# CHAPTER 4

# THE SIMPLE COMPRESSIBLE SUBSTANCE

### 4.1 Introduction

Since all matter can be compressed if a large enough pressure is applied, a study of the thermodynamic properties of the simple compressible substance is a good starting point for any description of the macroscopic properties of matter in equilibrium. Simple compressible substances are also by far the most important ones for engineering thermodynamics, since most (but not all) power plants and engines employ compression, heating, and expansion of a fluid to produce power.

A substance may be approximated as a simple compressible substance if effects due to other reversible work modes are negligible. For example, if the surface-to-volume ratio of a large body of water is small enough, then surface tension will not measurably affect the properties of the water except very near the surface. On the other hand, surface tension will have a dramatic influence on the properties of a very small water droplet, and will, for example, cause the pressure inside the droplet to be elevated above the value predicted if surface tension were neglected. Clearly, a very small water droplet can't be treated accurately as a simple compressible substance, while a large body of water is approximated very well in this way.

In this chapter, we examine the properties of simple compressible substances. We will restrict attention to *pure* substances, which contain only one type of molecule. Mixtures will be considered in a later chapter.

### 4.2 Phases of a Simple Compressible Substance

A simple compressible substance may exist in different phases: solid, liquid, or gas. Some substances have multiple solid phases, some even have multiple liquid phases (helium), but all have only one gas phase.

An experimental apparatus is shown in Fig. 4.1 which can be used to measure the properties and phases of a simple compressible substance as a function of temperature and pressure. A cylindrical solid sample is placed in a vertical cylinder of the same diameter, which is fitted with a piston. The ambient pressure is  $P_0$ , and the piston weight provides a constant downward force F =



Figure 4.1: Constant-pressure heating experiment.

 $M_p g$ . The pressure in the cylinder is

$$P = F/A = M_p g/A + P_0. (4.1)$$

The sample height is small enough that the pressure may be taken to be uniform within the sample. The cylinder and piston are well insulated, so there is no heat loss to the environment.

A small amount of heat Q is added by briefly passing current through a resistor mounted in the cylinder wall, after which the system is allowed to reestablish equilibrium. Once the system has come back to equilibrium, both the temperature and the volume may have changed. The new temperature is measured with a thermometer, and the new volume by the piston height.

If Q is sufficiently small, the expansion will occur slowly enough that friction between the piston and cylinder is negligible. In this case, even if the piston oscillates for a while due to the perturbation, once the oscillations have died out and the piston has settled down at a new height, the work done by the substance on the piston will be equal to the work done against atmospheric pressure, plus the change in the gravitational potential energy of the piston:<sup>1</sup>

$$W = (M_p g + P_0 A) \Delta y = (M_p g + P_0)(\Delta V/A) = (M_p g/A + P_0) \Delta V = P \Delta V.$$
(4.2)

An energy balance on the substance yields the change in its internal energy:

$$\Delta U = Q - P \Delta V. \tag{4.3}$$

<sup>&</sup>lt;sup>1</sup>If friction were not negligible, some kinetic energy of the piston would be converted to internal energy in the piston or cylinder due to friction, and therefore the work would be  $> P\Delta V$ .

The quantities Q, P, and  $\Delta V$  are all measured, so we can calculate  $\Delta U$ . Since P is a constant in this experiment, this equation may be rearranged in the form

$$\Delta(U + PV) = Q. \tag{4.4}$$

The combination U + PV occurs often in analysis of problems at constant pressure. Since U, P, and V are material properties, so is U + PV. Rather than always write U + PV, we give this property its own name and symbol: the *enthalpy!definition* H is defined by

$$H = U + PV. \tag{4.5}$$

Like U and V, H is an extensive property.

In terms of the enthalpy, Eq. (4.4) becomes

$$\Delta H = Q. \tag{4.6}$$

For heat addition at constant pressure, the heat added equals the change in enthalpy of the substance. In contrast, recall from the First Law that if heat is added at constant volume (W = 0), then  $\Delta U = Q$ .

Returning to our experiment, the process in now repeated many times, and the resulting property values are recorded at every step: heat Q is added, time is allowed to elapse to re-establish equilibium, the new T and V are measured, H is incremented by Q.

After n heat addition steps, the volume and temperature have values  $V_n$  and  $T_n$ , and enthalpy  $H_n$  of the substance relative to its starting value  $H_0$  is

$$H_n - H_0 = nQ. \tag{4.7}$$

Since the extensive properties (V and H) depend on how much of the substance was placed in the container, it is preferable to convert them to specific quantities (v = V/M, h = H/M). In Fig. 4.2, the measured temperature and change in specific enthalpy are shown plotted vs. the measured specific volume (connecting the individual measurements with solid lines).

When heat is first added to the solid, its temperature increases and it expands slightly (region a-b in Fig. 4.2). At point b, the temperature stops increasing, although the volume still increases. A look inside the cylinder reveals the presence of some liquid – the solid is melting.

At point c, all of the solid has melted, and precisely at this point the temperature begins to rise again. But when point d is reached, it stops again and the volume begins to increase significantly. Bubbles are observed to begin forming



Figure 4.2: Measured temperature (a) and specific enthalpy change (b) vs. measured specific volume for constant-pressure heating.

in the liquid at point d – the liquid is boiling. Moving across from point d to e, the amount of vapor in the cylinder increases, and the amount of liquid decreases. At point e, no liquid remains, and both temperature and volume increase upon further heat addition.

Figure 4.2 shows that when two phases are present (solid/liquid or liquid/vapor),  $h - h_0$  continues to increase with v even though T is constant, since energy input is required to convert solid to liquid, or liquid to vapor. Note that the only way to measure h is by means of Eq. (4.7), which actually only allows the change in h from the initial state to be determined. There is no experiment we could do to measure the value in the initial state  $h_0$ .<sup>2</sup> Since h = u + Pv, if  $h_0$  can't be determined, then  $u_0$  can't be either. This isn't a problem, however, since only differences of energy (or enthalpy) have any physical significance. We can start the experiment in some convenient, reproducible state, and simply assign any value we like to  $h_0$  (for example,  $h_0 = 0$ ). We call the initial state with arbitrarily-chosen  $h_0$  the reference state or datum state.

The results shown in Fig. 4.2 are for a single pressure,  $P = M_p g/A + P_0$ . By changing the mass of the piston, we can repeat the experiment for different pressures, determining T(v) and  $h(v) - h_0$  curves for a range of pressures.

Typical T(v) curves are shown in Fig. 4.3(a) with the points on different curves where the slope is discontinuous connected by dotted lines. The curve corresponding to Fig. 4.2(a) is labeled  $P_1$  on this plot. In Fig. 4.3(b), the dashes

 $<sup>^{2}</sup>$ We could measure it by starting in some other state, but it wouldn't be the initial state; the measured value would be relative to the enthalpy in this new initial state, which would still be undetermined.



Figure 4.3: (a) T - v curves for constant-pressure heating; (b) phase diagram.

lines are drawn solid, and each region is labeled by which phase or phases are present in the cylinder. Diagrams like this are called *phase diagrams*.

The experimental observations are as follows. As the pressure is increased, the temperature at which liquid appears (the melting point) and the temperature at which vapor appears (the boiling point) both increase. Also, the specific volume of the liquid increases to a larger value before boiling begins, and the specific volume of the vapor once the last liquid has evaporated decreases. Therefore, the change in specific volume upon boiling decreases as the pressure increases.

Beyond a particular pressure  $P_3$ , the T(v) curve changes character. As  $P_3$  is approached, the change in specific volume upon boiling goes to zero – the liquid and vapor approach the same density, and in fact become identical in all respects at  $P_3$ . For  $P > P_3$ , there is no longer a meaningful distinction between liquid and vapor, and there is no longer any conventional boiling behavior observed. In this pressure regime, as heat is added the high-density fluid simply expands continuously and homogeneously to a low-density fluid, without ever breaking up into separate liquid and vapor regions within the cylinder.

Pressure  $P_3$  is known as the *critical pressure*  $P_c$ . Below  $P_c$ , the transformation from liquid to vapor upon heating occurs by means of the fluid in the cylinder splitting into two separate regions (high-density liquid and low-density vapor); as more heat is added, the liquid portion shrinks, and the vapor portion grows. Above  $P_c$ , the transformation from liquid to vapor occurs continuously, with the fluid remaining uniform throughout the cylinder at all times.

As P approaches  $P_c$  from below, the limiting value approached by the boiling

		$\mathbf{D}$ (1) ( $\mathbf{D}$ )	(1 ( 2)
	$T_c$ (K)	$P_c (MPa)$	$ ho_c~( m kg/m^3)$
Helium-4	5.20	0.2275	69.64
Hydrogen	32.94	1.28	31.36
Nitrogen	126.2	3.4	314.03
Oxygen	154.6	5.04	436.15
Methane	190.6	4.60	160.43
Carbon Dioxide	304.2	7.38	464.00
Water	647.3	22.1	317.0

Table 4.1: Critical temperature, pressure, and density for a few substances.

temperature is known as the *critical temperature*  $T_c$ . The T(v) curve for  $P = P_c$  has an inflection point at  $T = T_c$ :

$$\left(\frac{\partial T}{\partial v}\right)_P = 0 \quad \text{and} \quad \left(\frac{\partial^2 T}{\partial v^2}\right)_P = 0 \quad \text{at } T = T_c, \ P = P_c.$$
 (4.8)

The specific volume of the fluid at the point where  $P = P_c$  and  $T = T_c$ is known as the *critical specific volume*  $v_c$ ; the reciprocal of  $v_c$  is the *critical density*  $\rho_c$ . The quantities  $T_c$ ,  $P_c$ , and  $v_c$  (or  $\rho_c$ ) define the *critical point*. The critical point quantities for a few substances are listed in Table 4.2.

If the pressure is now lowered below  $P_1$ , another change in the character of the T(v) curve is observed. On the  $P_0$  curve, there is only one segment where T is constant, not two. On the flat segment, a solid/vapor mixture is found in the cylinder, rather than a solid/liquid or liquid/vapor mixture. Evidently, at sufficiently low pressure no liquid phase forms – instead, the solid transforms directly to vapor. This process is known as *sublimation*.

### 4.3 P - v - T Surfaces

Since any two independent properties serve to define the thermodynamic state for a simple compressible substance, we may regard any other property as a function of these two. For example, at every (T, v) point in Fig. 4.3 we know the pressure, so we can construct P(T, v).

The function P(T, v) defines a surface over the T - v plane. A typical P - v - T surface is shown in Fig. 4.4. Every equilibrium state of the substance corresponds to some point on the P - v - T surface. In the pure solid region and in the pure liquid region below  $T_c$ , the slope of the surface is very steep, since compressing a solid or liquid even a little requires a huge increase in pressure. In the gas or vapor region, the surface is gently sloped, since gases are easily



Figure 4.4: A P - v - T surface for a substance which expands upon melting.

compressed. Of course, above the critical point the liquid and gas regions merge smoothly.

In Fig. 4.4 the term "gas" is used above the critical point, and "vapor" below it. This convention dates back to the early 19th century, when it was thought that "gases" like oxygen were different than "vapors" like steam. Vapors could be condensed to liquid, but gases (it was believed) could not be. When it was demonstrated in 1877 that oxygen and nitrogen could be liquified at sufficiently low temperature, it became clear that there was no fundamental distinction between gases and vapors; the only difference is that substances such as oxygen have critical temperatures well below room temperature, while the critical temperature of water is above room temperature. Thus, liquid water is commonplace, but liquid oxygen, nitrogen, hydrogen, or helium are not. However, processes to produce these as liquids are now straightforward, and liquid oxygen, nitrogen, and helium have very significant technological applications.<sup>3</sup>

The slope of the P - v - T surface is discontinuous on the boundary between the single-phase and the two-phase regions. Note that since T remains constant

 $<sup>^{3}</sup>$ For example, liquid hydrogen and oxygen as used as propellants in the Space Shuttle Main Engine; liquid nitrogen is widely used to cool electronic equipment and photodetectors; liquid helium is used to cool large superconducting magnets to temperatures a few degrees above absolute zero.

	$T_t$ (K)	$P_t$ (kPa)
Helium-4	2.18	5.1
Hydrogen	13.8	7.0
Nitrogen	63.15	12.5
Oxygen	54.34	0.14
Methane	90.68	11.7
Carbon Dioxide	216.54	517.3
Water	273.16	0.61

Table 4.2: Triple-point temperatures and pressures.

in the two-phase regions during constant-pressure heating, any horizontal slice through the surface in a two-phase region must produce a line perpendicular to the T axis; in other words, the slope of the surface in the T direction is zero in the two-phase regions.

The solid-vapor two-phase region intersects the solid-liquid and liquid-vapor regions in a single line parallel to the volume axis. This line is known as the *triple line*, since along this line all three phases may coexist in equilibrium. The pressure and temperature are the same everywhere along the triple line. Therefore, for a given substance, there is only one pressure  $P_t$  and one temperature  $T_t$ at which solid, liquid, and vapor may coexist in equilibrium. The combination  $(T_t, P_t)$  is known as the *triple point*. Of course it is only a *point* in the P - Tplane; when the volume axis is considered, it is a line. This is in contrast to the critical point, which is really a point in (P, v, T) space.

The triple points for several substances are listed in Table 4.3. Note that of the ones listed, only carbon dioxide has  $P_t > 1$  atm (1 atm = 101.325 kPa). Therefore, at 1 atm pressure, solid carbon dioxide ("dry ice") sublimates, while solid water melts.

Th P - v - T surface shown in Fig. 4.4 is appropriate for a substance which expands upon melting, which we assumed implicitly in our discussion above. However, a few substances – including water – contract when they melt. For these substances, the P - v - T surface looks like that shown in Fig. 4.5.

If a substance has multiple solid phases, the P - v - T surface can become very complex. A portion of the actual surface for water is shown in Fig. 4.6, showing the different phases of ice.

Two-dimensional phase diagrams may be obtained by projecting the P-v-T surface onto the P-T, T-v, or P-v planes. We have already looked at the T-v projection in constructing the P-v-T surface [Fig. 4.3(b)]. The P-T



Figure 4.5: A P - v - T surface for a substance which contracts upon melting.



Figure 4.6: A portion of the P - v - T surface for water.



Figure 4.7: P-T phase diagrams for (a) a substance which expands on melting; (b) a substance which contracts on melting.

projection is shown in Fig. 4.7 for a substance which expands on melting (a) and for one which contracts on melting (b). The critical point (c) and the triple point (t) are both shown.

The lines separating the single-phase regions on a P-T plot are known as *coexistence lines*, since on these lines two phases may coexist. The liquid-vapor coexistence line terminates at the critical point. In contrast, the solid-liquid coexistence line never terminates, no matter how high the pressure. This is because solid and liquid are fundamentally different – in a solid, atoms are arranged in a highly regular, periodic way, while in a liquid they are arranged randomly. There is no way for these states with very different symmetry to transform into one another continuously, and so it is not possible for a critical point to exist on the solid-liquid coexistence line.

Each of the coexistence lines in a P-T phase diagram can be described by some function P(T), so clearly P and T are not independent when two phases are simultaneously present. On the liquid-vapor and solid-vapor coexistence lines, the term *vapor pressure* is used to denote P(T), since this is the pressure of the vapor in equilibrium with the solid or liquid. An equivalent term is *saturation pressure*  $P_{sat}(T)$ . If pressure is specified, the *saturation temperature*  $T_{sat}(P)$  is defined to be the temperature on the coexistence curve where the pressure is P. The saturation temperature is just another name for the boiling temperature. For example, for water,  $T_{sat}(1 \text{ atm})$  is 373.15 K (100 °C), and  $P_{sat}(373.15 \text{ K}) = 1 \text{ atm}.$ 

### 4.4 Determining Properties in the Mixed-Phase Regions

Under conditions where two phases coexist in equilibrium, some care must be taken to correctly determine the properties and amount of each phase from a



Figure 4.8: In the liquid/vapor two-phase region, the liquid has specific volume  $v_f$  and the vapor has specific volume  $v_q$ .

phase diagram. The two phases have very different properties. For example, the specific volume of a liquid is much less than that of a gas. How can we determine *both* values from a phase diagram?

The key is to realize that in a two-phase region, the properties of each phase present are those at the "edges" of the region. For example, consider boiling a liquid at constant pressure. Just before the temperature where gas bubbles first appear, the cylinder is still filled with liquid. Call the specific volume at this point  $v_f$ .<sup>4</sup> As more heat is added at constant pressure, the only thing that happens is that some liquid becomes vapor – the properties (per unit mass) of the remaining liquid don't change. Although there is less liquid, the liquid remaining still has specific volume  $v_f$ .

What is the specific volume of the vapor which has been created? It too is constant during the constant-pressure boiling process, and thus must equal the value of v obtained once the cylinder contains only vapor. Call this value  $v_g$ .

Suppose now that the system is somewhere in the two-phase region on the isobar<sup>5</sup> labeled P in Fig. 4.8 and the measured total volume V results in a value for v = V/M as shown in this figure. This v does not actually correspond to the specific volume of either the liquid or the vapor in the container. These are  $v_f$  and  $v_g$ , respectively. Instead, v is an *average* of  $v_f$  and  $v_g$ , weighted by the mass of each in the container.

We use the term "saturated" to denote the states on either side of the vapor dome (Fig. 4.9). Thus, "saturated liquid" has specific volume  $v_f$ , and "saturated

 $<sup>^4</sup>$ Although it is not entirely logical, it is conventional to use the subscript "f" to denote properties of the liquid and "g" to denote properties of the vapor in an equilibrium liquid/vapor mixture.

 $<sup>^5\</sup>mathrm{An}$  isobar is a line of constant pressure. The P in a circle simply labels the pressure of this isobar.



Figure 4.9: Definition of saturated, superheated, and subcooled states.

vapor" has specific volume  $v_g$ . When liquid and vapor are present together in equilibrium, the liquid is always saturated liquid, and the vapor is saturated vapor. Vapor at a temperature above  $T_{sat}(P)$  is called *superheated vapor*, and liquid at a temperature below  $T_{sat}(P)$  is called *subcooled liquid*. Subcooled liquid is also called *compressed liquid*, since it is at a higher pressure than  $P_{sat}(T)$ .

Let the mass of the *vapor* in the container be Mx, where  $0 \le x \le 1$ . Then the mass of the liquid must be M(1-x), since the total mass is M. The total volume is then

$$V = M(1 - x)v_f + Mxv_g,$$
(4.9)

or

$$v = \frac{V}{M} = (1 - x)v_f + xv_g.$$
(4.10)

If we know v, we can then solve for x:

$$x = \frac{v - v_f}{v_g - v_f}.\tag{4.11}$$

The vapor mass fraction x is an intensive thermodynamic property of a liquid/vapor mixture. The common name in engineering thermodynamics for x is the quality. This name was given to x by engineers developing steam engines and power plants: the presence of liquid droplets in the steam damages engine parts such as turbine blades, hence from the engineer's perspective higher "quality" steam had less liquid content. Of course, for other applications the relative merits of liquid and vapor might be reversed. In this book, we will usually refrain from making a value judgement about liquid vs. vapor, and simply call x the vapor mass fraction.

Equation (4.11) is known as the *lever rule*. It may be interpreted in terms Fig. 4.8 as follows. To determine the mass fraction of a phase in a saturated vapor/liquid mixture, locate the system point in the two-phase region on a T-v or P-v plot. Now take the length of the horizontal line segment from v to the saturation line corresponding to the *other* phase, and divide this length by the total width of the 2-phase region  $(v_g - v_f)$ . Note that this rule works for any 2-phase region, for example for liquid/solid mixtures.

**Example 4.1** A bottle contains 10 kg of carbon dioxide at 260 K. If the volume of the bottle is 100 liters, does the bottle contain liquid, solid, gas, or a mixture? How much of each? What is the pressure?

Solution: Since 260 K is greater than the triple-point temperature for CO<sub>2</sub>, no solid will be present. Calculate v = V/M = (100 liters)/(10 kg):  $v = 0.01 \text{ m}^3/\text{kg}$ . From a phase diagram for CO<sub>2</sub> at 260 K, we find that  $v_f = 0.001001 \text{ m}^3/\text{kg}$ , and  $v_g = 0.01552 \text{ m}^3/\text{kg}$ . Since v is between these two values, the bottle contains a mixture of liquid and gaseous CO<sub>2</sub>. The vapor mass fraction is

$$x = \frac{0.01 - 0.001001}{0.01552 - 0.001001} = 0.62.$$

Since it is in the mixed phase region, the pressure is the saturation pressure at 260 K, which is 2.421 MPa.

# 4.5 Software for Property Evaluation

To solve problems involving real substances (such as the last example), some source of property data is required. Traditionally in thermodynamics courses, properties were looked up in tables, or estimated from detailed phase diagrams. A typical diagram for oxygen is shown in Fig. 4.10. Here the pressure is plotted against the enthalpy, and many curves representing particular values of other properties are shown. Since P and h are two valid, independent properties, the thermodynamic state is represented by a point on this plot. The point may be fixed by interpolation if any two properties are known for which curves are plotted on the chart. Once the state point is found, any other properties can be read off (with some care and practice).

Most thermodynamics textbooks now come with at least some rudimentary software to evaluate properties. In many cases, the programs are simply electronic versions of tables, which print to the screen the property values. In other cases, more elaborate software is provided which allows you to do a complete thermodynamic analysis. But even these packages are specialized applications, which you use for thermodynamics but nothing else.



Figure 4.10: A pressure-enthalpy plot for oxygen.

A new software package is provided as a supplement to this book which implements thermodynamic property functions in Microsoft Excel (a spreadsheet program). The thermodynamic property functions are provided by an "add-in" module called TPX ("Thermodynamic Properties for EXcel"). Details of how to load it into Excel and use it are given in Appendix A.

Calculating properties is easy with TPX. For example, if you want to know the specific enthalpy of oxygen at 1 MPa and 500 K, you simply type into a cell:

#### =h("o2","PT",1,500)

The parameters are: the substance name (case is unimportant); a string stating the properties which will be used to fix the state (here P and T); the value of the first parameter (P); the value of the second parameter (T). The value of the function returned in the cell is 655.83 kJ/kg. You can select any system of units you like; all inputs and outputs will then be in those units. (This example assumes the user selected units of Kelvin for temperature, MPa for pressure, kJ for energy, and kg for mass.)

The real power of using a spreadsheet becomes apparent in more complex analyses. For example, the temperature and pressure may not be specified inputs, but are themselves the result of calculations in other cells. In this case, simply replace the numerical value in the function parameters by the appropriate cell address (e.g. B4).

The same functions implemented by TPX are also available in a WWW property calculator. The calculator is convenient for simple calculations, if you have access to the Web but not to Excel.

**Example 4.2** One kg of water is placed in a closed container and heated at constant volume. The initial temperature is 300 K. If the desired final state is the critical point, determine the necessary container volume, initial pressure, initial vapor mass fraction, and energy transfer as heat.

Solution: Two properties are needed to specify the initial state. The temperature is given, so one more is required. Since the process occurs at constant volume, the initial volume  $V_1$  must equal the final volume  $V_2$ . The final state is the critical point, so

$$V_2 = (1 \text{ kg}) \times v_c.$$

The critical specific volume of water may be calculated using TPX:

$$v_c = vcrit("h2o") = 0.003155 \text{ m}^3/\text{kg}.$$

Therefore, state 1 is fixed by  $T_1 = 300$  K and  $v_1 = v_c$ . Using TPX, any other

desired property for state 1 may be computed:

$$\begin{split} P_1 &= 3528.2 \mbox{ Pa} & \mbox{P("H20", "TV", 300, vcrit("H20"))} \\ X_1 &= 5.49 \times 10^{-5} & \mbox{x("H20", "TV", 300, vcrit("H20"))} \\ u_1 &= 112.727 \mbox{ kJ/kg} & \mbox{u("H20", "TV", 300, vcrit("H20"))} \\ h_1 &= 112.738 \mbox{ kJ/kg} & \mbox{h("H20", "TV", 300, vcrit("H20"))} \end{split}$$

Note that the initial state is a mixed liquid/vapor state, and so  $P_1 = P_{sat}(300 \text{ K})$ . The vapor fraction is very small, since  $v_c$  is only slightly greater than the specific volume of the saturated liquid.

The required heat transfer Q is determined from the First Law:

$$\Delta U = Q + W.$$

Since the volume is constant, W = 0, so

$$Q = \Delta U = M(u_2 - u_1).$$

Using TPX,

 $u_2 = u("h2o", "tv", tcrit("h2o"), vcrit("h2o")) = 2029.6 \text{ kJ/kg}.$ 

so Q = (1 kg)(2029.6 kJ/kg - 112.7 kJ/kg) = 1916.9 kJ.

## 4.6 More Properties: Partial Derivatives of Equations of State

Consider an equation of state like P(T, v). Clearly, a partial derivative of this function, for example  $(\partial P/\partial T)_v$ , is some new function of (T, v) and may rightly be regarded as a thermodynamic property of the system. Some useful derivative properties are defined here.

#### 4.6.1 Thermal Expansion Coefficient

Most substances expand when heated. The property which tells us how much a substance expands when heated at constant pressure is the *thermal expansion* coefficient  $\beta$ , defined by

$$\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P \tag{4.12}$$

To calculate  $\beta$ , the equation of state v(T, P) would be differentiated with respect to T.

Note the 1/v in the definition  $-\beta$  is defined as the *fractional* change in volume per degree of temperature increase. Also, note that this definition is only really meaningful if a single phase is present, since otherwise T can't be increased holding P constant.

**Example 4.3** What is the thermal expansion coefficient of liquid water at 300 K and 1 atm?

**Solution:**  $\beta$  may be calculated approximately using TPX, evaluating the partial derivative by a finite-difference approximation. Taking a small increment of, say, 0.1 K, use TPX (with units set to K and atm) to evaluate  $(\partial v/\partial T)_P$ :

$$\left(\frac{\partial v}{\partial T}\right)_{P} \approx (v("h2o", "tp", 300.1, 1) - v("h2o", "tp", 300, 1)/0.1)$$
  
= 2.75 × 10<sup>-7</sup> m<sup>3</sup>/kg-K. (4.13)

Since

$$v=$$
 v("h2o", "tp", 300, 1)  $=0.001003378~{
m m}^3/{
m kg}$   
 $etapprox 2.74 imes 10^{-4}~{
m K}^{-1}.$ 

#### 4.6.2 Isothermal Compressibility

All matter decreases slightly in volume if the pressure is increased at constant temperature. The property how the volume varies with pressure at constant temperature is the *isothermal compressibility*  $\kappa$ , defined by

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T \tag{4.14}$$

As with  $\beta$ , if the equation of state v(T, P) is known, it can be differentiated to find  $\kappa(T, P)$ . And as with the thermal expansion coefficient,  $\kappa$  is only meaningful if the substance is in a single phase.

### 4.6.3 Specific Heats

Suppose a unit mass of a substance absorbs an amount of heat dQ; how much does the temperature increase? It depends in part on how the heating is done. From the First Law,

$$du = dQ + dW = dQ - Pdv. (4.15)$$

#### Constant Volume

If the heating is done at constant volume, the work term is zero. Therefore

$$du = dQ. \tag{4.16}$$

Differentiating the equation of state u(T, v) at constant v, we may also write for du

$$du = \left(\frac{\partial u(T, v)}{\partial T}\right)_{v} dT.$$
(4.17)

Equating these two expressions for du produces the desired relationship between dQ and dT:

$$dQ = \left(\frac{\partial u}{\partial T}\right)_v dT. \tag{4.18}$$

The specific heat at constant volume  $c_v$  is defined by

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \tag{4.19}$$

Then

$$du = c_v dT \tag{4.20}$$

for constant-volume heating. The SI units of  $c_v$  are J/kg/K.

#### Constant Pressure

At constant pressure, we have to be careful to remember to account for the work done against the environment as the sample expands. Rearranging Eq. (4.15), we find dQ = du + Pdv. But since P is constant in the process, du + Pdv = d(u + Pv). We recognize u + Pv to be the specific enthalpy h.

Therefore, for constant pressure heating, dQ = dh. We can also write

$$dh = \left(\frac{\partial h(T, P)}{\partial T}\right)_P dT, \tag{4.21}$$

since P is constant. Therefore, for *constant pressure* heating, dQ and dT are related by

$$dQ = \left(\frac{\partial h}{\partial T}\right)_P dT. \tag{4.22}$$

The specific heat at constant pressure  $c_p$  is defined by

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P \tag{4.23}$$

The units are the same as those for  $c_v$ .

Another common term for  $c_v$  and  $c_p$  is *heat capacity*. Heat capacities may also be defined per mole of substance  $(\hat{c}_v \text{ and } \hat{c}_p)$  or for a total amount of substance of mass M ( $C_v$  and  $C_p$ ).

Finally, it is worth noting that the names "heat capacity" and "specific heat" both derive from the old idea that a body can store "heat." The names shouldn't be taken too literally  $-c_v$  and  $c_p$  are simply defined in terms of the derivatives given above.

### 4.7 Model Equations of State

A software package like TPX evaluates properties using some mathematical functions which have been fit to a large number of experimental measurements. The measured data might be P(T, v),  $c_p(T, v)$ , or more indirect quantities like the speed of sound. The functions are empirical, and contain many adjustable constants which may be set to fit the measurements as accurately as possible. For example, the functions used by TPX to represent the properties of water contain more than 60 constants, with values chosen to provide the best fit to measurements. <sup>6</sup>

Sometimes it is desirable to work with much simpler approximate equations of state. The price for simplicity is lack of accuracy, but in some cases we are interested in examining qualitative behavior rather than calculating precise numbers. Here we examine some common approximate or *model* equations of state, starting with the simplest and working up to more complex but more accurate ones.

### 4.7.1 The Ideal Gas

The quantity  $P\hat{v}/T$  (where  $\hat{v}$  is the *molar* volume) is found to approach the same value for all fluids in limit of low density when the molecules are far from one another (Fig. 4.11). The limiting value is found to be

$$\lim_{P \to 0} \frac{P\hat{v}}{T} = \hat{R} = 8.314 \text{ kJ/mol-K}$$
(4.24)

The constant  $\hat{R}$  is known as the *universal gas constant*. If the pressure is low enough that  $P\hat{v}/T$  has reached this limiting value, then the equation of state is approximated by

$$P\hat{v} = \hat{R}T. \tag{4.25}$$

<sup>&</sup>lt;sup>6</sup>J. H. Keenan et al., *Steam Tables*, John Wiley and Sons, New York, 1969.



Figure 4.11: Demonstration that  $P\hat{v}/T$  approaches the same value for all fluids as  $P \to 0$ .

This equation of state is known as the *ideal gas law*, and represents the lowdensity limit of the equilibrium equation of state of all real simple compressible substances. An *ideal gas* (or *perfect gas*) is defined to be any gas which obeys Eq. (4.25).

Since  $\hat{v} = V/N$ , the ideal gas law can be written in terms of the total volume V and total number of moles N:

$$PV = N\hat{R}T.$$
(4.26)

The value of  $\hat{R}$  depends on how N is expressed. If N is expressed as a number of gram-moles (mol), then  $\hat{R} = 8.3143 \text{ kJ/mol-K}$ ; if N is expressed in kg-moles (1 kmol = 1000 mol), then  $\hat{R} = 8314.3 \text{ kJ/kmol-K}$ . Alternatively, we could dispense with using mole numbers, and express N as the actual number of molecules. In this case,  $\hat{R}$  needs to be converted from mol or kmol units to molecule units (1 mol =  $6.023 \times 10^{23}$  molecules; 1 kmol =  $6.023 \times 10^{26}$  molecules). In this case,

$$\hat{R} = (8.3143 \text{ kJ/mol-K})(1000 \text{ J/kJ})(1 \text{ mol}/6.023 \times 10^{23}) = 1.38 \times 10^{-26} \text{ J/K.}$$
(4.27)

In these units  $\hat{R}$  is usually called *Boltzmann's constant*  $k_B$ :

$$k_B = 1.38 \times 10^{-26} \text{ J/K.} \tag{4.28}$$

In this case, the ideal gas law becomes

$$PV = Nk_BT. (4.29)$$

It's important to remember that  $k_B$  and  $\hat{R}$  are really the same thing – just different units. We'll see Boltzmann's constant again in Chapter 6 when we discuss entropy.

We can also divide Eq. (4.26) by the total mass to obtain

$$Pv = \left(\frac{N\hat{R}}{M}\right)T = \left(\frac{\hat{R}}{\hat{M}}\right) = RT$$
(4.30)

where  $\hat{M} = M/N$  is the molecular weight, and  $R = \hat{R}/\hat{M}$ . Unlike  $\hat{R}$ , R is different for every gas. For helium, R = (8314.3 J/kmol-k)(1 kmol/4.0026 kg) = 2077.2 J/kg-k, while for water R = (8314.3 J/kmol-K)(1 kmol/18.016 kg) = 461.5 J/kg-K. It is often more convenient to work per unit mass rather than per mole, and so the form of the ideal gas law we will most often use is Eq. (4.30), Pv = RT.

It is important to bear in mind that the ideal gas law is not rigorously true, but becomes a good approximation at "sufficiently low" density. Some students reflexively invoke Pv = RT if a problem involves a substance they normally think of as a gas (e.g. helium, oxygen), forgetting that these substances not only can behave as non-ideal gases, but also can be liquid or solid – it all depends on the conditions.

It is simple to check whether the ideal gas law is a suitable approximation under specified conditions. Simply compute the *compressibility factor* Z, defined by

$$Z = \frac{Pv}{RT}.$$
(4.31)

If the ideal gas law is valid, then Z should equal 1. The deviation from Z = 1 is a measure of the error made in assuming ideal-gas behavior under the specified conditions.

**Example 4.4** How much error is made in using the ideal gas law to calculate the specific volume of hydrogen at 20 MPa and 90 K?

**Solution**: For hydrogen, R = 8314.3/2.016 = 4124 J/kg-K. Using TPX, v = v("h2", "tp", 90, 20) = 0.023 m<sup>3</sup>/kg under these conditions, so  $Z = (2 \times 10^7)(0.023)/4124 \times 90) = 1.24$ . Therefore, the actual volume is 24% larger than would be predicted by the ideal gas law.

### Internal Energy, Enthalpy, and Specific Heats

The specific internal energy of any simple compressible substance may be expressed as a function of T and v: u(T, v). Alternatively, we could take the independent variables to be  $(T, \rho)$  instead of (T, v), in which case we would write the specific internal energy as  $u(T, \rho)$ . Since every simple compressible substance approaches ideal gas behavior as  $\rho \to 0$ , the specific internal energy in the ideal-gas limit is  $u(T, \rho = 0)$ , which is a function of temperature alone:  $u(T, 0) = u^0(T)$ . We shall use a superscript "0" to denote properties in the ideal-gas,  $\rho \to 0$  limit.

The specific enthalpy of an ideal gas is

$$h^{0} = u^{0}(T) + Pv = u^{0}(T) + RT.$$
 (4.32)

Therefore, the specific enthalpy of an ideal gas is also a function only of temperature (independent of pressure).

From the definitions of  $c_v$  and  $c_p$ , in the ideal gas limit

$$c_v^0(T) = \frac{du^0(T)}{dT},$$
(4.33)

and

$$c_p^0(T) = \frac{dh^0(T)}{dT}.$$
 (4.34)

Since  $h^{0}(T) = u^{0}(T) + RT$ ,

$$c_p^0(T) = c_v^0(T) + R.$$
 (4.35)

The analogous equation on a molar basis would be  $\hat{c}_p^0(T) = \hat{c}_v^0(T) + \hat{R}$ . Of course, Eq. (4.35) holds only in the ideal gas limit, where Pv = RT applies.

The function  $c_p^0(T)/R$  is shown in Fig. 4.12 for several gases. Since  $c_p^0$  and  $c_v^0$  have the same units as R, the ratio  $c_p^0/R (= \hat{c}_p^0/\hat{R})$  is dimensionless. By multiplying the non-dimensional  $c_p^0/R$  by the appropriate appropriate R (or  $\hat{R}$ ) value,  $c_p^0$  or  $\hat{c}_p^0$  may be determined in any desired unit system.

If  $c_p^0(T)$  is known, Eq. (4.34) may be integrated between any two temperatures to find the change in enthalpy:

$$h^{0}(T_{1}) = h^{0}(T_{0}) + \int_{T_{0}}^{T_{1}} c_{p}^{0}(T) dT$$
 (4.36)



Figure 4.12: The ideal-gas specific heat  $c_p^0(T)$  for several gases.

If  $u^0(T_1)$  is desired, it could be computed by integrating Eq. (4.33), or from  $u^0(T_1) = h^0(T_1) - RT$ .

For the special case of  $c_p^0$  independent of T, Eq. (4.36) becomes

$$h^{0}(T_{1}) = h^{0}(T_{0}) + c_{p}^{0}(T_{1} - T_{0}), \qquad (4.37)$$

and the analogous expression for  $u^0$  is

$$u^{0}(T_{1}) = u^{0}(T_{0}) + c_{v}^{0}(T_{1} - T_{0}).$$
(4.38)

For some gases,  $c_p^0$  and  $c_v^0$  are truly independent of temperature. This is the case for any monatomic gas, such as argon, helium, neon, etc. In other cases, it may be approximately true for a limited temperature range (e.g., for N<sub>2</sub> from 300-500 K or from 2000-3000 K).

### Physics of the Temperature Dependence of $c_p(T)$

From Figure 4.12, it is apparent that the behavior of the function  $c_p^0(T)/R$  depends on the molecular structure of the gas. Using the methods of statistical physics, it is possible to calculate this dependence exactly. We will do this later, but for now we will discuss qualitatively the physics governing the ideal-gas specific heat, and learn how to compute at least the high-temperature limit of  $c_p^0(T)$  from molecular structure.

A principle of classical statistical physics known as the *principle of equipar*tition of energy says that every "square term" in the classical expression for the energy of a molecule will contribute a factor of (1/2)R to  $c_v^0$ . For example, the kinetic energy of a single atom contains three square terms:

$$= \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right).$$
(4.39)

So  $c_v^0 = (3/2)R$  and  $c_p^0 = c_v^0 + R = (5/2)R$ .

 $\epsilon$ 

For a diatomic molecule (assuming it can be approximated as two point masses joined by a linear spring), the energy is



where  $m_{12} = m_1 m_2 / (m_1 + m_2)$  is the reduced mass and  $v_r = dr/dt$ .



Center-of-mass motion (translation) contributes 3 square terms, rotation about 2 mutually orthogonal axes contributes 2 square terms, and vibration contributes 2 square terms (one for kinetic energy of vibration, and one for potential energy due to stretching the bond). The principle of equipartition of energy would predict  $c_v^0/R = 1/2(3+2+2) = 7/2$ , and thus  $c_v^0/R = 9/2$ .

This is in fact observed at high temperatures for diatomic gases (see the N<sub>2</sub> curve in Fig. 4.12). But at lower temperatures,  $c_p^0$  is found to be less than the value predicted by the equipartition principle. The reason for this is that equipartition of energy is a *classical* principle, which is valid only if classical physics provides an acceptable description of the molecular motion.

If we had calculated the energy of the molecule using quantum mechanics, we would have found that the possible energies for translation, rotation, and vibration are quantized. According to the correspondence principle, whenever the spacing between quantum levels is very small compared to the average energy a molecule possesses, the predictions of quantum mechanics approach those of classical mechanics. An appropriate comparison would be the average translational energy per molecule, which is just  $(3/2)k_BT$ . Actually, we're interested only in orders of magnitude so we can drop the 3/2 and just compare to  $k_BT$ .

Mode	$\epsilon/k_B~({ m K})$
Translation	$10^{-15}$
Rotation	2.9
Vibration	3390

Table 4.3: Characteristic quantum level spacings divided by  $k_B$ , in Kelvin. The value for translation assumes a 1 cm<sup>3</sup> box.

Typical numbers for the energy level spacings of N<sub>2</sub> are shown in Table 4.3. These energies are shown divided by  $k_B$ , giving them the units of Kelvin and making the comparison to  $k_BT$  easy.

We see that a classical description of translation is essentially always valid, and for rotation it is valid except at very low temperatures, when in any case  $N_2$  wouldn't be a gas. But vibration is another matter entirely. The spacing between vibrational levels for  $N_2$  predicted by quantum mechanics is large compared to the average energy per molecule at room temperature. For this reason, collisions of a room-temperature  $N_2$  molecule with others do not have enough energy to "excite" vibration, and so the molecule can't acquire vibrational energy. Higher temperatures are needed for vibration to become "fully excited."

This explains the  $c_p^0(T)$  behavior for N<sub>2</sub>. At room temperature,  $c_p^0 \approx 7/2$ . This suggests that the contribution from vibration is missing. The molecule is translating and rotating, but essentially not vibrating at all, since the lowest vibrational level is too high to be reached by collisions with other roomtemperature molecules. As the temperature increases,  $c_p^0$  approaches 9/2 as expected, as vibration becomes excited.

#### High Temperature Limit for Polyatomic Molecules

Molecules containing more than 2 atoms have several different vibration modes, with different frequencies and therefore different spacings between vibrational levels. The vibrational modes become excited at different temperatures in general. As each mode becomes active, the value of  $c_p^0$  increases by R.

The vibrational modes of  $CO_2$  are shown below, along with the vibrational frequencies of each. (The units used are the standard spectroscopic units of wavenumbers. To convert to Hz, multiply by the speed of light.) There are actually two bending modes with the same frequency, since the molecule may bend in the plane of the paper (as shown) or out of the plane, so  $CO_2$  has a total of four vibrational modes.



We can determine the high-temperature limit for  $c_p^0$  for any polyatomic molecule using the equipartition principle. Suppose the molecule contains Natoms, has  $N_R$  rotational modes, and  $N_V$  vibrational modes.

If the molecule is linear (such as  $CO_2$ ), it has only 2 possible rotations, just like a diatomic, so  $N_R = 2$ . (It is impossible to rotate about the molecular axis, since the nuclei are effectively point masses.) But a nonlinear, bent molecule (such as H<sub>2</sub>O) has 3 possible independent rotations ( $N_R = 3$ ).

The number of vibrational modes is given by <sup>7</sup>

$$N_V = 3N - 3 - N_R. (4.41)$$

From the discussion of the equipartition principle above, we see that each rotational mode contributes (1/2)R to  $c_p^0$ , while each vibrational mode contributes a full R. (Vibration has 2 square terms – one for kinetic energy, one for potential energy.) So the general formula for a polyatomic molecule is

$$\frac{c_p(T \to \infty)}{R} = \frac{5}{2} + \frac{1}{2}N_R + N_V.$$
(4.42)

Therefore,

$$\frac{c_p(T \to \infty)}{R} = \begin{cases} 3N - 3/2 & \text{linear} \\ 3N - 2 & \text{nonlinear} \end{cases}$$
(4.43)

### 4.7.2 The van der Waals Equation of State

In 1873, The Dutch physicist van der Waals proposed (as part of his doctoral thesis) two simple, empirical modifications to the ideal gas law, in an attempt to find a gas law valid over a wider range of conditions. The first modification was to replace v in the ideal gas law by (v - b), where b is a small positive constant. This accounts for the fact that real gases are not infinitely compressible, since the

<sup>&</sup>lt;sup>7</sup>It takes 3N numbers to specify the instantaneous configuration of the molecule (x, y, and z for each atom). Therefore, the molecule has 3N "degrees of freedom." We can alternatively describe the molecular configuration by specifying its center-of-mass position (3 numbers), angular orientation (1 angle for each rotational mode), and amplitude of each vibrational mode (1 number for each mode). The sum of these must equal 3N.

molecules have finite volume (v does not approach zero as P increases holding T constant). The constant b corresponds roughly to the specific volume of the fluid when the molecules are packed together — essentially the liquid or solid specific volume.

The second modification accounts approximately for the attractive forces between molecules. Molecules about to strike the wall feel a net restraining force due to their attraction to the other molecules in the gas behind them; this lowers the speed with which they strike the wall and the impulse delivered to the wall in the collision. Since any pressure measurement can be thought of as measuring the force on a wall due to the impulse of many collisions per second, the measured pressure P will be somewhat lower than the value which would be measured if the attractive forces were absent. The magnitude of the lowering, van der Waals argued, should be proportional to  $1/v^2$ , since the wall collision frequency per unit area is proportional to 1/v, and to first approximation the net restraining force should be proportional to the number of "nearby" molecules, which also scales with 1/v.

Based on these considerations, van der Waals proposed replacing P in the ideal gas law by  $P + a/v^2$ , since the measured P is lower than it "should be" in the ideal gas law by a factor  $a/v^2$ , where a is a positive constant.

With these modifications to the ideal gas law, the van der Waals equation

$$(P + a/v^2)(v - b) = RT (4.44)$$

is obtained. For large v (low density), this equation reduces to the ideal gas law, as it should.

Unlike the ideal gas equation of state, the van der Waals equation has a critical point, where  $(\partial T/\partial v)_P = 0$  and  $(\partial^2 T/\partial v^2)_P = 0$ . It is left as an excercise to show that setting these two partial derivatives to zero results in the solution for  $T_c$  and  $P_c$ 

$$RT_c = \frac{8a}{27b} \tag{4.45}$$

$$P_c = \frac{a}{27b^2}.$$
 (4.46)

Solving for a and b in terms of  $T_c$  and  $P_c$ ,

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c} \tag{4.47}$$

$$b = \frac{RT_c}{8P_c}.$$
 (4.48)

If we pick a and b using these expressions, the van der Waals equation is guaranteed to reproduce the correct critial temperature and pressure, although this certainly does not mean it must produce any other accurate property values.

In Fig. 4.13, the predictions of the van der Waals equation, the ideal gas equation, and TPX are compared near the critical point of methane. Three isotherms at  $0.94T_c$ ,  $T_c$ , and  $1.06T_c$  are shown, along with the actual vapor dome of methane. All three agree fairly well at large v, where the ideal gas law holds approximately. For smaller v, the ideal gas law does not adequately approximate the actual P(v, T) at all.

The van der Waals equation does much better. For  $T > T_c$ , the shape of the isotherm is qualitatively right, although quantitatively it overpredicts P(v,T) at small v. It also overpredicts the critical volume  $v_c$  slightly. An interesting thing happens below  $T_c$ : the van der Waals P(v,T) is no longer monotonic in v – instead, the isotherm exhibits a local maximum and a local minimum.

### Stability and the Liquid-Vapor Phase Transition

Suppose we prepare a van der Waals gas in a cylinder at  $T_0 < T_c$ , with  $v_0$  chosen such that the state lies on the portion of the  $T_0$  isotherm where  $(\partial P/\partial v)_T > 0$ (Fig. 4.14). The piston weight is chosen to balance  $P_0 = P(v_0, T_0)$  exerted by the gas. But due to very small random fluctuations in the number of molecules striking the piston from both sides, the piston position (and therefore v) will fluctuate very slightly.

Suppose due to a small fluctuation v increases very, very slightly. Then since  $(\partial P/\partial v)_T > 0$  on this portion of the isotherm, P will *increase*. This will create a net upward force on the piston, so v will increase even more. The process will stop only when point b is reached, where the pressure again balances the piston weight.

Now consider the other case: suppose v decreases very slightly. Now the pressure in the gas *drops*, so there is a net downward force on the piston, and it falls until point a is reached.

We conclude from this thought experiment that the entire portion of the isotherm with  $(\partial P/\partial v)_T > 0$  is unstable. A small fluctuation in v, no matter how small, results in the system changing state: it will either go to the low-volume state a, or the high-volume state b (both of which are stable to small fluctuations, since  $(\partial P/\partial v)_T < 0$  for these states).

Thus, the van der Waals equation predicts that for a given  $T < T_c$ , there is a range of pressures for which there are two possible states which are stable to small fluctuations. One state has  $v < v_c$ , and may be regarded as the liquid



Figure 4.13: Isotherms for methane predicted by TPX, the van der Waals equation, and the ideal gas equation. The temperatures are 179.1, 190.5, and 202.0 K.



Figure 4.14: An isotherm of the van der Waals equation for  $T < T_c$ .



Figure 4.15: Comparison of actual behavior during isothermal compression to prediction of van der Waals equation.

state, and the other has  $v > v_c$ , and may be regarded as the vapor state.

In reality, of course, we don't observe isotherms which have the shape in Fig. 4.14 for  $T < T_c$ . Instead, at some pressure  $P_{sat}(T)$  the fluid abruptly switches from the low-density (vapor) state to the high-density (liquid) state or visa versa, as shown in Fig. 4.15. The reason this happens is that although both the liquid and vapor states for pressures within the shaded region are stable to *small* perturbations, only one is stable to "big" perturbations. For  $P > P_{sat}(T)$ , it is the liquid state which is most stable, and for  $P < P_{sat}(T)$  it is the vapor state. We'll see how to predict  $P_{sat}(T)$  soon.

This qualitative behavior applies to real fluids, not only to idealized van der Waals fluids: the liquid-vapor phase transition results from an instability of an "underlying" smooth P(v,T) function. By carefully avoiding "big" perturbations (like dirt particles or scratches on the container wall where vapor bubbles can get a start) it is actually possible experimentally to prepare liquid at  $P < P_{sat}(T)$ . Similarly, by carefully compressing a vapor in very clean conditions pressures greater than  $P_{sat}(T)$  can be reached without liquid droplets forming. Such states are called *metastable states*. Metastable states are not thermodynamic equilibrium states, since if the system is given a big enough perturbation (a dust particle, a scratch, gently shaking the container), it switches to the more stable state.

To experimentally prepare metastable states, it is actually more common to vary temperature at a given P. In this case, liquid is stable below  $T_{sat}(P)$  (the boiling point), and metastable above it. Liquid heated above the boiling point without boiling is called *superheated liquid* and vapor cooled below the boiling point without condensing is called *supercooled vapor*.

#### A Generalized Equation of State

The van der Waals equation of state may be put in non-dimensional form by defining the nondimensional reduced pressure  $P^* = P/P_c$  and reduced temperature  $T^* = T/T_c$ . If we write Eq. (4.44) in terms of  $P^*$  and  $T^*$ , and substitute for a and b from Eq. (4.47) and Eq. (4.48), it reduces to

$$Z^{3} - \left(\frac{P^{*}}{8T^{*}} + 1\right)Z^{2} + \left(\frac{27P^{*}}{64T^{*2}}\right)Z - \frac{27P^{*2}}{512T^{*3}} = 0, \qquad (4.49)$$

where Z is the compressibility factor Pv/RT. The roots of this cubic equation determine  $Z(T^*, P^*)$ . Depending on  $T^*$  and  $P^*$ , this equation will have either one root, or three. (If three, then as discussed above the middle one is unstable.)

Note that a and b do not appear in Eq. (4.49). Thus, the van der Waals equation of state reduces to a single equation for all fluids, independent of a and b, as long as T and P are expressed in reduced form. Equations of state which depend only on  $T^*$  and  $P^*$  are called *generalized equations of state*. The van der Waals equation is the simplest example of a generalized equation of state.

At the critical point  $(P^* = 1, T^* = 1)$  the solution to Eq. (4.49) is Z = 3/8. Thus, the van der Waals equation predicts that all fluids should have  $Z_c = P_c v_c / RT_c = 0.375$ .

Unfortunately,  $Z_c$  for real fluids is not 0.375, and differs from one fluid to the next. Most fluids have  $Z_c$  in the range from about 0.23 to about 0.33 – less than the van der Waals equation of state would predict. So clearly the van der Waals equation of state is not very accurate for real fluids. This is also clear from Fig. 4.13: the critical specific volume is overpredicted, as is the liquid specific



Figure 4.16: Compressibility factor Z vs.  $P^*(P_r)$  for several values of  $T^*(T_r)$ .

volume at high pressure.

### 4.7.3 The Principle of Corresponding States

Even though the van der Waals equation is not particularly accurate, the ability to write it as a universal function  $Z(T^*, P^*)$  is intriguing — maybe Z really can be expressed as a function of only  $T^*$  and  $P^*$ , but the function resulting from the van der Waals equation simply isn't the right one.

To test this hypothesis, we can take measured P - v - T data for different fluids, calculate Z = Pv/RT, and the plot Z as a function of  $P^* = P/P_c$  and  $T^* = T/T_c$ , where of course  $T_c$  and  $P_c$  differ for each fluid.

If  $Z = Z(T^*, P^*)$ , plotting Z in this way should collapse the experimental P - v - T data onto the same set of curves for all fluids. A plot of this type is shown in Fig. 4.16, in which Z is plotted vs.  $P^*$  for  $T^*$  values from 1 to 2. It is observed that the experimental values for different fluids do tend to fall onto the same curves for a given  $T^*$ , independent of the particular fluid.

However, it is also clear that this result is only approximate. For example, on the  $T^* = 1.5$  curve in Fig. 4.16, the propane data points are systematically above the mean, and the methane points systematically below. Also, we have already stated that  $Z_c$  varies slighly from one fluid to another, which could not be true if  $Z = Z(T^*, P^*)$  were exactly true, since  $Z_c = Z(1, 1)$ .

The statement that  $Z = Z(T^*, P^*)$  is known as the *Principle of Correspond*ing States. As we have already seen, it an *approximate* principle, not an exact one. Several empirical fits for  $Z(T^*, P^*)$  have been proposed which seek to reproduce the "average" behavior shown in Fig. 4.16. The earliest was a set of charts due to Nelson and Obert in 1954.

A more recent, popular generalized equation of state is one proposed by Lee and Kesler in 1975. The function they propose for  $Z(T^*, P^*)$  for "simple" fluids is shown graphically in Fig. 4.17. It can be seen that this function corresponds fairly closely to the experimental data shown in Fig. 4.16. Simple fluids are basically ones composed of small, simple molecules, but the precise definition of a simple fluid is circular: it is one for which  $Z(T^*, P^*)$  is as shown in Fig. 4.17.

Lee and Kesler (following earlier work by Pitzer) also introduced a third parameter, the so-called acentric factor  $\omega$ , to allow better correlation of experimental data than can be achieved using only the parameters  $T^*$  and  $P^*$ . They observe that simple fluids have  $P_{sat}(T)/P_c = 0.1$  when  $T/T_c = 0.7$ . To parameterize deviations from the behavior of Fig. 4.17, they define  $\omega$  as

$$\omega = -\log_{10} \left( \frac{P_{sat}(0.7T_c)}{P_c} \right) - 1.0.$$
(4.50)

The acentric parameter is zero for a simple fluid, and usually positive for other fluids.

Lee and Kesler assume that the effects of non-zero  $\omega$  can be accounted for by adding a correction term linear in  $\omega$ :

$$Z = Z^{(0)}(T^*, P^*) + \omega Z^{(1)}(T^*, P^*).$$
(4.51)

Here  $Z^{(0)}$  is the function shown in Fig. 4.17, and  $Z^{(1)}$  is a correction factor to account for non-simple-fluid effects. Specifically,  $Z^{(1)}$  is computed so that an accurate  $Z(T^*, P^*)$  function is obtained for octane (C<sub>8</sub>H<sub>18</sub>), which is not a "simple" fluid and has  $\omega = 0.3978$ . Of course, Eq. (4.51) is still approximate, but it is found to be accurate to within 2% or 3% for most non-polar or slightly polar fluids. For highly-polar fluids (e.g. water) or very light ones (e.g. hydrogen, helium, or neon) for which quantum effects are important, it is less accurate.

Equation 4.51 is implemented in TPX as the function ZLK(T\*, P\*, Omega). The Omega parameter is optional – if omitted, the result will be calculated for  $\omega = 0$  (a simple fluid).

#### 4.7.4 The Incompressible Substance

Finally, now that we have considered some rather complex model equations of state, we turn to the simplest possible equation of state. The compressibility



Figure 4.17: The Lee-Kesler generalized compressibility function  $Z^{(0)}$  for a simple fluid.

of most liquids and solids is quite low. Unless very large pressures are applied, the specific volume hardly changes at all.

If we wish to ignore entirely the compressibility of a liquid or a solid, we can replace the real P(v, T) behavior by a simple model:

$$v = v_0, \tag{4.52}$$

where  $v_0$  is a constant. A idealized substance which obeys Eq. (4.52) is called an *incompressible substance*. It is not possible to do compression work on an incompressible substance, since by definition dv = 0. Therefore, the First Law for an incompressible substance is

$$du = dQ. \tag{4.53}$$

Therefore, the only way to change u is by heat addition. This implies that an incompressible substance has only *one* degree of freedom, so u = u(T).

If we choose to approximate a real liquid as incompressible in solving a particular problem, we simply neglect the small pressure dependence of v and u. A common choice is to evaluate v and u at the saturation pressure at the local temperature, and use these values no matter what the real liquid pressure is.

Note that by definition h = u + Pv, so h will still depend on P for an incompressible substance, even though u does not. Therefore, for a process in which T and P change,  $\Delta h = \Delta u + v\Delta P$ . For most liquids and solids, v is small enough that the  $v\Delta P$  term is small compared to  $\Delta u$ .

Note also that  $(\partial h/\partial T)_P = du/dT$  in this case, so

$$c_p(T) = c_v(T) \tag{4.54}$$

for an incompressible substance. This relationship is very different than the one for ideal gases [Eq. (4.35)].

### Problems

4.1 Some properties of ice, liquid water, and water vapor at the triple point T = 273.16 K are given below.

Phase	Density $(kg/m^3)$	Specific enthalpy (kJ/kg)
Ice	917.0	-333.5
Liquid	999.8	0.0
Vapor	$4.84  imes 10^{-3}$	2501.4

The enthalpy values are relative to the liquid enthalpy.

A closed, *constant volume* 1 liter container initially is at a temperature infinitesimally below 273.16 K. It holds solid and vapor in equilibrium, with 80% solid by mass. Heat is now added until equal masses of liquid and solid are present. Write down equations expressing energy, mass, and volume balance. Determine numerically how much heat must be added.

- **4.2** The air pressure in aircraft cabins is kept lower than sea level atmospheric pressure, since otherwise the pressure force on the airframe would be too great at high altitude. A typical value for a transatlantic flight would be a cabin pressure equivalent to atmospheric pressure at an elevation of 8,000 ft. On such a flight, to what temperature should the flight attendants heat water for it to boil? How much heat must be added to boil a unit mass of water, and how does it compare to the heat needed at sea level? Make any reasonable assumptions you need for the analysis, but state what you are assuming.
- **4.3** Five kg of methane are contained in a closed, 150 liter container. If the pressure is 1 MPa, determine:
  - 1. Whether any liquid is present, and if so how many kg
  - 2. The temperature
  - 3. The internal energy U of the methane (J)
- **4.4** A particular substance has an isothermal compressibility  $\kappa = aT^4/P^3$  and a thermal expansion coefficient  $\beta = bT^3/P^2$ . Determine the equation of state v(T, P) to within an additive constant and the ratio a/b.
- 4.5 Ten kg of saturated nitrogen vapor at 90 K is heated at constant pressure until its volume is 3  $m^3$ . Determine
  - 1. The pressure
  - 2. The final temperature
  - 3. The heat added
  - 4. The work done by the nitrogen on the environment.
- 4.6 Using TPX, plot the compressibility factor Z for hydrogen and for oxygen at 300 K vs. pressure. For hydrogen, plot Z over the pressure range of 1 atm to 100 MPa, and for oxygen over the pressure range of 0.02 MPa to 20 MPa. Use a logarithmic scale for pressure.

For a particular gas storage tank design, it is necessary to estimate to within 1% accuracy the tank volume required for a given mass of gas and pressure at T = 300 K. For both hydrogen and oxygen, determine the pressure below which use of the ideal gas equation provides acceptable accuracy.

- 4.7 Estimate the temperature water at the bottom of a 500 ft deep lake would have to be heated before it begins to boil.
- **4.8** The specific heat at constant volume  $c_v$  for insulating solids at low temperature is given by the equation

$$\frac{c_v}{R} = \left(\frac{12\pi^4}{5}\right) \left(\frac{T}{\theta}\right)^3,$$

which is known as the Debye  $T^3$  law. The constant  $\theta$  is known as the *Debye temperature*, and is a characteristic of the material in question.

For diamond,  $\theta = 2200$  K. Treating diamond as incompressible, how much heat in Joules must be added to raise the temperature of 1 kg of diamond from 1 K to 50 K?

4.9 Show that for any simple compressible substance

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\beta}{\kappa}$$

and

$$\left(\frac{\partial\beta}{\partial P}\right)_T = -\left(\frac{\partial\kappa}{\partial T}\right)_P$$

 $4.10\,$  Derive the results for a van der Waals gas

$$RT_c = \frac{8a}{27b}$$

and

$$P_c = \frac{a}{27b^2}$$

4.11 A particular substance is found to obey the Dieterici equation of state

$$P(v-b)\exp(a/vRT) = RT.$$

1. Derive expressions for the properties at the critical point  $P_c$ ,  $v_c$ , and  $T_c$  in terms of the constants a, b, and R.

- 2. Compare the values for  $Z_c = P_c v_c / RT_c$  predicted by this equation with the values from Table 4.2 or calculated using TPX for hydrogen, carbon dioxide, and water.
- **4.12** A particular fluid has critical state parameters  $T_c = 300$  K and  $P_c = 6$  MPa, and a molecular weight of 30. Estimate its specific volume at T = 330 K and P = 12 MPa using
  - 1. the van der Waals equation of state
  - 2. the Lee-Kesler generalized compressibility function, assuming it is a simple fluid.
- **4.13** Determine the high-temperature limit for  $c_p$  for Ar, N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub>, and compare to the results in Figure 4.12. What is the value of  $c_p$  (kJ/kg/K) in the high-temperature limit for C<sub>60</sub>?
- **4.14** Calculate the acentric parameter  $\omega$  for N<sub>2</sub>, CH<sub>4</sub>, and CF<sub>4</sub>H<sub>2</sub> ("HFC134a") using TPX. Compare the predictions for Z at  $T^* = 1.2$ ,  $P^* = 1.5$  using
  - 1. TPX
  - 2. Lee-Kesler with  $\omega = 0$
  - 3. Lee-Kesler with the actual  $\omega$ .

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