated that it cannot be expressed in terms of simple mathematical functions. For a closed system, the equation of state relates the temperature to two other thermodynamic variables.

An equation of state expresses the individual peculiarities of one system as compared with another system and must, therefore, be determined either by experiment or by molecular theory. A general theory like thermodynamics, based on general laws of nature, is incapable of generating an equation of state for any substance. An equation of state is not a theoretical deduction from the theory of thermodynamics, but is an experimentally derived law of behavior for any given pure substance. It expresses the results of experiments in which the thermodynamic coordinates of a system were measured as accurately as possible, over a range of values. An equation of state is only as accurate as the experiments that led to its formulation, and holds only within the range of values measured. As soon as this range is exceeded, a different form of equation of state may be required.

Note that in any of the three homogeneous phases discussed in Sect. 2.2.1 in above, a relationship exists that gives $P = P(V, T)$. Or any of the variables can be expressed in terms of the other two. These equations are called *Equations of State*. In the two-phase regions, including their borders, specifying temperature alone will set the pressure and vice versa. Giving both pressure and temperature will not define the volume because we will need to know the relative proportion of the two phases present. The mass fraction of the vapor in a two-phase liquid-vapor region is called the quality.

2.3 Ideal Gas

Any equation that relates the pressure, temperature, and specific volume of a substance is called an equation of state. There are many equations of state, some simple and others very complex. The simplest and best-known equation of state for substances in the gas phase is the Ideal Gas equation of state. This equation predicts the p - v - T behavior of a gas quite accurately for dilute or low-pressure gases. Probably the definition of a low pressure or dilute gas is that it obeys the Ideal Gas Law. *It is based on the two modeling assumptions that (1) each molecule is a point mass with no volume, and (2) they only interact by billiard ball-like collision conserving energy and momentum of the colliding particles.* The Ideal Gas equation of state was formulated long before the atomic hypothesis was demonstrated, but these two assumptions quickly lead to the properties of the Ideal Gas equation of state.

An *Ideal Gas* is one that obeys the following *Equation of State*.

$$pV = n\Re T \quad (2.1)$$

p Absolute pressure

V Volume of gas

n Number of moles of the gas

\Re Universal Gas Constant = 8314 J/kmol/K = 1545 ft-lbf/lbmol/°R = 1.986 Btu/lbmol/°R

T Absolute temperature in degrees Rankine or Kelvins

Note that \Re is the Universal Gas Constant. A gas constant for a particular gas can be obtained by dividing the universal constant by the molar mass to obtain the following equation.

$$R = \Re / M \quad (2.2)$$

where M is molecular weight of gas. If we identify m as the mass of gas in kg or lbm , then another form of the Ideal Gas Law can be written as:

$$pV = m\Re T \quad (2.3)$$

Identifying $\rho = m / V$ as the gas density, then another form of the Ideal Gas Law is:

$$p = \rho \Re T \quad (2.4)$$

Normally an Ideal Gas must be a pure substance. However, air is a mixture that obeys the Ideal Gas Equation over a broad range of values for temperature and pressure. Most gases obey the Ideal Gas Equation of State if the pressure is not too high or the temperature too low.

The Ideal Gas law gives is a simple enough equation that given any two of the thermodynamic variables, p , v , and T , the third can easily be found. Consider 2 kg-moles of H_2 at 1000 °K and 0.2 MPa. Calculate the volume required to store the gas at this temperature and pressure. The required volume is,

$$V = \frac{n\Re T}{p} = 2.0 \text{ kg-moles} * 8314.47 \text{ J/kg-mole/K} * 1000^\circ \text{K} / 200,000 \text{ nt/m}^2 = 83.1 \text{ m}^3$$

Obviously, given temperature and density, or specific volume, the pressure could be found in a similar manner. Given pressure and density, or specific volume, the temperature is easily found from the same equation. For this reason, applying the Ideal Gas Law is usually a good first guess when trying to solve for pressure, density, or temperature.

2.4 Real Gases and Vapors

In this section, the behavior and properties of real gases and vapors are described and equations of state are identified.

An ideal gas is made up of particles that do not attract or repel one another. Real gases are made up of atoms or molecules that may attract one another strongly, like ammonia, water vapor, or sulfur dioxide. On the other hand, they may attract one another hardly at all, like helium.

Real gases behave like ideal gases at “ordinary” temperatures and pressures. However, if you heat them up and compress them to high pressure, then their behavior departs from ideal. If the molecules attract one another, a molecule in the center of the gas is attracted equally on all sides and its motion is not affected. For a molecule, which is very close to the wall of container, exerts less force on the wall, due to the intermolecular attractive forces with other molecules.

2.4.1 Simple Real Gas Equations of State

At higher pressures or lower temperatures, the equation of state becomes more complicated. The volume taken up by the molecules of the gas must be considered and the attraction of the molecules for each other lessens the pressure they exert on their container. The first Equation of State to take these two effects into account was the Van der Waals Equation of State given by,

$$p = \frac{\Re T}{(v-b)} - \frac{a}{v^2} \quad (2.5)$$

where a and b are constants appropriate to the specific gas. As far as thermodynamics is concerned, the important idea is that an equation of state exists, not whether it can be written down in a simple mathematical form. Also there exists no equation of state for the states traversed by a system that is not in mechanical and thermal equilibrium, since such states cannot be described in terms of thermodynamic coordinates referring to the system as a whole.

It is generally impossible to express the complete behavior of a substance over the whole range of measured values of p , v , and T by means of one simple equation with two adjustable parameters (a and b). Several equations of state, such as the Ideal Gas Law and those found below can be used to characterize the gas or vapor phase. Several Equations of State that have found utility in thermodynamic analysis are listed here.

a. $p = \frac{\Re T}{(v-b)} - \frac{a}{v^2}$ Van der Waals equation of state

b. $p = \frac{\Re T}{v-b} - \frac{a}{T^{1/2}v(v+b)}$ Redlich-Kwong equation of state

- c. $p = \frac{\Re T}{v-b} - \frac{\alpha a}{v^2 + 2bv - b^2}$ Peng-Robinson equation of state
- d. $pv = \Re T(1 + BP + CP^2 + \dots)$ Virial Expansion
- e. $(pe^{a/\Re Tv})(v-b) = \Re T$ Dieterici equation of state
- f. $\left(p + \frac{a}{v^2 T}\right)(v-b) = \Re T$ Berthelot equation of state
- g. $\left(p + \frac{a}{(v+c)^2 T}\right)(v-b) = \Re T$ Clausius equation of state.
- h. $pv = \Re T \left(1 + \frac{B'}{v} + \frac{C'}{v^2} + \dots\right)$ Another type of virial expansion

2.4.2 Determining the Adjustable Parameters

Every equation of state must satisfy a number of conditions.

1. It must reduce to the Ideal Gas Law as the pressure approaches zero or the temperature increases without bound.
2. The critical isotherm must show a point of inflection at the critical point.
3. The isometrics on a p - T diagram should approach straight lines with either decreasing density or increasing temperature. The critical isometric should be a straight line.

Since the critical point is the limiting position on a p - v diagram (see Fig. 2.5 below) as the two end-points (saturated liquid and saturated vapor) on the same isotherm approach each other, it follows that the slope of the isotherm passing through the critical point (the critical isotherm) is zero, or stated mathematically as;

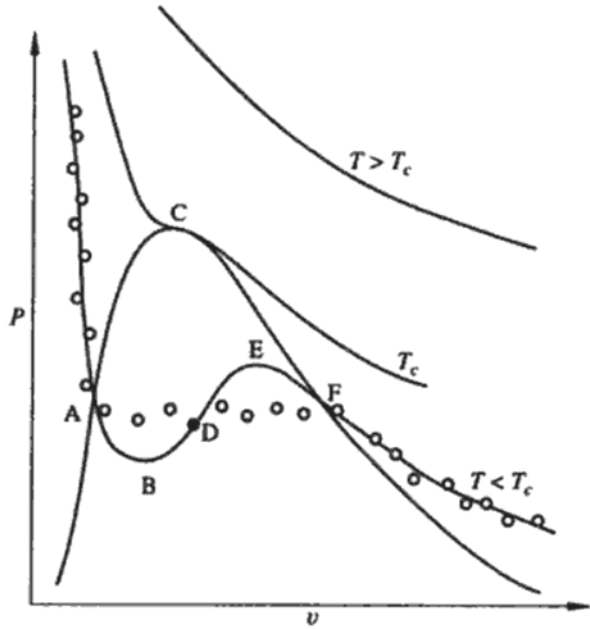
$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \quad (2.6a)$$

Also, the critical point is a point of inflection on the critical isotherm, because the isotherm is concave upward at volumes less than the critical volume and concave downward at specific volumes more than the critical volume; hence

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0 \quad (2.6b)$$

Equations 2.6a and 2.6b, along with the equation of state itself, enable one to evaluate the constants in any two parameter equation of state based on the critical values P_C , V_C , and T_C . Consider, for example, the Van der Waals equation of state, which can be written:

Fig. 2.5 p - v diagram for pure substance showing isotherms in the region of critical point. Solid lines represent the values predicted by the Van der Waals equation of state. Points represents the experimental values



$$p = \frac{\Re T}{v-b} - \frac{a}{v^2} \quad (2.7)$$

where $v = V/n$ is the molar volume. This equation holds fairly well in the vapor region near and above the critical point. Equations 2.6a and 2.6b for molar volume yield, respectively;

$$\left(\frac{\partial P}{\partial v} \right)_{T=T_c} = -\frac{\Re T}{(v-b)^2} + \frac{2a}{v^3} = 0 \quad (2.8a)$$

and

$$\left(\frac{\partial^2 P}{\partial v^2} \right)_{T=T_c} = \frac{2\Re T}{(v-b)^3} - \frac{6a}{v^4} = 0 \quad (2.8b)$$

Equations 2.8a and 2.8b can be rewritten as;

$$\frac{2a}{v^3} = \frac{\Re T}{(v-b)^2} \quad (2.9)$$

and

$$\frac{3a}{v^4} = \frac{\Re T}{(v-b)^3} \quad (2.10)$$

Dividing the first equation by the second to obtain the critical molar volume as;

$$v_C = 3b \quad (2.11)$$

Substituting this value for v in the first of the two equations, we obtain a relationship for the critical temperature as;

$$T_C = \frac{8a}{27b\Re} \quad (2.12)$$

and finally, substituting these two values in the Van der Waals equation to obtain the critical pressure as

$$P_C = \frac{a}{27b^2} \quad (2.13)$$

At the critical point these equations can be written as follows;

$$\left(\frac{\partial P}{\partial v} \right)_{T=T_C} = -\frac{\Re T_C}{(v_C-b)^2} + \frac{2a}{v_C^3} = 0 \quad (2.14)$$

and

$$\left(\frac{\partial^2 P}{\partial v^2} \right)_{T=T_C} = \frac{2\Re T_C}{(v_C-b)^3} - \frac{6a}{v_C^4} = 0 \quad (2.15)$$

so that at the critical point, Van der Waals equation is given by

$$\left(P_C + \frac{a}{v_C^2} \right) (v_C - b) = \Re T_C \quad (2.16)$$

Based on the critical point data then, we can calculate the Van der Waals constants a and b in terms of the critical constants. Since it is possible to experimentally measure the critical temperature and critical pressure, a and b can be evaluated from knowledge of P_C and T_C through the following relations

$$a = \frac{27\Re^2 T_C^2}{64P_C} \quad \text{and} \quad b = \frac{\Re T_C}{8P_C} \quad (2.17)$$

Table 2.1 Calculated values of Z_c

Substance	Z_c
Water	0.230
Ammonia	0.242
Carbon dioxide	0.275
Nitrogen	0.287
Helium	0.291
Hydrogen	0.307
Van der Waals gas	0.375
Ideal gas	1.00

The values of a and b are provided for a number of gases in the Appendix.

It follows for the Van der Waals equation of state at the critical point,

$$Z_c = \frac{P_c v_c}{\Re T_c} = \frac{\frac{a}{27b^2} \cdot 3b}{\Re \cdot \frac{8a}{27b\Re}} = \frac{3}{8} = 0.375 \quad (2.18)$$

where Z_c is the critical compressibility factor. If a substance behaved like an Ideal Gas at the critical point, then Z_c would equal 1.0. If it obeys the Van der Waals equation, then this ratio should equal 0.375, which would be a measure of the departure of the Van der Waals gas from an Ideal Gas. In Table 2.1 below, the calculated values of Z_c are listed for a number of interesting gases, and in no case is this ratio equal to 0.375, or even close. Above the critical point, at higher pressure, the Van der Waals equation is fairly satisfactory and is useful in many cases. Other equations of state give better values of Z_c , but no two parameters Equation of State adequately describes all properties of pure substances near the vapor dome.

2.4.3 Other Useful Two Parameter Equations of State

Many equations of state have been proposed to represent $P - V - T$ data more accurately than the Ideal Gas Law for those regions where it does not apply. Most of the equations of state that have been proposed are empirical and only a few of them are in wide use in thermodynamics and related engineering and physics fields. Two other equations of state, commonly used in engineering analysis, are presented below.

2.4.3.1 Redlich-Kwong Equation of State

The Redlich-Kwong (RK) equation of state is an empirical equation that is widely used for engineering calculations.

$$P = \frac{\Re T}{v-b} - \frac{a}{T^{0.5}v(v+b)} \quad (2.19)$$

The constants a and b of the Redlich-Kwong equation of state can be estimated from the critical constants by the following relations. It is generally thought to provide satisfactory results above the critical temperature for any pressure.

$$a = \frac{0.42748\Re^2 T_c^{2.5}}{P_c} \quad (2.20a)$$

$$b = \frac{0.0867\Re T_c}{P_c} \quad (2.20b)$$

This gives $Z_c = 0.333$ which is significantly closer to the range of interest for most gases. The constants a and b are evaluated in the Appendix for a number of gases.

2.4.3.2 Peng-Robinson Equation of State

The Peng-Robinson equation of state gives a slightly better approximation below the critical temperature by adding another parameter, ω , the acentricity factor given by,

$$\omega = -1 - \log_{10} \left(\frac{p^{sat}}{P_C} \right)_{T/T_c = 0.7} \quad \kappa = 0.37464 + 1.54226\omega - 0.26993\omega^2 \quad (2.21a)$$

$$\alpha = \left[1 + \kappa \left(1 - \sqrt{T/T_c} \right) \right]^2 \quad P = \frac{\Re T}{v-b} - \frac{\alpha a}{v^2 + 2bv - b^2} \quad (2.21b)$$

The Peng-Robinson constants are determined by

$$a = 0.45723553 \frac{\Re^2 T_c^2}{P_c} \quad b = 0.07779607 \frac{\Re T_c}{P_c} \quad (2.21c)$$

It gives a $Z_c = 0.307$, closer to the range of a number of gases. The constants for the Peng-Robinson Equation of State are provided for a number of gasses in the Appendix.

2.4.4 Common Equations of State with Additional Parameters

Equations of state play an important role in chemical engineering design and they have assumed an expanding role in the study of the phase equilibrium of fluids and fluid mixtures. Originally, equations of state were used mainly for pure components. Many equations of state have been proposed in the literature with either an empirical, semi-empirical or a theoretical basis. Brief reviews can be found in the following sections.

2.4.4.1 Beattie-Bridgeman Equation of State

The Beattie-Bridgeman equation of state is given by

$$Pv^2 = \Re T \left(1 - \frac{c}{vT^3} \right) \left(v - B_0 - \frac{bB_0}{v} \right) - A_0 \left(1 - \frac{a}{v} \right) \quad (2.22)$$

The constants A_0 , B_0 , a , b , and c are characteristic of a gas. These constants for some substances are given in Table 2.2.

Table 2.2 Constants of Beattie-Bridgeman equation of state

Gas	$A_0 \left(\frac{\text{Pam}^3}{\text{mol}^2} \right)$	$B_0 \times 10^6 \left(\frac{\text{m}^3}{\text{mol}} \right)$	$a \times 10^6 \left(\frac{\text{m}^3}{\text{mol}} \right)$	$b \times 10^6 \left(\frac{\text{m}^3}{\text{mol}} \right)$	$c \left(\frac{\text{m}^3\text{K}^3}{\text{mol}} \right)$
Air	0.1318	46.11	19.31	-11.010	43.40
Ammonia	0.2425	34.15	170.31	19.112	4768.70
n-Butane	1.8030	246.20	121.61	94.230	3500.00
Carbon dioxide	0.5073	104.76	71.32	72.350	660.00
Ethane	0.5958	94.00	58.61	19.150	900.00
Ethylene	0.6234	121.56	49.64	35.970	226.80
Helium	0.00219	14.00	59.84	0.000	0.04
Hydrogen	0.0200	20.96	-5.06	-43.590	5.04
Methane	0.2307	55.87	18.55	-158.700	128.30
Neon	0.0215	20.60	21.96	0.000	1.01
Nitrogen	0.1362	50.46	26.17	-6.910	42.00
Oxygen	0.1511	46.24	25.62	4.208	48.00
n-Pentane	2.8634	394.00	150.99	139.600	4000.00
Propane	1.2078	181.00	73.21	42.930	1200.00

Table 2.3 Source Kenneth Wark, thermodynamics, 4th ed., p. 141

Gas	a	A_0	B	B_0	$c \times 10^{-4}$	$C_0 \times 10^{-5}$	$\alpha \times 10^5$	Γ
n-Butane, C_4H_{10}	190.68	1021.6	0.039998	0.12436	3205	1006	110.1	0.0340
Carbon dioxide, CO_2	13.86	277.30	0.007210	0.04991	151.1	140.4	8.470	0.0054
Carbon monox- ide, CO	3.71	135.87	0.002632	0.05454	10.54	8.673	13.50	0.0060
Methane, CH_4	5.00	187.91	0.003380	0.04260	25.78	22.86	12.44	0.0060
Nitrogen, N_2	2.54	106.73	0.002328	0.04074	7.379	8.164	12.72	0.0053

2.4.4.2 Benedict-Webb-Rubin Equation of State

The Benedict-Webb-Rubin (BWR) equation of state is given by;

$$P = \frac{\Re T}{v} + \frac{1}{v^2} \left(\Re T \left(B_0 + \frac{b}{v} \right) - \left(A_0 + \frac{a}{v} + \frac{a\alpha}{v^4} \right) - \frac{1}{T^2} \left(C_0 - \frac{c}{v} \left(1 + \frac{\gamma}{v^2} \right) \exp \left(\frac{-\gamma}{v^2} \right) \right) \right) \quad (2.23)$$

where A_0 , B_0 , C_0 , a , b , c , α and γ are constants for a given fluid. The BWR constants for a few selected gases can be found in Table 2.3 above or in Perry's Chemical Engineer's Handbook. This equation of state is quite complex and contains eight constants, and is able to predict the $p-v-T$ data with higher accuracy compared to many other equations of state.

The Equations of State used to calculate the steam properties in the Appendix was broken down into five regions. Each region required between 10 and 43 constants to adequately represent the data.

2.4.4.3 Virial Equation of State

The word virial comes from the Latin meaning force, thus it refers to the interaction forces between molecules. In 1901 Kamerlingh Onnes suggested the virial equation of state expressed as a power series in reciprocal volume; it is given by

$$\frac{pv}{\Re T} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} \quad (2.24a)$$

where B , C , D , etc. are known as second virial coefficient, third virial coefficient etc. Virial coefficients express the deviations from the Ideal Gas Law due to intermolecular forces. These virial coefficients are functions of temperature only. The advantage of the virial equation of state is that it may be made to represent

the experimental $p-v-T$ data as accurately as required by increasing the number of constants. The values of the second virial coefficients have been determined experimentally for a number of gases. The third virial coefficients are not known for many substances and much less information is available beyond the third virial coefficient. Moreover, the virial equation of state with more than three terms is difficult to handle. The virial equation of state and the ideal gas law have a strong theoretical base. They have been derived through *statistical mechanical methods*. All other equations of state are empirical or semi-empirical. The virial equation of state is sometimes written as a power series in the pressure as;

$$\frac{pv}{\Re T} = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (2.24b)$$

where the coefficients B' , C' , D' , etc. are functions of temperature only. The coefficients B' , C' , D' , etc. are related to the virial coefficients B , C , D , etc. by the following relations:

$$B' = \frac{B}{\Re T} \quad (2.25a)$$

$$C' = \frac{C - B^2}{(\Re T)^2} \quad (2.25b)$$

$$D' = \frac{D - 3BC + 3B^3}{(\Re T)^3} \quad (2.25c)$$

It has been found that the virial Eq. 2.24a adequately represents the experimental data over a wide range of pressure, compared to the virial Eq. 2.24b when both these equations are truncated after the third term [1]. The general form of Eq. 2.24a can be written as;

$$\frac{pv}{\Re T} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots = \sum_{i=0}^R \frac{c_i}{v^i} \quad (2.26)$$

The parameters in the equation ($B, C, D = c_i$) are again called “virial coefficients”. If $c_i = 0$ for $i > 0$, the virial equation reduces to the ideal gas equation. The accuracy required determines the number of terms that are kept—more terms makes the equation more accurate, but also more complicated to work with. Virial coefficients are different for each gas, but other than that are functions of temperature only.

Coefficients are normally obtained by making measurements of p , v , and T , and fitting the equation. These values are then published so that others may use them.

Many forms of the virial equation exist. Truncating this equation after one coefficient gives a quadratic equation in v . Thus, it retains some of the simplicity of the Ideal Gas law allowing quick analytic solutions for v given p and T .

$$\frac{Pv}{\Re T} = 1 + \frac{B}{v} \quad (2.27a)$$

A number of methods (correlations, etc.) are available to determine B . In order to improve accuracy and capture more behaviors, additional parameters are sometimes added. One example is the Benedict-Webb-Rubin (BWR) Equation of State Eq. 2.23.

This equation provides a first order correction to the Ideal Gas Law for non-polar species. It should not be attempted for polar compounds such as water that have a non-zero dipole moment [1]. The following procedure may be used to estimate v or P for a given T for a non-polar species, one with a dipole moment close to zero, such as hydrogen or oxygen and all other symmetrical molecules.

To use the truncated virial Equation of State proceeds in the following manner.

- Look up the critical temperature and pressure (T_c and P_c) for the species of interest in Appendix. Also, look up the acentric factor, ω , a parameter that reflects the geometry and polarity of a molecule, in the constants table for the Peng-Robinson Equation of State in the Appendix. (A more complete list can be found in Reid et al. [2].)
- Calculate the reduced temperature T_r using the relationship $T_r = T / T_c$.
- Calculate the following coefficients:

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (2.27b)$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (2.27c)$$

$$B = \frac{\Re T_c}{P_c} (B_0 + \omega B_1) \quad (2.27d)$$

- Substitute into Eq. 2.27 the value of B and whichever of the variables p and v is known and solve for the other variable. Solution for p is straightforward. If v is to be determined, the equation can be rearranged into a quadratic and solved using the quadratic formula.

$$v^2 - \frac{\Re T}{p} v - \frac{\Re T}{p} B = 0$$

- Normally one of the two solutions is reasonable and the other is not and should be discarded; if there is any doubt, estimate v from the ideal gas equation of state and accept the virial equation solution that comes closest to v_{ideal} .

2.4.4.4 Equation of State Comparison

Virial equations with one coefficient cannot represent thermodynamic systems where both liquid and vapor are present. A “cubic” equation of state is needed to do this. We have identified three two-parameter equations of state above for which data

is presented in the Appendix. The most sophisticated of these is the Peng-Robinson equation because it corrects the “a” coefficient for the acentric factor.

$$P = \frac{\Re T}{(v-b)} - \frac{\alpha a}{v^2 + 2bv - b^2} \quad (2.28a)$$

where the constants are given by;

$$a = 0.45723553 \frac{\Re^2 T_c^2}{P_c} \quad (2.28b)$$

$$b = 0.07779607 \frac{\Re T_c}{P_c} \quad (2.28c)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26993\omega^2 \quad (2.28d)$$

$$\alpha = \left(1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right)^2 \quad (2.28e)$$

In this equation, the b term is a volume correction, while a is a molecular interaction parameter. The constants all depend on the critical temperature and pressure of the gas. These can be looked up easily in a data table.

The “*acentric factor*”, omega ω , is also easily looked up. It is related to the geometry of the gas molecule.

To use the Peng-Robinson equation:

1. Look up T_c , P_c , and the *acentric factor* for the species of interest in the Appendix.
2. Plug in and find a , b , and alpha α .
3. Plug these into the Peng-Robinson equation; the result will be a cubic equation in v depending on p and T .
4. Solve for the unknown you seek.

Solving the cubic equation can be accomplished with a binary search using the computer or by analytically solving the cubic equation. The equation can be transformed to

$$v^3 + \left(b - \frac{\Re T}{p} \right) v^2 + \left(\frac{\alpha a}{p} - 3b^2 - 2 \frac{\Re T}{p} b \right) v + \left(b^3 + \frac{\Re T}{p} b^2 - \frac{\alpha a}{p} b \right) = 0$$

$$v^3 + a_1 v^2 + a_2 v + a_3 = 0$$

The analytic solution is given by,

$$v^3 + a_1 v^2 + a_2 v + a_3 = 0$$

Transform to

$$x^3 + b_1 x + b_2 = 0 \quad v = x - \frac{a_1}{3}$$

$$b_1 = \frac{3a_2 - a_1^2}{3} \quad b_2 = \frac{2a_1^3 - 9a_1 a_2 + 27a_3}{27}$$

$$\frac{b_2^2}{4} + \frac{b_1^3}{27} > 0, \text{ 1 real, 2 imaginary, } \frac{b_2^2}{4} + \frac{b_1^3}{27} = 0, \text{ 3 real, 2 equal,}$$

$$\frac{b_2^2}{4} + \frac{b_1^3}{27} < 0, \text{ 3 real \& distinct}$$

For the first case

$$C = \sqrt[3]{-\frac{b_2}{2} + \sqrt{\frac{b_2^2}{4} + \frac{b_1^3}{27}}} \quad D = \sqrt[3]{-\frac{b_2}{2} - \sqrt{\frac{b_2^2}{4} + \frac{b_1^3}{27}}}$$

$$x = C + D \quad x = -\frac{C+D}{2} + \frac{C-D}{2}\sqrt{-3} \quad x = -\frac{C+D}{2} - \frac{C-D}{2}\sqrt{-3}$$

$$v = x - \frac{a_1}{3}$$

For the third case of three real unequal roots let,

$$\cos \phi = \frac{-a_2/2}{\sqrt{-a_1^3/27}}$$

$$x_1 = 2\sqrt{-b_1/3} \cos(\phi/3) \quad x_2 = 2\sqrt{-b_1/3} \cos(\phi/3 + 2\pi/3) \quad x_3 = 2\sqrt{-b_1/3} \cos(\phi/3 + 4\pi/3)$$

Example 2.1 Carbon dioxide at 500 K and 6.5 MPa flows at 100 kg/h. Use the one parameter Virial Equation of State and the Peng-Robinson Equation of State to determine the volumetric flow.

Solution The pressure and temperature are known, so look up the critical properties, the acentric factor, and the Peng-Robinson constants in the Appendix.

The critical properties are $T_c = 304.2^\circ\text{K}$, $p_c = 7.39\text{ MPa}$, and the acentric factor is 0.225.

Evaluating the B coefficients,

$$T_r = 500.0 / 304.2 = 1.64365 \quad B_0 = 0.083 - 0.422 / T_r^{1.6} = -0.1076$$

$$B_1 = 0.139 - 0.422 / T_r^{4.2} = 0.0867$$

$$B = 8314.47 * 304.2 / 7.39 \text{E}+6 * (-0.1076 + 0.225 * 0.0867) = -0.03014$$

$$v = \frac{\Re T}{2p} \pm \sqrt{\left(\frac{\Re T}{2p}\right)^2 + \frac{\Re TB}{p}} = (0.31978 + 0.081651) / 44 = 0.01382 \text{ m}^3/\text{kg}$$

The Peng-Robinson coefficients are

$$a = 0.39576 \text{ MPa}\cdot\text{m}^3/\text{kgmol}^2 \quad b = 0.02662 \text{ m}^3/\text{kgmol}$$

$$\kappa = 0.37464 + 1.5422 * 0.225 - 0.26993 * 0.225^2 = 0.70797$$

$$\alpha = \left(1.0 + 0.70797 \left\{1 - \sqrt{T/T_c}\right\}\right)^2 = 0.6357$$

$$p = \frac{\Re T}{v-b} - \frac{\alpha a}{v^2 + 2bv - b^2}$$

$$v^3 + \left(b - \frac{\Re T}{p}\right)v^2 + \left(\frac{\alpha a}{p} - 3b^2 - 2\frac{\Re T}{p}b\right)v + b^3 + \frac{\Re T}{p}b^2 - \frac{\alpha a}{p}b = 0$$

Applying the cubic formula gives

$$a_1 = -0.61295, \quad a_2 = 0.002526, \quad a_3 = -0.00055844, \quad b_1 = -0.12271, \quad b_2 = -0.017101$$

$$\frac{b_2^2}{4} + \frac{b_1^3}{27} > 0, \quad 1 \text{ real, } 2 \text{ imaginary}$$

$$C = 0.22044 \quad D = 0.18555$$

$$v = 0.5 * (0.22044 + 0.18555) / 44.0 = 0.01387 \text{ m}^3/\text{kg}$$

It is worth noting that the Ideal Gas solution is

$$v = \frac{\Re T}{p_{AM}} = \frac{8314.47 * 500}{6500000.0 * 44} = 0.01454 \text{ m}^3/\text{kg} \text{ and the tables give } 0.01389 \text{ m}^3/\text{kg}$$

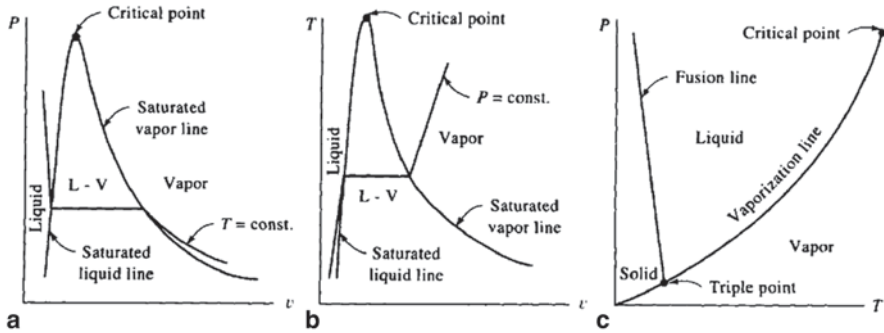


Fig. 2.6 The $P-V$, $T-V$, and $P-T$ diagrams

So the Ideal Gas solution is high by 4.65%. The virial solution is low by 0.54%, and the Peng-Robinson solution is low by 0.14%.

The volumetric flow rate with the virial solution will be $100 \times 0.01382 = 1.382 \text{ m}^3/\text{h}$

The volumetric flow rate with the Peng-Robinson solution would be $100 \times 0.01387 = 1.387 \text{ m}^3/\text{h}$

2.4.5 The Liquid-Vapor Region

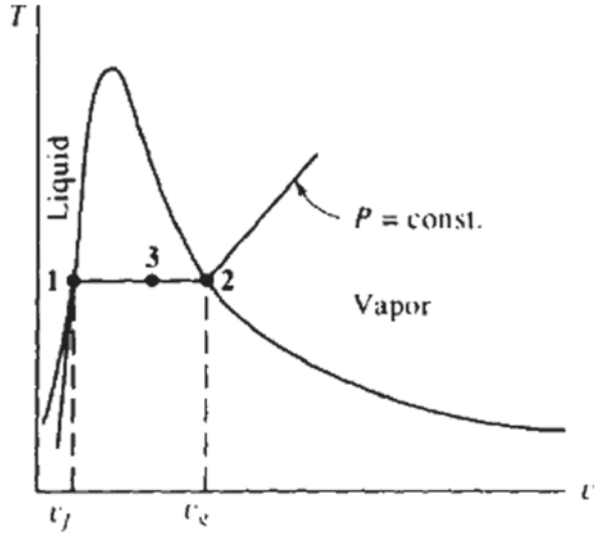
Applying Fig. 2.6 shows that at any given (T, v) between saturated points **1** and **2**, liquid and vapor exist as a mixture in equilibrium. Let v_f and v_g to represent the specific volumes of the *saturated liquid* and the *saturated vapor*, respectively, while m is the total mass of the system that is shown in Fig. 2.6 and m_f the mass amount of mass in the liquid phase, and m_g the amount of mass in the vapor phase, then for a state of the system represented by (T, v) the total volume of the mixture is the same of the volume occupied by the liquid and the occupied by the vapor as [3]:

$$mv = m_f v_f + m_g v_g \quad (2.29)$$

$$m = m_f + m_g \quad (2.30)$$

or dividing both side of Eq. 2.29 by m , then utilizing Eq. 2.30, we have;

Fig. 2.7 The $T - V$ diagram showing the saturated liquid and saturated vapor points



(2.31)

$$\begin{aligned}
 v &= \left(\frac{m_f}{m} \right) v_f + \left(\frac{m_g}{m} \right) v_g \\
 &= \left(\frac{m - m_g}{m} \right) v_f + \left(\frac{m_g}{m} \right) v_g \\
 &= v_f + \left(\frac{m_g}{m} \right) v_g - \left(\frac{m_g}{m} \right) v_f \\
 &= v_f + \left(\frac{m_g}{m} \right) (v_g - v_f) \\
 &= v_f + x(v_g - v_f) \\
 &= v_f + x v_{fg}
 \end{aligned}$$

The ratio $x = \frac{m_g}{m}$ is called quality because steam that has a larger proportion of vapor is considered “higher quality” than steam with a lesser mass of vapor. $v_{fg} = v_g - v_f$ is the heat of vaporization. If we take a slice through the 3-D plot to form the P - T plane and include the **Critical Point** we will obtain the plot that is shown in Fig. 2.4.

Note that the percentage liquid by mass in a mixture is $1000(1 - x)$ and the percentage vapor is $100x$. See Fig. 2.7.

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations. Therefore, properties are frequently presented in the form of tables. Some thermodynamic properties can be measured easily and those that can't are calculated by using the thermodynamic relations that they must satisfy and the measurable properties.

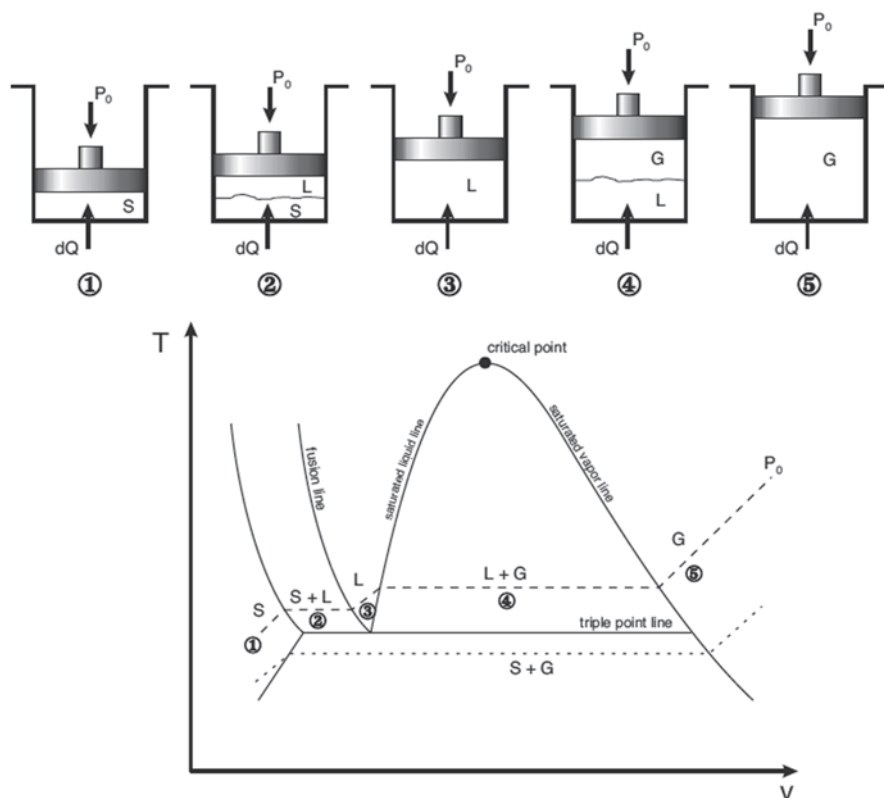


Fig. 2.8 Illustration of T - v process steps and its diagram

The working fluid of most interest to engineer's and by far the fluid most studied is water. Its properties have been tabulated for years in what are called Steam Tables. A set of *Steam Tables* are provided in the back of the book, within the Appendix. The Tables are Appendix 14.1–14.7.

2.5 $T-V$ Diagram for a Simple Compressible Substance

Consider an experiment in which a substance starts as a solid and is heated up at constant pressure until it becomes a gas. The process is depicted in Fig. 2.8.

As heat is applied to the solid, the temperature increases and the volume increases slightly. When the melt temperature is reached, the temperature remains constant but the volume continues to increase as the solid is converted to a liquid. Once all of the material has been converted to a liquid, the temperature begins to increase again as more heat is added. When the vaporization temperature is reached, the liquid begins to be converted to a vapor and the temperature remains constant as more heat is added. Once all of the liquid has been converted to vapor, adding more heat will once again cause the temperature to rise.[3–7].

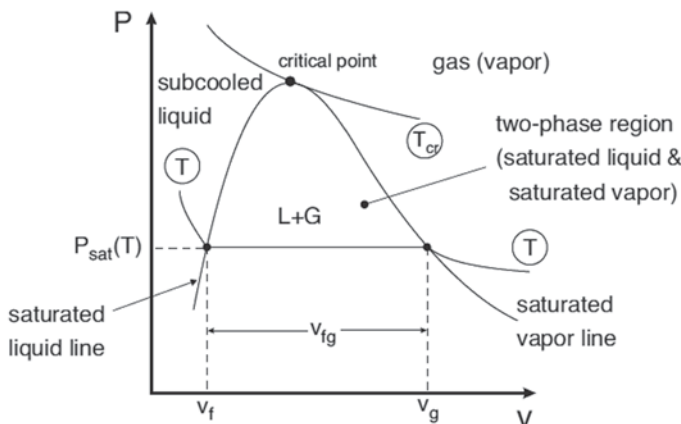


Fig. 2.9 Illustration of $P-V$ diagram

2.6 $P-V$ Diagram for a Simple Compressible Substance

The general shape of a $p-v$ diagram for a pure substance is very similar to that of a $T-V$ diagram and its representation by the **vapor dome** as discussed before. Figure 2.9 is a presentation of a $p-v$ diagram.

On this diagram the subscript f denotes a saturated liquid (fluid) and g denotes a saturated vapor (gas).

2.7 $P-V-T$ Diagram for a Simple Compressible Substance

All the data that are represented on both the $p-v$ and $p-T$ diagrams can be shown one diagram if the three coordinates p , v , and T are plotted along orthogonal axes. The result is called the $p-v-T$ surface and two such surfaces are shown in Figs. 2.10 and 2.11, the first for a kilogram of an unusual substance like water that contracts upon melting, and the second for a kilogram of a typical substance like carbon dioxide that expands upon melting.

Where the critical point is denoted by the letter C and the triple point by TP . The critical isotherm is marked T_C . Every point on the $P-V-T$ surface represents a state of equilibrium for the substance. If the $p-v-T$ surface is projected on the $p-v$ plane, then the usual $p-v$ diagram is seen and upon projecting the $p-v-T$ surface onto the $p-T$ plane, the entire solid-vapor region projects into the vaporization curve, the entire liquid-vapor region projects into the fusion curve, and, finally, the *Triple-Point Line* projects into the triple point on the phase diagram [4].

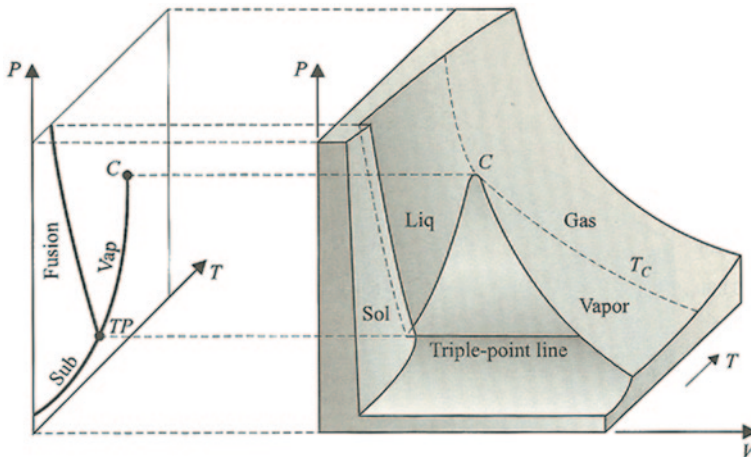


Fig. 2.10 P - V - T surface for H_2O , which contracts while melting

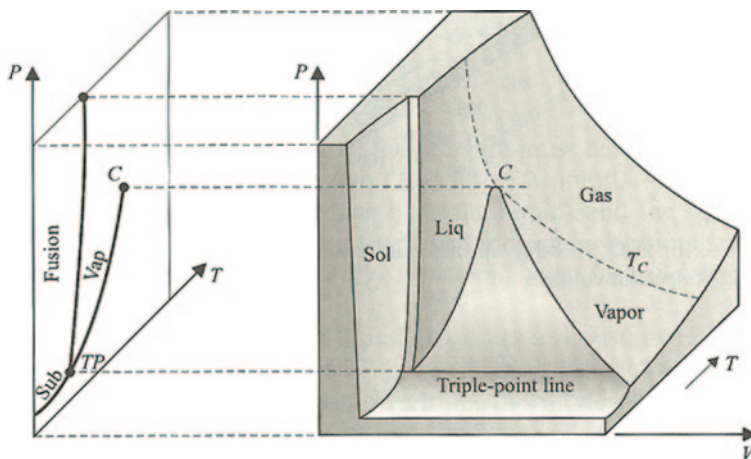


Fig. 2.11 P - V - T surface for CO_2 , which expands while Melting

The P - V - T surfaces present a great deal of information at once, but in typical thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the p - v and T - v diagrams (Fig. 2.12).

Example 2.2 Determine the volume change when 1 kg of saturated water is completely vaporized at a pressure of (a) 1 kPa, (b) 100 kPa, and (c) 10000 kPa.

Solution Appendix A14.2 provides the necessary values. The quantity being sought is $v_{fg} = v_g - v_f$. Note that p is given in MPa

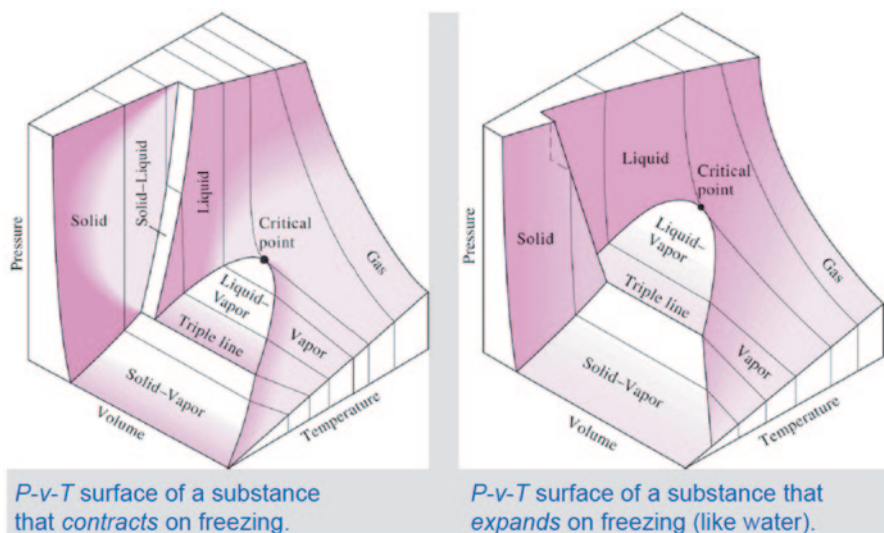


Fig. 2.12 Illustration of $P-V-T$ diagram for two cases

- 1 kPa. Thus, $v_{fg} = 129.183 - 0.001 = 129.182 \text{ m}^3/\text{kg}$.
- 100 kPa MPa. Again $v = 1.673 - 0.001 = 1.672 \text{ m}^3/\text{kg}$.
- 10,000 kPa = 10 MPa. Finally, $v_{fg} = 0.018034 - 0.001453 = 0.016581 \text{ m}^3/\text{kg}$.

Example 2.3 Four kg of water is placed in an enclosed volume of 1 m^3 . Heat is added until the temperature is 420°K . Find (a) the pressure, (b) the mass of vapor, and (c) the volume of the vapor.

Solution Appendix A14.1 is used. The volume of 4 kg of saturated vapor at 420°K is $(0.425255)(4) = 1.701 \text{ m}^3$. Since the given volume is less than this, we assume the state to be in the quality region.

- In the quality region the pressure is given as $p = 437.24 \text{ kPa}$.
- To find the mass of the vapor we must determine the quality. It is found from Eq. 2.3, using the actual $v = 1/4 \text{ m}^3/\text{kg}$, as;

$$0.25 = 0.001087 + (0.425255 - 0.001087)$$

thus $x = 0.2489/0.425255 = 0.5853$. Using the relationship of $x = \frac{m_g}{m}$, the vapor mass is

$$m_g = mx = (4)(0.5853) = 2.341 \text{ kg}$$

- Finally, the volume of the vapor is found from

$$V_g = v_g m_g = (0.4253)(2.341) = 0.9956 \text{ m}^3$$

Note that in a mixture where the quality is not very close to zero, the vapor phase occupies most of the volume. In this example, with a quality of 58.53 % it occupies 99.56 % of the volume.

Example 2.4 Four kg of water is heated at a pressure of 220 kPa to produce a mixture with quality $x = 0.8$. Determine the final volume occupied by the mixture.

Solution Using Appendix A14.2 to determine the appropriate number at 220 kPa we linearly interpolate between 0.2 and 0.3 MPa. This provides, at 220 kPa.

$$v_g = \left(\frac{220 - 200}{250 - 200} \right) (0.718697 - 0.885735) + 0.885735 = 0.8189 \text{ m}^3/\text{kg}$$

Note that no interpolation is necessary for v_f , since for both pressures v_f is the same to four decimal places. Using Eq. 2.6, we now find

$$v = v_f + x(v_g - v_f) = 0.0011 + (0.8)(0.8189 - 0.001) = 0.6554 \text{ m}^3/\text{kg}$$

The total volume occupied by 4 kg is $V = mv = (4 \text{ kg})(0.6640 \text{ m}^3/\text{kg}) = 2.621 \text{ m}^3$.

Example 2.5 Two lb of water is contained in a constant-pressure container held at 540 psia. Heat is added until the temperature reaches 1100 °R. Determine the final volume of the container.

Solution: Use Appendix 14.7. Since 540 psia lies between the table entry values, the specific volume is simply

$$v = 1.2223 + (0.4)(1.0017 - 1.2223) = 1.1341 \text{ ft}^3/\text{lbm}$$

The final volume is then $V = mv = (2)(1.2115) = 2.2681 \text{ ft}^3$

Example 2-6 Calculate the pressure of steam at a temperature of 500 °C and a density of 24 kg/m³ using (a) the ideal-gas equation, (b) the van der Waals equation, (c) the Redlich-Kwong equation, (d) the Peng-Robinson equation, and (e) the steam table.

Solution

- Using the ideal-gas equation, $P = \rho RT = (24/18)(8.31447)(773) = 8569.4 \text{ kPa}$.
- Using values for a and b from the Appendix for the Van der Waals equation provides;

$$P = \frac{RT}{v - b} - \frac{a}{v^2} = \frac{8.31447(773)}{\frac{18}{24} - 0.03084} - \frac{553.04}{\left(\frac{18}{24}\right)^2} = 7954 \text{ kPa}$$

- c. Using values for a and b from the Appendix for the Redlich-Kwong equation gives;

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)\sqrt{T}} = \frac{(8.31447)(773)}{\frac{18}{24} - 0.02110} - \frac{14258.5}{\left(\frac{18}{24}\right)\left(\frac{18}{24} + 0.02110\right)\sqrt{773}} = 7931 \text{ kPa}$$

- d. For the Peng-Robinson equation the acentric factor for water is 0.3437.

$$\kappa = 0.37464 + 1.54226\omega - 0.26993\omega^2$$

$$\alpha = \left(1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2$$

$$\alpha = 0.8447 :$$

$$P = \frac{8.31447 * 773}{0.75 - 0.01895} - \frac{0.8447 * 599.4}{(0.75^2 + 2 * 0.01895 * 0.75 - 0.01895^2)} = 7934.24 \text{ kPa}$$

- e. The steam table provides the most precise value for the pressure. Using $T = 500^\circ\text{C}$ and $v = 1/24 = 0.04166 \text{ m}^3/\text{kg}$, we find $P = 8141 \text{ kPa}$. Note that the ideal-gas law has an error of 5.3 %, and the errors of each of the other three equations are Van der Waals = -2.29 %, Redlich Kwong = -2.58 %, Peng-Robinson = -2.54 %

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Thermodynamics In Nuclear Power Plant Systems

Zohuri, B.; McDaniel, P.

2015, XXIII, 724 p. 321 illus., 146 illus. in color.,

Hardcover

ISBN: 978-3-319-13418-5