

Thermodynamics

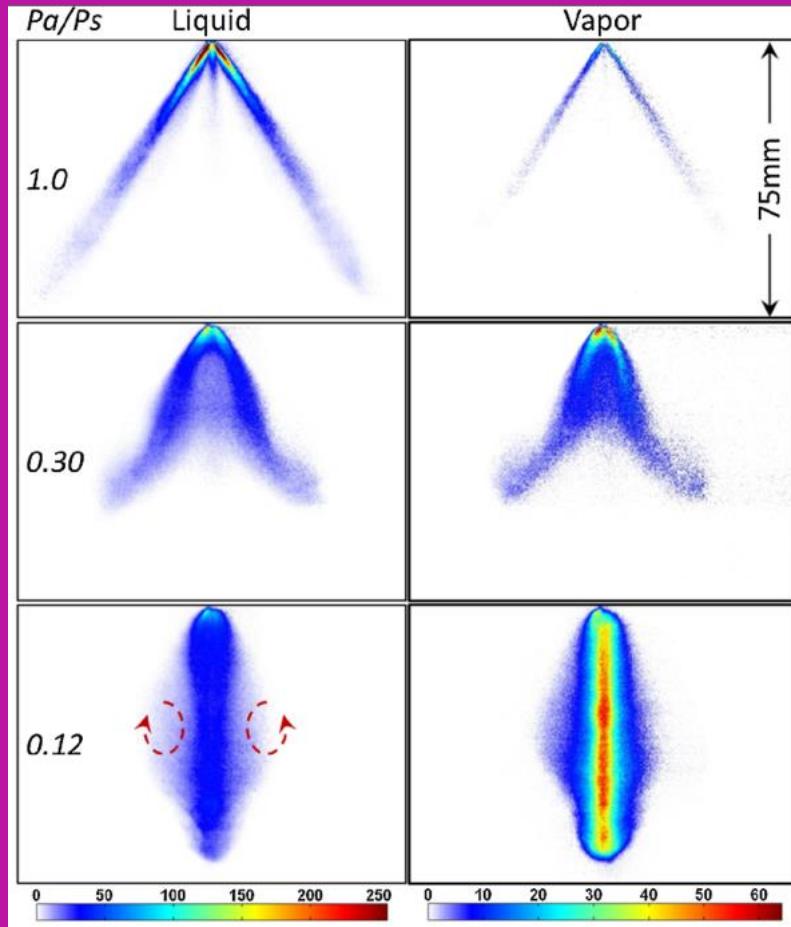
An Engineering Approach

Lecture 3: Properties of Pure Substance

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Learning Outcomes

When you complete your study of this chapter, you will be able to...

- explain key concepts, including phase and pure substance, state principle for simple compressible systems, p–v–T surface, saturation temperature and saturation pressure, two-phase liquid–vapor mixture, quality, enthalpy, and specific heats.
- analyze closed systems, including applying the energy balance with property data.
- sketch T–v, p–v, and phase diagrams, and locate states on these diagrams.
- Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.
- Describe the hypothetical substance “ideal gas” and the ideal-gas equation of state.
- Apply the ideal-gas equation of state in the solution of typical problems.
- Introduce the compressibility factor, which accounts for the deviation of real gases from ideal-gas behavior.
- Present some of the best-known equations of state.

Phase and Pure Substance

phase

The term **phase** refers to a quantity of matter that is homogeneous throughout in both chemical composition and physical structure.

Homogeneity in physical structure means that the matter is all solid, or all liquid, or all vapor (or equivalently all gas). A system can contain one or more phases.

pure substance

A pure substance is one that is uniform and invariable in chemical composition.

A pure substance can exist in more than one phase, but its chemical composition must be the same in each phase.

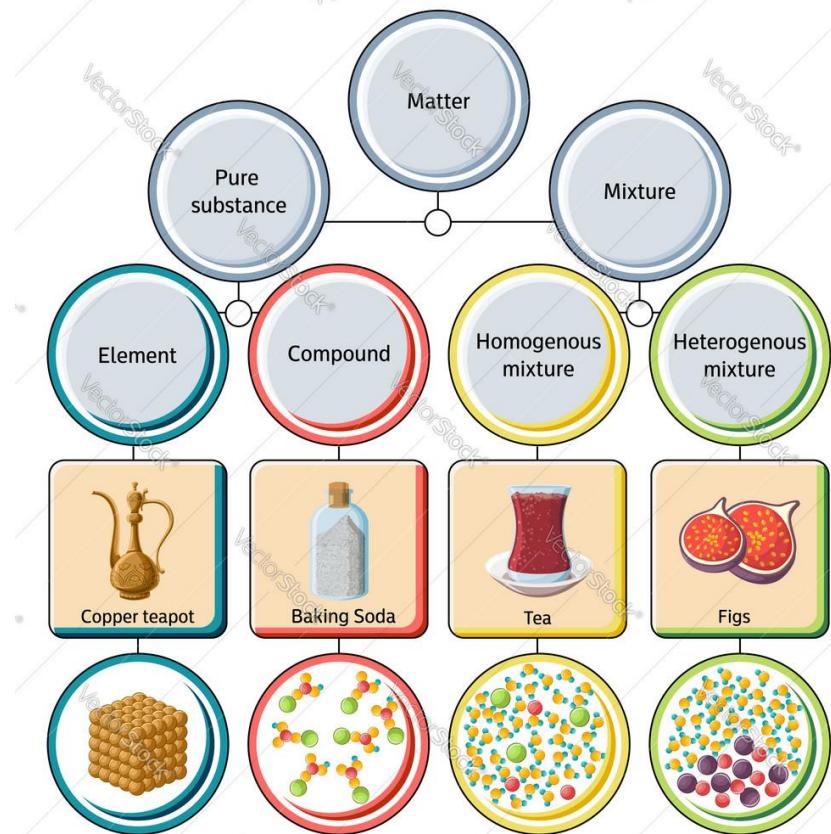
► **FOR EXAMPLE** if liquid water and water vapor form a system with two phases, the system can be regarded as a pure substance because each phase has the same composition. A uniform mixture of gases can be regarded as a pure substance provided it remains a gas and doesn't react chemically. Air can be regarded as a pure substance as long as it is a mixture of gases, but if a liquid phase should form on cooling, the liquid would have a different composition than the gas phase, and the system would no longer be considered a pure substance. ◀◀◀◀◀

Pure Substance

A pure substance does not have to be of a single chemical element or compound, however. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous. Air, for example, is a mixture of several gases, but it is often considered to be a pure substance because it has a uniform chemical composition.

A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same. (water and ice)

A mixture of liquid air and gaseous air, however, is not a pure substance since the composition of liquid air is different from the composition of gaseous air, and thus the mixture is no longer chemically homogeneous. This is due to different components in air condensing at different temperatures at a specified pressure.



Phase of Pure Substance

The most commonly known phase changes are those six between solids, liquids, and gasses. However, plasma also is a state of matter, so a complete list requires all eight total phase changes.

Phase changes typically occur when the temperature or pressure of a system is altered.

Phase Changes of States of Matter

- **Solids:** Solids can melt into liquids or sublime into gases. Solids form by deposition from gases or freezing of liquids.
- **Liquids:** Liquids can vaporize into gases or freeze into solids. Liquids form by condensation of gases and melting of solids.
- **Gases:** Gases can ionize into plasma, condense into liquids, or undergo deposition into solids. Gases form from the sublimation of solids, vaporization of liquids, and recombination of plasma.
- **Plasma:** Plasma can recombine to form a gas. Plasma most often forms from ionization of a gas, although if sufficient energy and enough space are available, it's presumably possible for a liquid or solid to ionize directly into a gas.

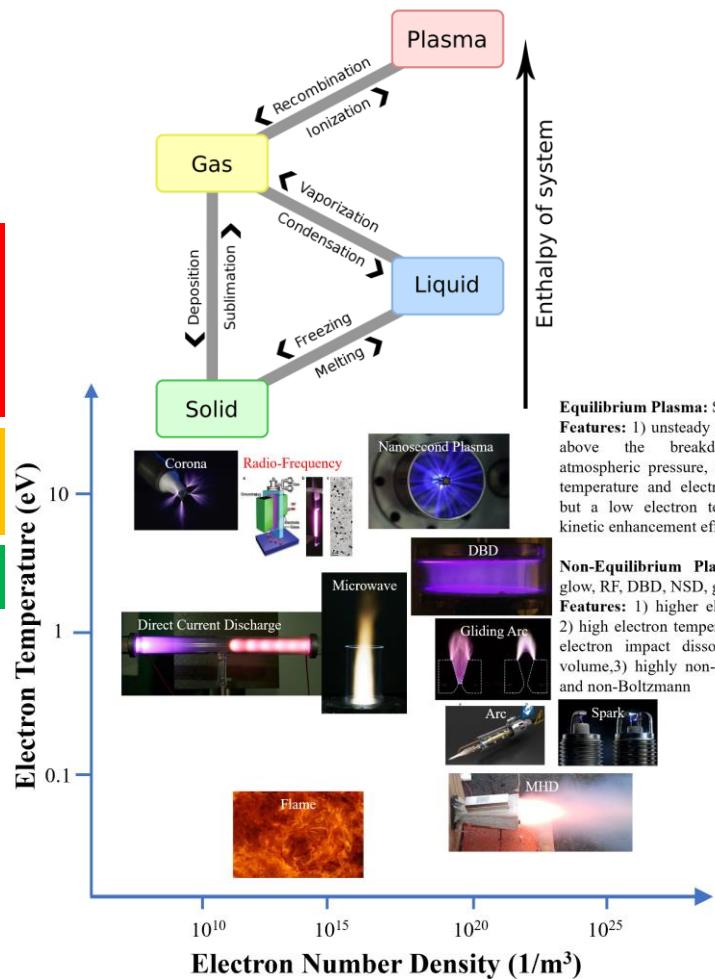


Fig. 2. Schematic of electron temperature and number density for different discharges, Corona, direct current (DC) discharge, microwave (MW) discharge; dielectric barrier discharge (DBD), radio-frequency discharge (RF), glow discharge, gliding arc, nanosecond pulsed discharge (NSD), arc, magneto-hydrodynamic discharge (MHD), and flame.

Equilibrium Plasma: Spark and arc
Features: 1) unsteady process at a voltage above the breakdown level and atmospheric pressure, 2) high neutral gas temperature and electron number density but a low electron temperature, 3) less kinetic enhancement effect in combustion

Non-Equilibrium Plasma: corona, DC, glow, RF, DBD, NSD, gliding arc, and MW
Features: 1) higher electron temperature, 2) high electron temperature to enable fast electron impact dissociation in a large volume, 3) highly non-equilibrium process and non-Boltzmann

Fixing the State

The **intensive state** of a closed system at **equilibrium** is its condition as described by the values of its intensive thermodynamic properties.

From observation of many thermodynamic systems, we know that not all of these properties are independent of one another, and the state can be uniquely determined by giving the values of a subset of the independent intensive properties.

Values for all other intensive thermodynamic properties are determined once this independent subset is specified.

state principle

the state principle has been developed as a guide in determining the number of independent properties required to fix the state of a system.

simple compressible systems

The simple compressible system is described as the state principle about the intensive states of systems of commonly encountered pure substances, such as water or a uniform mixture of nonreacting gases.

Experience shows simple compressible systems occur in a wide range of engineering applications. For such systems, the state principle indicates that specification of the values for any **two independent intensive** thermodynamic properties will fix the values of all other intensive thermodynamic properties.

Evaluating Properties: General Considerations

$p - v - T$ Relation

as independent and pressure determined as a function of these two: $p = p(T, v)$. The graph of such a function is a surface, the $p - v - T$ surface.

The state of a simple compressible substance is fixed by any two independent, intensive properties. Once the two appropriate properties are fixed, all the other properties become dependent properties.

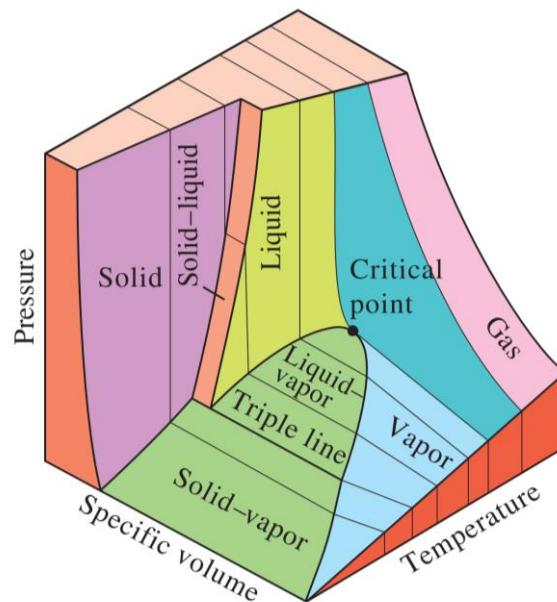


FIGURE 3-23

P - v - T surface of a substance that
contracts on freezing.

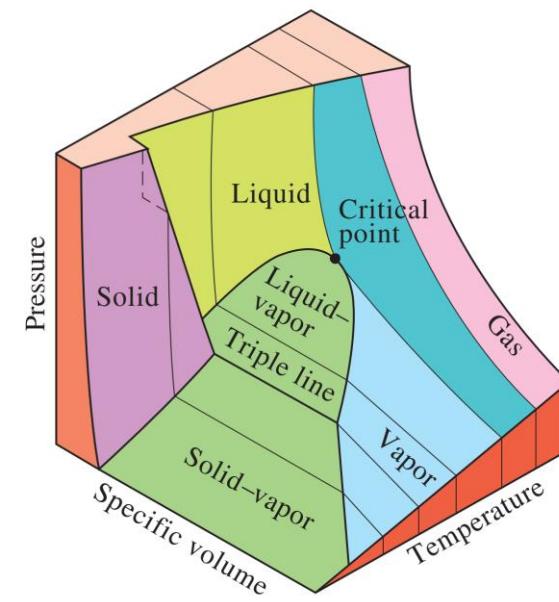


FIGURE 3-24

P - v - T surface of a substance that
expands on freezing (like water).



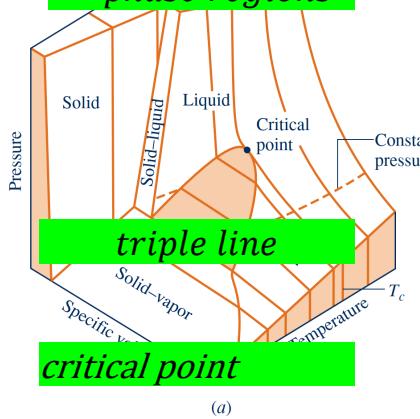
Evaluating Properties: General Considerations

*single
– phase regions*

In these single-phase regions, the state is fixed by any two of the properties: pressure, specific volume, and temperature, since all of these are independent when there is a single phase present.

*two
– phase regions*

Located between the single-phase regions are two-phase regions where two phases exist in equilibrium: liquid–vapor, solid–liquid, and solid–vapor. Two phases can coexist during changes in phase such as vaporization, melting, and sublimation.



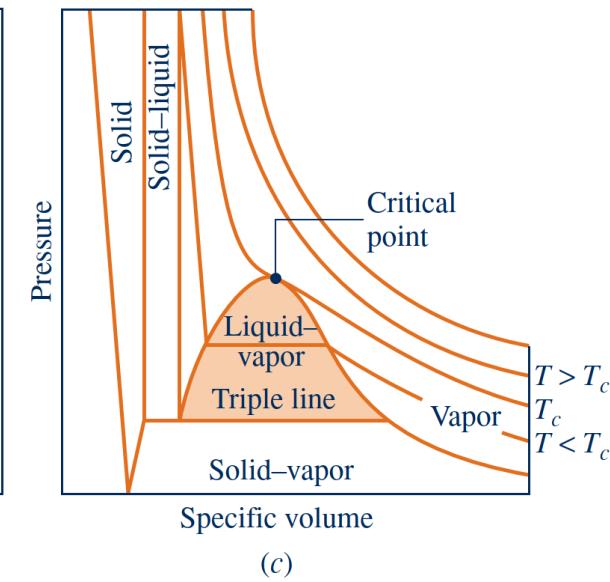
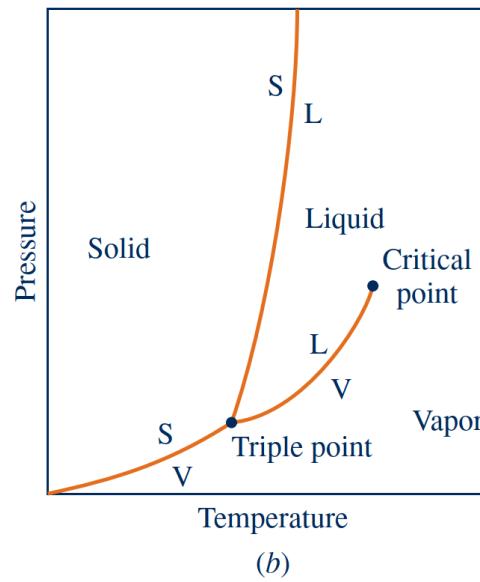
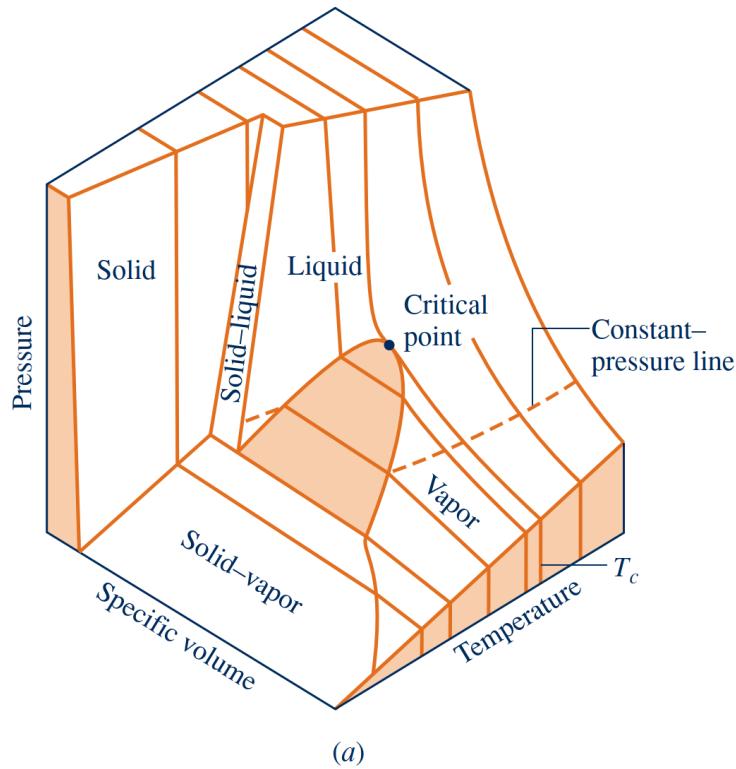
Within the two-phase regions pressure and temperature are not independent; one cannot be changed without changing the other. In these regions the state cannot be fixed by temperature and pressure alone; however, the state can be fixed by specific volume and either pressure or temperature.

Three phases can exist in equilibrium along the line labeled triple line.

At the top of the vapor dome, where the saturated liquid and saturated vapor lines meet, is the critical point. The critical temperature T_c of a pure substance is the maximum temperature at which liquid and vapor phases can coexist in equilibrium.

A state at which a phase change begins or ends is called a saturation state.

Evaluating Properties: General Considerations



Projections of the p–v–T Surface

phase diagram

If the p–v–T surface is projected onto the pressure–temperature plane, a property diagram known as a phase diagram results.

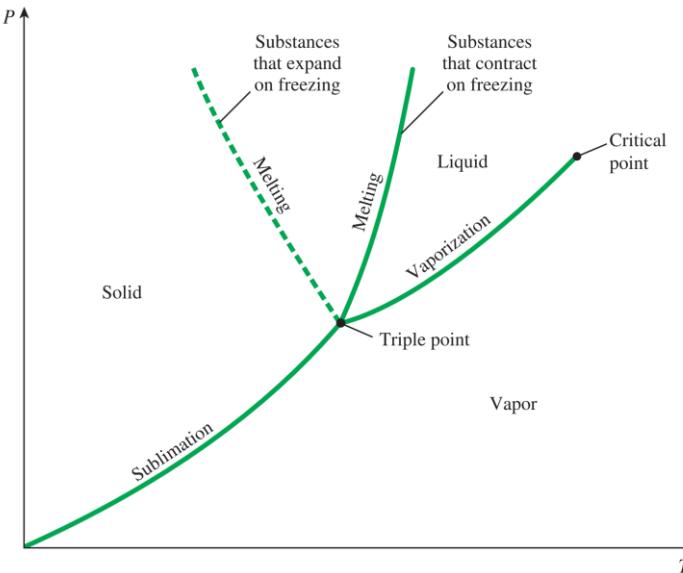
when the surface is projected in this way, the two-phase regions reduce to lines. A point on any of these lines represents all two-phase mixtures at that particular temperature and pressure.

saturation temperature and pressure

The term saturation temperature designates the temperature at which a phase change takes place at a given pressure, and this pressure is called the saturation pressure for the given temperature.

triple point

The triple line of the three-dimensional p–v–T surface projects onto a point on the phase diagram. This is called the triple point.

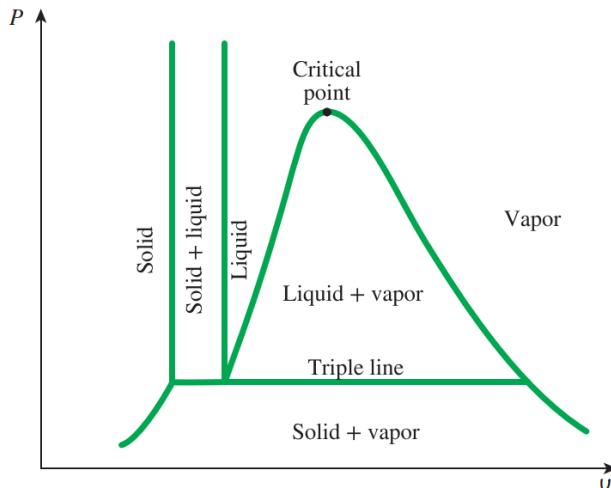


Projections of the p-v-T Surface

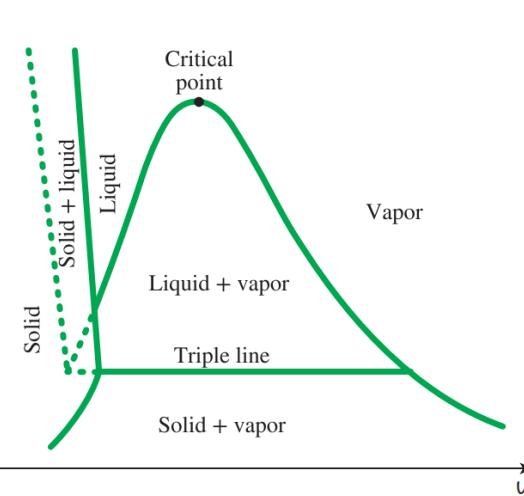
p-v diagram

If the p-v-T surface is projected onto the pressure–specific volume plane results in a p-v diagram.

When solving problems, a sketch of the p-v diagram is frequently convenient.



(a) $P\text{-}v$ diagram of a substance that contracts on freezing



(b) $P\text{-}v$ diagram of a substance that expands on freezing (such as water)

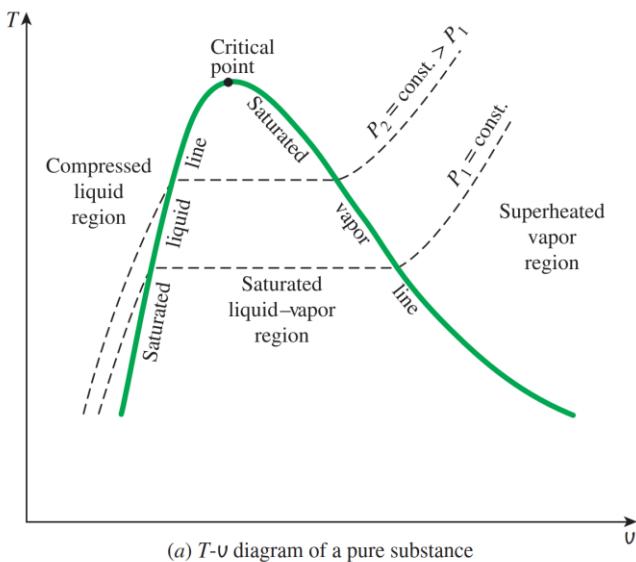
FIGURE 3-19

$P\text{-}v$ diagrams of different substances.

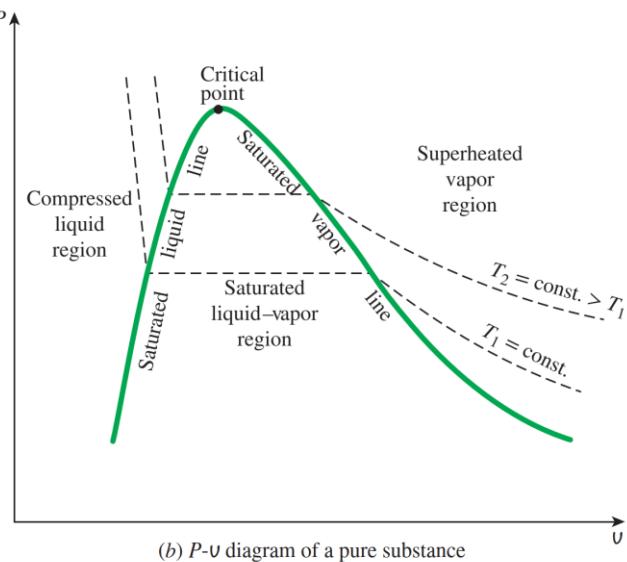
Projections of the p-v-T Surface

T-v diagram

Projecting the liquid, two-phase liquid-vapor, and vapor regions of the p-v-T surface onto the temperature-specific volume plane results in a T-v diagram



(a) T-v diagram of a pure substance



(b) P-v diagram of a pure substance

FIGURE 3-17

Property diagrams of a pure substance.

Studying Phase Change

Liquid States

As the system is heated at constant pressure, the temperature increases considerably while the specific volume increases slightly. Eventually, the system is brought to the state represented by f on Fig. 3.3. This is the saturated liquid state corresponding to the specified pressure. For water at 1.014 bar the saturation temperature is 100°C.

subcooled liquid

At subcooled liquid state, the temperature is less than the saturation temperature at the given pressure.

compressed liquid

These states are also referred to as compressed liquid states because the pressure at each state is higher than the saturation pressure corresponding to the temperature at the state. The names liquid, subcooled liquid, and compressed liquid are used interchangeably.

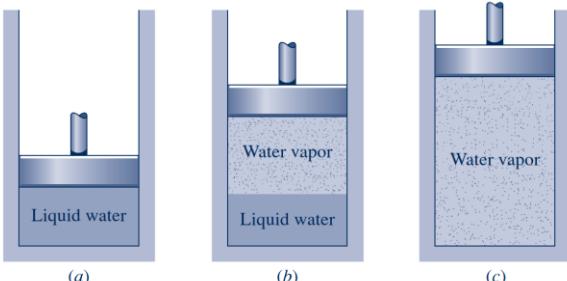


Fig. 3.4 Illustration of constant-pressure change from liquid to vapor for water.

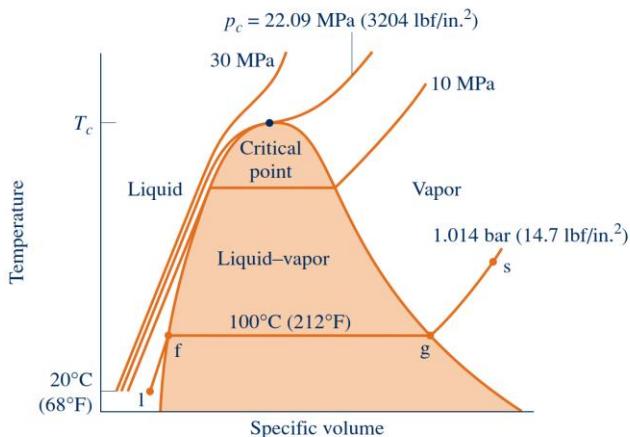


Fig. 3.3 Sketch of a temperature–specific volume diagram for water showing the liquid, two-phase liquid–vapor, and vapor regions (not to scale).

Studying Phase Change

Two-Phase
Liquid–Vapor
Mixture

When a mixture of liquid and vapor exists in equilibrium, the liquid phase is a saturated liquid and the vapor phase is a saturated vapor. If the system is heated further until the last bit of liquid has vaporized, it is brought to point g on Fig. 3.3, the saturated vapor state. The intervening two-phase liquid–vapor mixture states can be distinguished from one another by the quality, an intensive property.

quality

For a two-phase liquid–vapor mixture, the ratio of the mass of vapor present to the total mass of the mixture is its quality, x . In symbols,

$$x = \frac{m_{\text{vapor}}}{m_{\text{liquid}} + m_{\text{vapor}}}$$

Studying Phase Change

Vapor States

When the system is at the saturated vapor state (state g on Fig. 3.3), further heating at fixed pressure results in increases in both temperature and specific volume. The condition of the system would now be as shown in Fig. 3.4c. The state labeled s on Fig. 3.3 is representative of the states that would be attained by further heating while keeping the pressure constant. A state such as s is often referred to as a superheated vapor state because the system would be at a temperature greater than the saturation temperature corresponding to the given pressure.

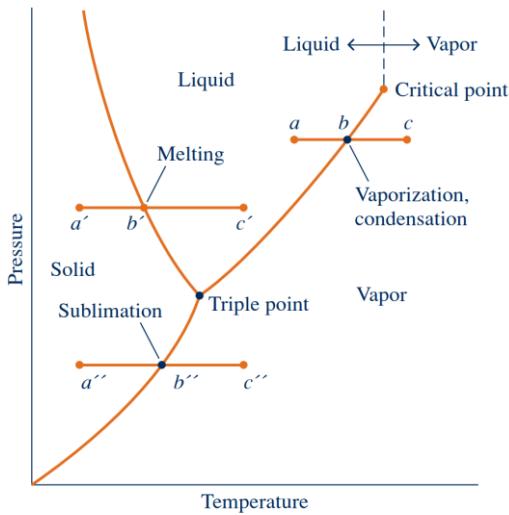
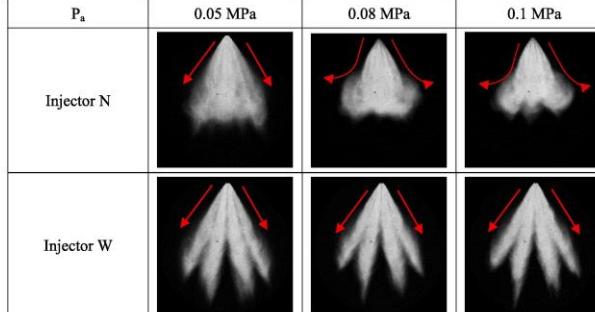
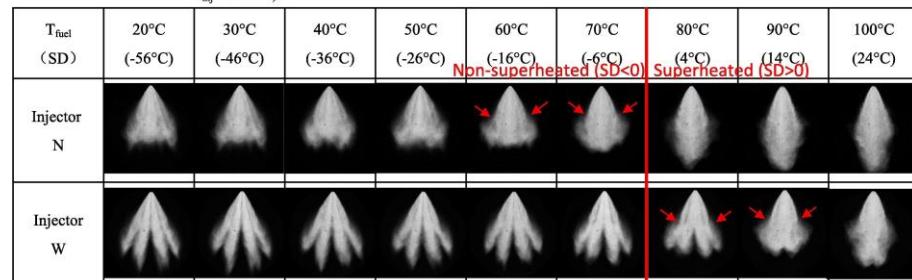


Fig. 3.5 Phase diagram for water (not to scale).



(a) Comparison of spray images about injector N and W under different ambient pressures ($T_{fuel}=20^{\circ}C$, $P_{inj}=10 \text{ MPa}$).



(b) Comparison of the spray images of injector N and injector W under different fuel temperatures ($P_a=0.05 \text{ MPa}$, $P_{inj}=10 \text{ MPa}$).

Retrieving Thermodynamic Properties

- 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, but others cannot, and the latter are calculated by using the relations between them and measurable properties.

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Analysis: Two independent properties are required to fix states 1 and 2. At the initial state, the pressure and quality are known. As these are independent, the state is fixed. State 1 is shown on the T - v diagram in the two-phase region. The specific volume at state 1 is found using the given quality and Eq. 3.2. That is,

$$v_1 = v_{f1} + x(v_{g1} - v_{f1})$$

From Table A-3 at $p_1 = 1$ bar, $v_{f1} = 1.0432 \times 10^{-3}$ m 3 /kg and $v_{g1} = 1.694$ m 3 /kg. Thus,

$$v_1 = 1.0432 \times 10^{-3} + 0.5(1.694 - 1.0432 \times 10^{-3}) = 0.8475$$
 m 3 /kg

At state 2, the pressure is known. The other property required to fix the state is the specific volume v_2 . Volume and mass are each constant, so $v_2 = v_1 = 0.8475$ m 3 /kg. For $p_2 = 1.5$ bar, Table A-3 gives $v_{f2} = 1.0582 \times 10^{-3}$ m 3 /kg and $v_{g2} = 1.59$ m 3 /kg. Since

$$v_f < v_2 < v_{g2}$$

① state 2 must be in the two-phase region as well. State 2 is also shown on the T - v diagram above.

(a) Since states 1 and 2 are in the two-phase liquid-vapor region, the temperatures correspond to the saturation temperatures for the given pressures. Table A-3 gives

$$T_1 = 99.63^\circ\text{C} \quad \text{and} \quad T_2 = 111.4^\circ\text{C}$$

(b) To find the mass of water vapor present, we first use the volume and the specific volume to find the total mass, m . That is,

$$m = \frac{V}{v} = \frac{0.5 \text{ m}^3}{0.8475 \text{ m}^3/\text{kg}} = 0.59 \text{ kg}$$

Then, with Eq. 3.1 and the given value of quality, the mass of vapor at state 1 is

$$m_{g1} = x_1 m = 0.5(0.59 \text{ kg}) = 0.295 \text{ kg}$$

The mass of vapor at state 2 is found similarly using the quality x_2 . To determine x_2 , solve Eq. 3.2 for quality and insert specific volume data from Table A-3 at a pressure of 1.5 bar, along with the known value of v , as follows

$$\begin{aligned} x_2 &= \frac{v - v_{f2}}{v_{g2} - v_{f2}} \\ &= \frac{0.8475 - 1.0528 \times 10^{-3}}{1.159 - 1.0528 \times 10^{-3}} = 0.731 \end{aligned}$$

Then, with Eq. 3.1

$$m_{g2} = 0.731(0.59 \text{ kg}) = 0.431 \text{ kg}$$

(c) If heating continued, state 3 would be on the saturated vapor line, as shown on the T - v diagram of Fig. E3.2. Thus, the pressure would be the corresponding saturation pressure. Interpolating in Table A-3 at $v_g = 0.8475$ m 3 /kg, we get $p_3 = 2.11$ bar.

- ① The procedure for fixing state 2 is the same as illustrated in the discussion of Fig. 3.8.
- ② Since the process occurs at constant specific volume, the states lie along a vertical line.

Skills Developed

Ability to...

- ❑ define a closed system and identify interactions on its boundary.
- ❑ sketch a T - v diagram and locate states on it.
- ❑ retrieve property data for water at liquid-vapor states, using quality.

EXAMPLE 3.2

Heating Water at Constant Volume

A closed, rigid container of volume 0.5 m 3 is placed on a hot plate. Initially, the container holds a two-phase mixture of saturated liquid water and saturated water vapor at $p_1 = 1$ bar with a quality of 0.5. After heating, the pressure in the container is $p_2 = 1.5$ bar. Indicate the initial and final states on a T - v diagram, and determine

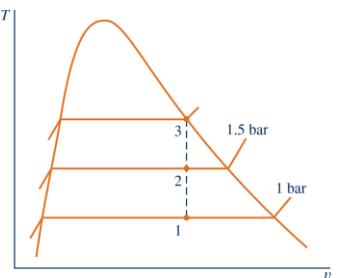
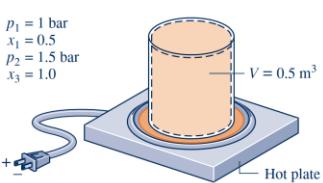
- the temperature, in $^\circ\text{C}$, at states 1 and 2.
- the mass of vapor present at states 1 and 2, in kg.
- If heating continues, determine the pressure, in bar, when the container holds only saturated vapor.

SOLUTION

Known: A two-phase liquid-vapor mixture of water in a closed, rigid container is heated on a hot plate. The initial pressure and quality and the final pressure are known.

Find: Indicate the initial and final states on a T - v diagram and determine at each state the temperature and the mass of water vapor present. Also, if heating continues, determine the pressure when the container holds only saturated vapor.

Schematic and Given Data:



Engineering Model:

- The water in the container is a closed system.
- States 1, 2, and 3 are equilibrium states.
- The volume of the container remains constant.

Quick Quiz

If heating continues at constant specific volume from state 3 to a state where pressure is 3 bar, determine the temperature at that state, in $^\circ\text{C}$. Ans. 282 $^\circ\text{C}$



Saturation Tables

Tables A-2, A-3, and A-6 provide property data for water at saturated liquid, saturated vapor, and saturated solid states.

The specific volume of a two-phase liquid–vapor mixture can be determined by using the saturation tables and the definition of quality given by Eq. 3.1 as follows. The total volume of the mixture is the sum of the volumes of the liquid and vapor phases

$$V = V_{\text{liq}} + V_{\text{vap}}$$

Dividing by the total mass of the mixture, m , an average specific volume for the mixture is obtained

$$\nu = \frac{V}{m} = \frac{V_{\text{liq}}}{m} + \frac{V_{\text{vap}}}{m} \quad \nu = \left(\frac{m_{\text{liq}}}{m} \right) \nu_f + \left(\frac{m_{\text{vap}}}{m} \right) \nu_g$$

► FOR EXAMPLE let us determine the pressure of water at each of three states defined by a temperature of 100°C and specific volumes, respectively, of $\nu_1 = 2.434 \text{ m}^3/\text{kg}$, $\nu_2 = 1.0 \text{ m}^3/\text{kg}$, and $\nu_3 = 1.0423 \times 10^{-3} \text{ m}^3/\text{kg}$. Using the known temperature, Table A-2 provides the values of ν_l and ν_g : $\nu_l = 1.0435 \times 10^{-3} \text{ m}^3/\text{kg}$, $\nu_g = 1.673 \text{ m}^3/\text{kg}$. Since ν_1 is 0.70 times the critical specific volume, $\nu_l > \nu_1$, so state 1 is compressed liquid. State 2 is at the critical point because $\nu_2 = \nu_c$. State 3 is superheated vapor because $\nu_3 < \nu_g$. The pressure of state 1 is $p_1 = p_c$. The pressure of state 2 is $p_2 = p_c$. The pressure of state 3 is $p_3 = 100 \text{ kPa}$.

Finding States in the Steam Tables: Overview Using p - ν Diagram

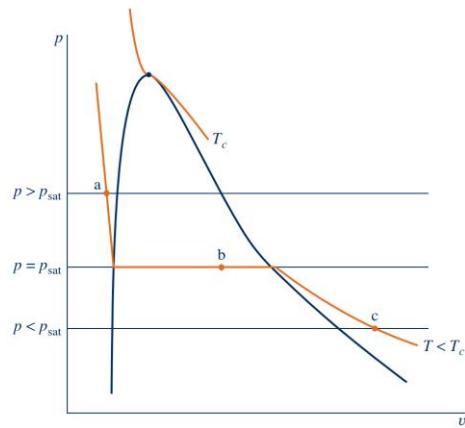


Fig. 3-10 Finding states in the steam tables: overview using p - ν diagram for water in the two-phase region.

Given Properties	Test to Determine Region	Where/How to Obtain Properties
p and $T < T_c$	Look up T in Table A-2/2E: a. If $p > p_{\text{sat}}$, compressed liquid b. If $p = p_{\text{sat}}$, two-phase liquid–vapor mixture c. If $p < p_{\text{sat}}$, superheated vapor	a. Table A-5/5E or Table A-2/2E (approximate as saturated liquid at T) b. T and p are not independent; need another intensive property c. Table A-4/4E
p and $T > T_c$	Superheated vapor	Table A-4/4E

Evaluating Specific Internal Energy and Enthalpy

Enthalpy

Because the sum $U + pv$ occurs so frequently in subsequent discussions, it is convenient to give the combination a name, enthalpy, and a distinct symbol, H . By definition

$$H = U + pV \quad h = u + pv \quad \bar{h} = \bar{u} + \bar{p}v$$

Data for specific internal energy u and enthalpy h are retrieved from the property tables in the same way as for specific volume. For saturation states, the values of u_f and u_g , as well as h_f and h_g , are tabulated versus both saturation pressure and saturation temperature. The specific internal energy for a two-phase liquid–vapor mixture is calculated for a given quality in the same way the specific volume is calculated:

$$u = (1 - x)u_f + xu_g = u_f + x(u_g - u_f)$$

Similarly, the specific enthalpy for a two-phase liquid–vapor mixture is given in terms of the quality by

$$h = (1 - x)h_f + xh_g = h_f + x(h_g - h_f)$$

Evaluating Specific Internal Energy and Enthalpy

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f (that is $v_{fg} = v_g - v_f$)

Sat. Temp. °C <i>T</i>	Sat. press. kPa <i>P_{sat}</i>	Specific volume m ³ /kg	
		Sat. liquid <i>v_f</i>	Sat. vapor <i>v_g</i>
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

Temperature Corresponding saturation pressure Specific volume of saturated liquid Specific volume of saturated vapor

FIGURE 3-27

A partial list of Table A-4.

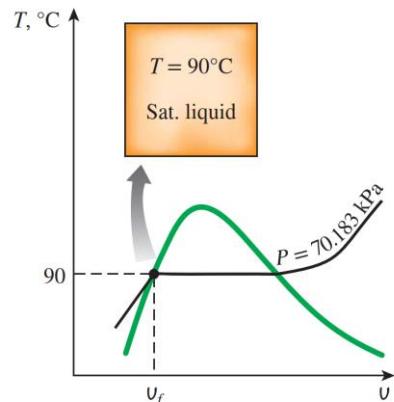


FIGURE 3-28

Schematic and *T-v* diagram for Example 3-1.

EXAMPLE 3-1

Pressure of Saturated Liquid in a Tank

- A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.

SOLUTION A rigid tank contains saturated liquid water. The pressure and volume of the tank are to be determined.

Analysis The state of the saturated liquid water is shown on a *T-v* diagram in Fig. 3-28. Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90°C:

$$P = P_{\text{sat}} @ 90^\circ\text{C} = \mathbf{70.183 \text{ kPa}} \quad (\text{Table A-4})$$

The specific volume of the saturated liquid at 90°C is

$$v = v_f @ 90^\circ\text{C} = 0.001036 \text{ m}^3/\text{kg} \quad (\text{Table A-4})$$

Then the total volume of the tank becomes

$$V = m v = (50 \text{ kg})(0.001036 \text{ m}^3/\text{kg}) = \mathbf{0.0518 \text{ m}^3}$$

Evaluating Specific Internal Energy and Enthalpy

► FOR EXAMPLE to illustrate the use of Eqs. 3.6 and 3.7, we determine the specific enthalpy of Refrigerant 22 when its temperature is 12°C and its specific internal energy is 144.58 kJ/kg. Referring to Table A-7, the given internal energy value falls between u_f and u_g at 12°C, so the state is a two-phase liquid–vapor mixture. The quality of the mixture is found by using Eq. 3.6 and data from Table A-7 as follows:

$$x = \frac{u - u_f}{u_g - u_f} = \frac{144.58 - 58.77}{230.38 - 58.77} = 0.5$$

Then, with the values from Table A-7, Eq. 3.7 gives

$$\begin{aligned} h &= (1 - x)h_f + xh_g \\ &= (1 - 0.5)(59.35) + 0.5(253.99) = 156.67 \text{ kJ/kg} \end{aligned}$$

In the superheated vapor tables, u and h are tabulated along with v as functions of temperature and pressure.

► FOR EXAMPLE let us evaluate T , v , and h for water at 0.10 MPa and a specific internal energy of 2537.3 kJ/kg. Turning to Table A-3, note that the given value of u is greater than u_g at 0.1 MPa ($u_g = 2506.1$ kJ/kg). This suggests that the state lies in the superheated vapor region. By inspection of Table A-4 we get $T = 120^\circ\text{C}$, $v = 1.793 \text{ m}^3/\text{kg}$, and $h = 2716.6$ kJ/kg. Alternatively, h and u are related by the definition of h :

$$\begin{aligned} h &= u + pv \\ &= 2537.3 \frac{\text{kJ}}{\text{kg}} + \left(10^5 \frac{\text{N}}{\text{m}^2}\right) \left(1.793 \frac{\text{m}^3}{\text{kg}}\right) \Bigg| \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \\ &= 2537.3 + 179.3 = 2716.6 \text{ kJ/kg} \end{aligned}$$

► EXAMPLE 3.4 ►

Analyzing Two Processes in Series

Water contained in a piston–cylinder assembly undergoes two processes in series from an initial state where the pressure is 10 bar and the temperature is 400°C.

Process 1–2: The water is cooled as it is compressed at a constant pressure of 10 bar to the saturated vapor state.

Process 2–3: The water is cooled at constant volume to 150°C.

(a) Sketch both processes on T – v and p – v diagrams.

(b) For the overall process determine the work, in kJ/kg.

(c) For the overall process determine the heat transfer, in kJ/kg.

SOLUTION

Known: Water contained in a piston–cylinder assembly undergoes two processes: It is cooled and compressed, while keeping the pressure constant, and then cooled at constant volume.

Find: Sketch both processes on T – v and p – v diagrams. Determine the net work and the net heat transfer for the overall process per unit of mass contained within the piston–cylinder assembly.

Schematic and Given Data:

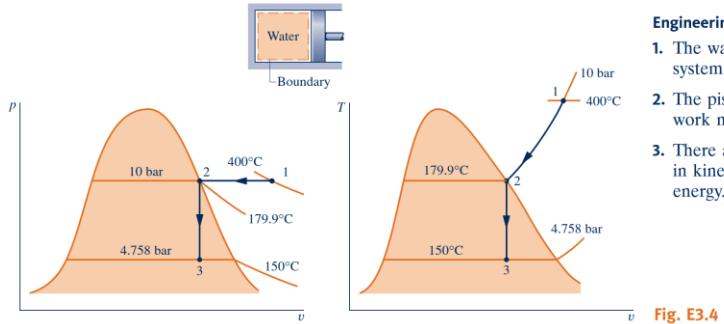


Fig. E3.4

Analysis:

(a) The accompanying T – v and p – v diagrams show the two processes. Since the temperature at state 1, $T_1 = 400^\circ\text{C}$, is greater than the saturation temperature corresponding to $p_1 = 10 \text{ bar}$: 179.9°C , state 1 is located in the superheat region.

(b) Since the piston is the only work mechanism

$$W = \int_1^3 p \, dV = \int_1^2 p \, dV + \int_2^3 p \, dV$$

The second integral vanishes because the volume is constant in Process 2–3. Dividing by the mass and noting that the pressure is constant for Process 1–2

$$\frac{W}{m} = p(v_2 - v_1)$$

The specific volume at state 1 is found from Table A-4 using $p_1 = 10 \text{ bar}$ and $T_1 = 400^\circ\text{C}$: $v_1 = 0.3066 \text{ m}^3/\text{kg}$. Also, $u_1 = 2957.3 \text{ kJ/kg}$. The specific volume at state 2 is the saturated vapor value at 10 bar: $v_2 = 0.1944 \text{ m}^3/\text{kg}$, from Table A-3. Hence,

$$\begin{aligned} \frac{W}{m} &= (10 \text{ bar})(0.1944 - 0.3066) \left(\frac{\text{m}^3}{\text{kg}} \right) \left| \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \right| \left| \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \right| \\ &= -112.2 \text{ kJ/kg} \end{aligned}$$

The minus sign indicates that work is done *on* the water vapor by the piston.

(c) An energy balance for the *overall* process reduces to

$$m(u_3 - u_1) = Q - W$$

By rearranging

$$\frac{Q}{m} = (u_3 - u_1) + \frac{W}{m}$$

To evaluate the heat transfer requires u_3 , the specific internal energy at state 3. Since T_3 is given and $v_3 = v_2$, two independent intensive properties are known that together fix state 3. To find u_3 , first solve for the quality

To evaluate the heat transfer requires u_3 , the specific internal energy at state 3. Since T_3 is given and $v_3 = v_2$, two independent intensive properties are known that together fix state 3. To find u_3 , first solve for the quality

$$x_3 = \frac{v_3 - v_{f3}}{v_{g3} - v_{f3}} = \frac{0.1944 - 1.0905 \times 10^{-3}}{0.3928 - 1.0905 \times 10^{-3}} = 0.494$$

where v_{f3} and v_{g3} are from Table A-2 at 150°C. Then

$$\begin{aligned} u_3 &= u_{f3} + x_3(u_{g3} - u_{f3}) = 631.68 + 0.494(2559.5 - 631.68) \\ &= 1584.0 \text{ kJ/kg} \end{aligned}$$

where u_{f3} and u_{g3} are from Table A-2 at 150°C.

Substituting values into the energy balance

$$\frac{Q}{m} = 1584.0 - 2957.3 + (-112.2) = -1485.5 \text{ kJ/kg}$$

The minus sign shows that energy is transferred *out* by heat transfer.

Skills Developed

Ability to...

- define a closed system and identify interactions on its boundary.
- evaluate work using Eq. 2.17.
- apply the energy balance with steam table data.
- sketch T – v and p – v diagrams and locate states on them.

Introducing Specific Heats c_v and c_p

specific heats

The specific heats, denoted c_v and c_p , are particularly useful for thermodynamic calculations involving the ideal gas model

The intensive properties c and c_p are defined for pure, simple compressible substances as partial derivatives of the functions $u(T, v)$ and $h(T, p)$, respectively,

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

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p$$

specific heat ratio

$$k = \frac{c_p}{c_v}$$

(3.8)

(3.9)

(3.10)

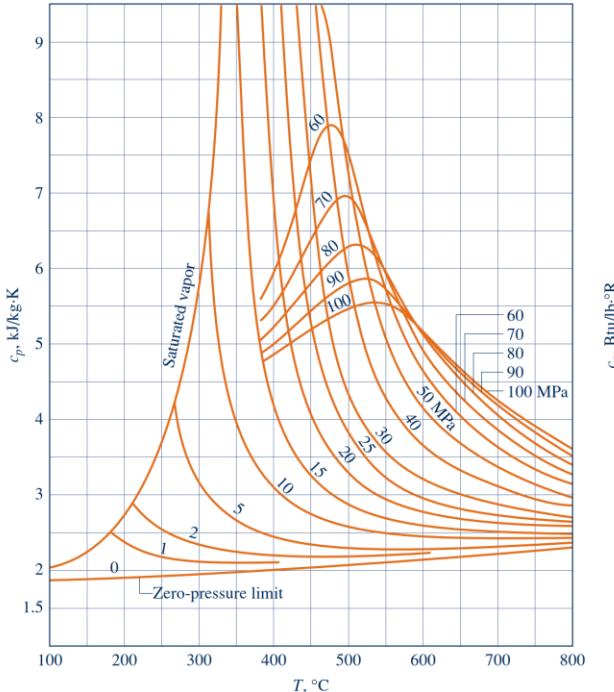


Fig. 3.9 c_p of water vapor as a function of temperature and pressure.



Incompressible Substance Model

Incompressible Substance Model

To simplify evaluations involving liquids or solids, the specific volume (density) is often assumed to be constant and the specific internal energy assumed to vary only with temperature. A substance idealized in this way is called incompressible.

$$c_v(t) = \frac{du}{dT} \quad (\text{incompressible}) \quad (3.15)$$

$$h(T, p) = u(T) + pv \quad (\text{incompressible}) \quad (3.16)$$

$$\left(\frac{\partial h}{\partial T} \right)_p = \frac{du}{dT}$$

$$c_p = c_v \quad (\text{incompressible}) \quad (3.17)$$

$$u_2 - u_1 = \int_{T_1}^{T_2} c(T) dT \quad (\text{incompressible}) \quad (3.18)$$

$$\begin{aligned} h_2 - h_1 &= u_2 - u_1 + v(p_2 - p_1) \\ &= \int_{T_1}^{T_2} c(T) dT + v(p_2 - p_1) \quad (\text{incompressible}) \end{aligned} \quad (3.19)$$

If the specific heat c is taken as constant,

$$u_2 - u_1 = c(T_2 - T_1) \quad (3.20a)$$

$$h_2 - h_1 = c(T_2 - T_1) + v(p_2 - p_1) \quad (\text{incompressible, constant } c) \quad (3.20b)$$

EXAMPLE 3.6 ►

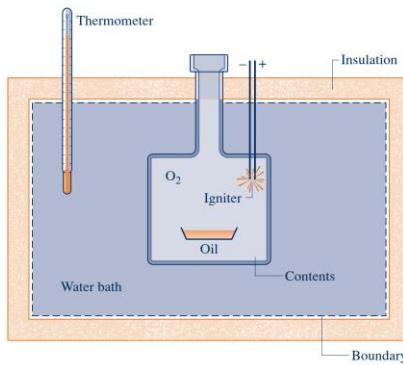
Measuring the Calorie Value of Cooking Oil

One-tenth milliliter of cooking oil is placed in the chamber of a constant-volume calorimeter filled with sufficient oxygen for the oil to be completely burned. The chamber is immersed in a water bath. The mass of the water bath is 2.15 kg. For the purpose of this analysis, the metal parts of the apparatus are modeled as equivalent to an additional 0.5 kg of water. The calorimeter is well insulated, and initially the temperature throughout is 25°C. The oil is ignited by a spark. When equilibrium is again attained, the temperature throughout is 25.3°C. Determine the change in internal energy of the chamber contents, in kcal per mL of cooking oil and in kcal per tablespoon of cooking oil.

Known: Data are provided for a constant-volume calorimeter testing cooking oil for calorie value.

Find: Determine the change in internal energy of the contents of the calorimeter chamber.

Schematic and Given Data:



Engineering Model:

1. The closed system is shown by the dashed line in the accompanying figure.
2. The total volume remains constant, including the chamber, water bath, and the amount of water modeling the metal parts.
3. Water is modeled as incompressible with constant specific heat c .
4. Heat transfer with the surroundings is negligible, and there is no change in kinetic or potential energy.

Fig. E3.6

Analysis: With the assumptions listed, the closed system energy balance reads

$$\Delta U + \Delta KE^0 + \Delta PE^0 = Q^0 - W^0$$

or

$$(\Delta U)_{\text{contents}} + (\Delta U)_{\text{water}} = 0$$

thus

$$(\Delta U)_{\text{contents}} = -(\Delta U)_{\text{water}} \quad (a)$$

The change in internal energy of the contents is equal and opposite to the change in internal energy of the water.

Since water is modeled as incompressible, Eq. 3.20a is used to evaluate the right side of Eq. (a), giving

① ②

$$(\Delta U)_{\text{contents}} = -m_w c_w (T_2 - T_1) \quad (b)$$

With $m_w = 2.15 \text{ kg} + 0.5 \text{ kg} = 2.65 \text{ kg}$, $(T_2 - T_1) = 0.3 \text{ K}$, and $c_w = 4.18 \text{ kJ/kg} \cdot \text{K}$ from Table A-19, Eq. (b) gives

$$(\Delta U)_{\text{contents}} = -(2.65 \text{ kg})(4.18 \text{ kJ/kg} \cdot \text{K})(0.3 \text{ K}) = -3.32 \text{ kJ}$$

Converting to kcal, and expressing the result on a per milliliter of oil basis using the oil volume, 0.1 mL, we get

$$\frac{(\Delta U)_{\text{contents}}}{V_{\text{oil}}} = \frac{-3.32 \text{ kJ}}{0.1 \text{ mL}} \left| \frac{1 \text{ kcal}}{4.1868 \text{ kJ}} \right| \\ = -7.9 \text{ kcal/mL}$$

The calorie value of the cooking oil is the magnitude—that is, 79 kcal/mL. Labels on cooking oil containers usually give calorie value for a serving size of 1 tablespoon (15 mL). Using the calculated value, we get 119 kcal per tablespoon.

Skills Developed

Ability to...

- define a closed system and identify interactions within it and on its boundary.
- apply the energy balance using the incompressible substance model.

1. The change in internal energy for water can be found alternatively using Eq. 3.12 together with saturated liquid internal energy data from Table A-2.
2. The change in internal energy of the chamber contents cannot be evaluated using a specific heat because specific heats are defined (Sec. 3.9) only for *pure* substances—that is, substances that are unchanging in composition.

Quick Quiz

Using Eq. 3.12 together with saturated liquid internal energy data from Table A-2, find the change in internal energy of the water, in kJ, and compare with the value obtained assuming water is incompressible. Ans. 3.32 kJ

BIO CONNECTIONS

 Is your diet bad for the environment? It could be. The fruits, vegetables, and animal products found in grocery stores require a lot of fossil fuel just to get there. While study of the linkage of the human diet to the environment is in its infancy, some preliminary findings are interesting.

One study of U.S. dietary patterns evaluated the amount of fossil fuel—and, implicitly, the level of greenhouse gas production—required to support several different diets. Diets rich in meat and fish were found to require the most fossil fuel, owing to the significant energy resources required to produce these products and bring them to market. But for those who enjoy meat and fish, the news is not all bad. Only a fraction of the fossil fuel needed to get food to stores is used to grow the food; most is spent on processing and distribution. Accordingly, eating favorite foods originating close to home can be a good choice environmentally.

Still, the connection between the food we eat, energy resource use, and accompanying environmental impact requires further study, including the vast amounts of agricultural land needed, huge water requirements, emissions related to fertilizer production and use, methane emitted from waste produced by billions of animals raised for food annually, and fuel for transporting food to market.



Aalto University
School of Engineering

Generalized Compressibility Chart

Universal Gas Constant, \bar{R}

$$\lim_{p \rightarrow 0} \frac{p\bar{v}}{T} = \bar{R} \quad (3.21)$$

$$\bar{R} = \begin{cases} 8.314 \text{ kJ/kmol} \cdot \text{K} \\ 1.986 \text{ Btu/lbmol} \cdot {}^{\circ}\text{R} \\ 1545 \text{ ft} \cdot \text{lbf/lbmol} \cdot {}^{\circ}\text{R} \end{cases} \quad (3.22)$$

Compressibility Factor, Z

$$Z = \frac{p\bar{v}}{\bar{R}T}$$

With $\bar{v} = Mv$ (Eq. 1.9), where M is the molar mass, the compressibility factor can be expressed alternatively as

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

where

$$R = \frac{\bar{R}}{M}$$

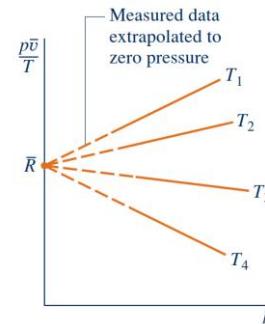
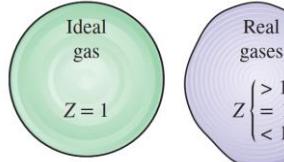


Fig. 3.10 Sketch of $p\bar{v}/T$ versus pressure for a gas at different temperatures.

Values of the Gas Constant R of Selected Elements and Compounds

Substance	Chemical Formula	R (kJ/kg · K)	R (Btu/lb · °R)
Air	—	0.2870	0.06855
Ammonia	NH ₃	0.4882	0.11662
Argon	Ar	0.2082	0.04972
Carbon dioxide	CO ₂	0.1889	0.04513
Carbon monoxide	CO	0.2968	0.07090
Helium	He	2.0769	0.49613
Hydrogen	H ₂	4.1240	0.98512
Methane	CH ₄	0.5183	0.12382
Nitrogen	N ₂	0.2968	0.07090
Oxygen	O ₂	0.2598	0.06206
Water	H ₂ O	0.4614	0.11021

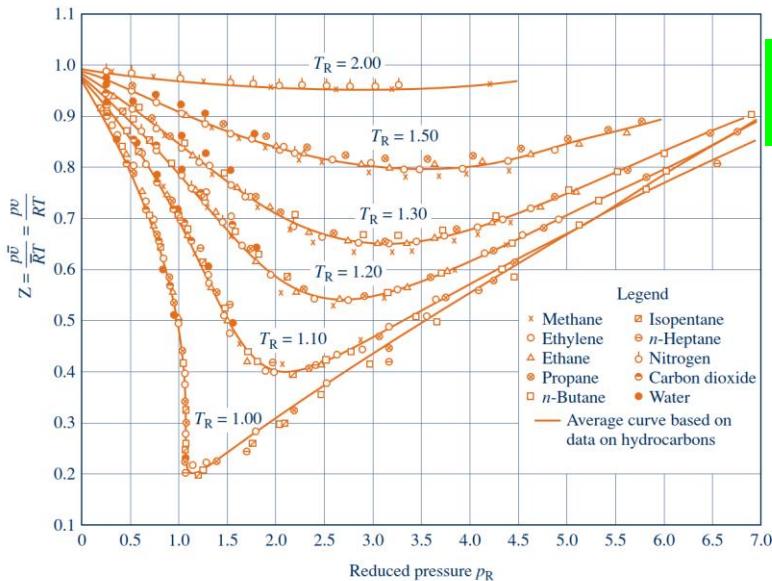
Generalized Compressibility Chart, Z Chart

reduced pressure
 p_R and reduced
temperature T_R

$$p_R = p/p_c$$

$$T_R = T/T_c$$

where p_c and T_c denote the critical pressure and temperature, respectively.



pseudoreduced
specific volume

Values of specific volume are included on the generalized chart through the variable v'_R , called the pseudoreduced specific volume, defined by

$$v'_R = \frac{\bar{v}}{RT_c/p_c}$$

TAKE NOTE...

Study of Fig. A-2 shows that the value of Z tends to unity at fixed reduced temperature T_R as reduced pressure p_R tends to zero. That is, $Z \rightarrow 1$ as $p_R \rightarrow 0$ at fixed T_R .

Figure A-2 also shows that Z tends to unity at fixed reduced pressure as reduced temperature becomes large.

Fig. 3.12 Generalized compressibility chart for various gases.

EXAMPLE 3.7 ►

Using the Generalized Compressibility Chart

A closed, rigid tank filled with water vapor, initially at 20 MPa, 520°C, is cooled until its temperature reaches 400°C. Using the compressibility chart, determine

(a) the specific volume of the water vapor in m^3/kg at the initial state.

(b) the pressure in MPa at the final state.

Compare the results of parts (a) and (b) with the values obtained from the superheated vapor table, Table A-4.

SOLUTION

Known: Water vapor is cooled at constant volume from 20 MPa, 520°C to 400°C.

Find: Use the compressibility chart and the superheated vapor table to determine the specific volume and final pressure and compare the results.

Schematic and Given Data:

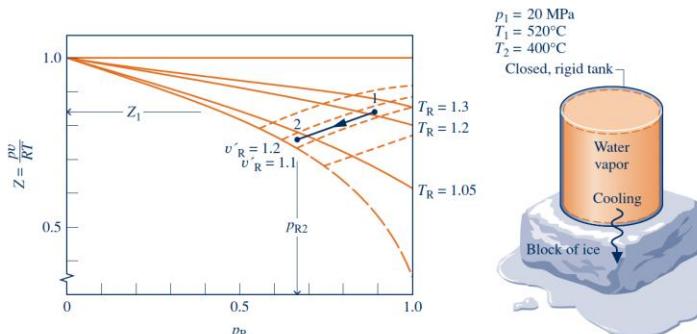


Fig. E3.7

Analysis:

(a) From Table A-1, $T_c = 647.3 \text{ K}$ and $p_c = 22.09 \text{ MPa}$ for water. Thus,

$$T_{R1} = \frac{793}{647.3} = 1.23, \quad p_{R1} = \frac{20}{22.09} = 0.91$$

①

Engineering Model:

1. The water vapor is a closed system.
2. The initial and final states are at equilibrium.
3. The volume is constant.

With these values for the reduced temperature and reduced pressure, the value of Z obtained from Fig. A-1 is approximately 0.83. Since $Z = pv/RT$, the specific volume at state 1 can be determined as follows:

$$\begin{aligned} v_1 &= Z_1 \frac{RT_1}{p_1} = 0.83 \frac{\bar{R}T_1}{Mp_1} \\ &= 0.83 \left(\frac{8314 \frac{\text{N} \cdot \text{m}}{\text{kmol} \cdot \text{K}}}{18.02 \frac{\text{kg}}{\text{kmol}}} \right) \left(\frac{793 \text{ K}}{20 \times 10^6 \frac{\text{N}}{\text{m}^2}} \right) = 0.0152 \text{ m}^3/\text{kg} \end{aligned}$$

② The molecular weight of water is from Table A-1.

Turning to Table A-4, the specific volume at the initial state is $0.01551 \text{ m}^3/\text{kg}$. This is in good agreement with the compressibility chart value, as expected.

(b) Since both mass and volume remain constant, the water vapor cools at constant specific volume and, thus, at constant v'_R . Using the value for specific volume determined in part (a), the constant v'_R value is

$$v'_R = \frac{vp_c}{RT_c} = \frac{\left(0.0152 \frac{\text{m}^3}{\text{kg}} \right) \left(22.09 \times 10^6 \frac{\text{N}}{\text{m}^2} \right)}{\left(8314 \frac{\text{N} \cdot \text{m}}{\text{kmol} \cdot \text{K}} \right) (647.3 \text{ K})} = 1.12$$

At state 2

$$T_{R2} = \frac{673}{647.3} = 1.04$$

Locating the point on the compressibility chart where $v'_R = 1.12$ and $T_R = 1.04$, the corresponding value for p_R is about 0.69. Accordingly

$$p_2 = p_c(p_{R2}) = (22.09 \text{ MPa})(0.69) = 15.24 \text{ MPa}$$

Interpolating in the superheated vapor tables gives $p_2 = 15.16 \text{ MPa}$. As before, the compressibility chart value is in good agreement with the table value.

- ① Absolute temperature and absolute pressure must be used in evaluating the compressibility factor Z , the reduced temperature T_R , and reduced pressure p_R .
- ② Since Z is unitless, values for p , v , R , and T must be used in consistent units.

Skills Developed

Ability to...

- retrieve $p-v-T$ data from the generalized compressibility chart.
- retrieve $p-v-T$ data from the steam tables..

Quick Quiz

Using the compressibility chart, determine the specific volume, in m^3/kg , for water vapor at 14 MPa, 440°C. Compare with the steam table value. Ans. $0.0195 \text{ m}^3/\text{kg}$

Evaluating Properties Using the Ideal Gas Model

ideal gas equation of state

$$pv = RT \quad (3.32)$$

$$pV = mRT \quad (3.33)$$

$$p\bar{v} = \bar{R}T \quad (3.34)$$

or, with $\bar{v} = V/n$, as

$$pV = n\bar{R}T \quad (3.35)$$

ideal gas model

$$pv = RT \quad (3.32)$$

$$u = u(T) \quad (3.36)$$

$$h = h(T) = u(T) + RT \quad (3.37)$$

TAKE NOTE...

To expedite the solutions of many subsequent examples and end-of-chapter problems involving air, oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), and other common gases, we indicate in the problem statements that the ideal gas model should be used. If not indicated explicitly, the suitability of the ideal gas model should be checked using the Z chart or other data.

EXAMPLE 3–10 Temperature Rise of Air in a Tire During a Trip

The gage pressure of an automobile tire is measured to be 210 kPa before a trip and 220 kPa after the trip at a location where the atmospheric pressure is 95 kPa (Fig. 3–45). Assuming the volume of the tire remains constant and the air temperature before the trip is 25°C, determine air temperature in the tire after the trip.

SOLUTION The pressure in an automobile tire is measured before and after a trip. The temperature of air in the tire after the trip is to be determined.

Assumptions 1 The volume of the tire remains constant. 2 Air is an ideal gas.

Properties The local atmospheric pressure is 95 kPa.

Analysis The absolute pressures in the tire before and after the trip are

$$P_1 = P_{\text{gage},1} + P_{\text{atm}} = 210 + 95 = 305 \text{ kPa}$$

$$P_2 = P_{\text{gage},2} + P_{\text{atm}} = 220 + 95 = 315 \text{ kPa}$$

Note that air is an ideal gas and the volume is constant. The air temperature after the trip is determined to be

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow T_2 = \frac{P_2}{P_1} T_1 = \frac{315 \text{ kPa}}{305 \text{ kPa}} (25 + 273) \text{ K} = 307.8 \text{ K} = \mathbf{34.8^\circ\text{C}}$$

Therefore, the absolute temperature of air in the tire will increase by 3.3 percent during this trip.

Discussion Note that the air temperature has risen nearly 10°C during this trip. This shows the importance of measuring the tire pressures before long trips to avoid errors due to the temperature increase of air in tires. Also note that the unit kelvin is used for temperature in the ideal-gas relation.



FIGURE 3–45

©Stockbyte/Getty Images RF

Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree.

In thermodynamics, we are interested in two kinds of specific heats: specific heat at constant volume c_v and specific heat at constant pressure c_p .

the specific heat c_v

$$c_v(T) = \frac{du}{dT} \quad (\text{ideal gas})$$

$$du = c_v(T) dT$$

(3.38)

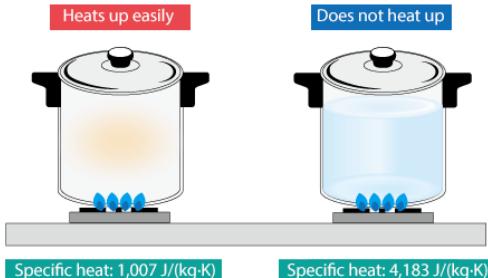
(3.39)

For a gas obeying the ideal gas model, specific internal energy depends only on temperature.

specific heat c_p

$$c_p(T) = \frac{dh}{dT} \quad (\text{ideal gas})$$

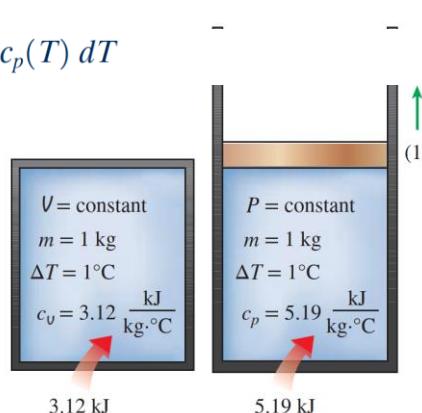
$$dh = c_p(T) dT$$



(3.41)

Similarly, for a gas obeying the ideal gas model, the specific enthalpy depends only on

(3)



$c_v = \left(\frac{\partial u}{\partial T}\right)_v$
= the change in internal energy with temperature at constant volume

$c_p = \left(\frac{\partial h}{\partial T}\right)_p$
= the change in enthalpy with temperature at constant pressure

Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

the change in specific internal energy is

$$u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v(T) dT \quad (\text{ideal gas}) \quad (3.40)$$

the change in specific enthalpy is

$$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T) dT \quad (\text{ideal gas}) \quad (3.43)$$

$$c_p(T) = c_v(T) + R \quad (\text{ideal gas}) \quad (3.44)$$

$$\bar{c}_p(T) = \bar{c}_v(T) + \bar{R} \quad (\text{ideal gas}) \quad (3.45)$$

For an ideal gas, the specific heat ratio, k , is also a function of temperature only

$$k = \frac{c_p(T)}{c_v(T)} \quad (\text{ideal gas}) \quad (3.46)$$

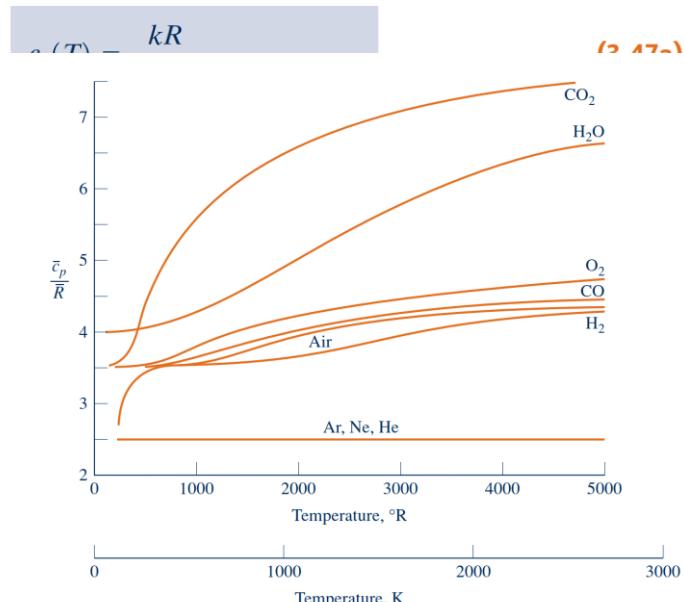


Fig. 3.13 Variation of \bar{c}_p/\bar{R} with temperature for a number of gases modeled as ideal gases.

Applying the Energy Balance Using Ideal Gas Tables, Constant Specific Heats

For a number of common gases, evaluations of specific internal energy and enthalpy changes are facilitated by the use of the ideal gas tables, Tables A-22 and A-23, which give u and h (or \bar{u} and \bar{h}) versus temperature.

To obtain enthalpy versus temperature,

$$h(T) = \int_{T_{\text{ref}}}^T c_p(T) dT + h(T_{\text{ref}})$$

Accordingly, a tabulation of enthalpy versus temperature is developed through the integral

$$h(T) = \int_0^T c_p(T) dT \quad (3.49)$$

When the specific heats are taken as constants,

$$u(T_2) - u(T_1) = c_v(T_2 - T_1) \quad (3.50)$$

$$h(T_2) - h(T_1) = c_p(T_2 - T_1) \quad (3.51)$$

$$c_v = \frac{\int_{T_1}^{T_2} c_v(T) dT}{T_2 - T_1}, \quad c_p = \frac{\int_{T_1}^{T_2} c_p(T) dT}{T_2 - T_1}$$

Analyzing Two Processes in Series

Water contained in a piston–cylinder assembly undergoes two processes in series from an initial state where the pressure is 10 bar and the temperature is 400°C.

Process 1–2: The water is cooled as it is compressed at a constant pressure of 10 bar to the saturated vapor state.

Process 2–3: The water is cooled at constant volume to 150°C.

(a) Sketch both processes on T – v and p – v diagrams.

(b) For the overall process determine the work, in kJ/kg.

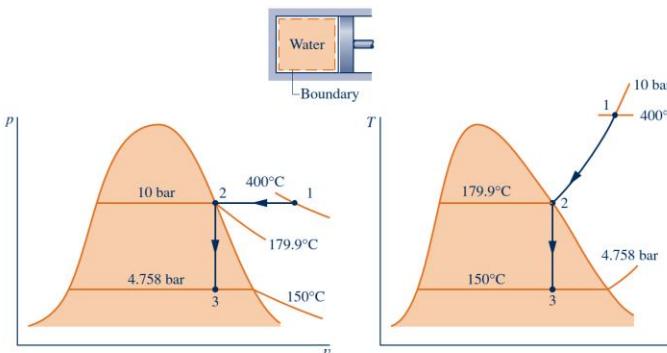
(c) For the overall process determine the heat transfer, in kJ/kg.

SOLUTION

Known: Water contained in a piston–cylinder assembly undergoes two processes: It is cooled and compressed, while keeping the pressure constant, and then cooled at constant volume.

Find: Sketch both processes on T – v and p – v diagrams. Determine the net work and the net heat transfer for the overall process per unit of mass contained within the piston–cylinder assembly.

Schematic and Given Data:



Engineering Model:

1. The water is a closed system.
2. The piston is the only work mode.
3. There are no changes in kinetic or potential energy.

Fig. E3.4

Analysis:

(a) The accompanying T – v and p – v diagrams show the two processes. Since the temperature at state 1, $T_1 = 400^\circ\text{C}$, is greater than the saturation temperature corresponding to $p_1 = 10$ bar: 179.9°C, state 1 is located in the superheat region.

(b) Since the piston is the only work mechanism

$$W = \int_1^3 p \, dV = \int_1^2 p \, dV + \int_2^3 p \, dV^0$$

The second integral vanishes because the volume is constant in Process 2–3. Dividing by the mass and noting that the pressure is constant for Process 1–2

$$\frac{W}{m} = p(v_2 - v_1)$$

The specific volume at state 1 is found from Table A-4 using $p_1 = 10$ bar and $T_1 = 400^\circ\text{C}$: $v_1 = 0.3066 \text{ m}^3/\text{kg}$. Also, $u_1 = 2957.3 \text{ kJ/kg}$. The specific volume at state 2 is the saturated vapor value at 10 bar: $v_2 = 0.1944 \text{ m}^3/\text{kg}$, from Table A-3. Hence,

$$\begin{aligned} \frac{W}{m} &= (10 \text{ bar}) \left(0.1944 - 0.3066 \right) \left(\frac{\text{m}^3}{\text{kg}} \right) \left| \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \right| \left| \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \right| \\ &= -112.2 \text{ kJ/kg} \end{aligned}$$

The minus sign indicates that work is done *on* the water vapor by the piston.

(c) An energy balance for the *overall* process reduces to

$$m(u_3 - u_1) = Q - W$$

By rearranging

$$\frac{Q}{m} = (u_3 - u_1) + \frac{W}{m}$$

To evaluate the heat transfer requires u_3 , the specific internal energy at state 3. Since T_3 is given and $v_3 = v_2$, two independent intensive properties are known that together fix state 3. To find u_3 , first solve for the quality

$$x_3 = \frac{v_3 - v_{f3}}{v_{g3} - v_{f3}} = \frac{0.1944 - 1.0905 \times 10^{-3}}{0.3928 - 1.0905 \times 10^{-3}} = 0.494$$

where v_{f3} and v_{g3} are from Table A-2 at 150°C. Then

$$\begin{aligned} u_3 &= u_{f3} + x_3(u_{g3} - u_{f3}) = 631.68 + 0.494(2559.5 - 631.68) \\ &= 1584.0 \text{ kJ/kg} \end{aligned}$$

where u_{f3} and u_{g3} are from Table A-2 at 150°C.

Substituting values into the energy balance

$$\frac{Q}{m} = 1584.0 - 2957.3 + (-112.2) = -1485.5 \text{ kJ/kg}$$

The minus sign shows that energy is transferred *out* by heat transfer.

Skills Developed

Ability to...

- define a closed system and identify interactions on its boundary.
- evaluate work using Eq. 2.17.
- apply the energy balance with steam table data.
- sketch T – v and p – v diagrams and locate states on them.

Quick Quiz

If the two specified processes were followed by Process 3–4, during which the water expands at a constant temperature of 150°C to saturated vapor, determine the work, in kJ/kg, for the *overall* process from 1 to 4. **Ans.** $W/m = -17.8 \text{ kJ/kg}$

Using the Energy Balance and Constant Specific Heats

Two tanks are connected by a valve. One tank contains 2 kg of carbon monoxide gas at 77°C and 0.7 bar. The other tank holds 8 kg of the same gas at 27°C and 1.2 bar. The valve is opened and the gases are allowed to mix while receiving energy by heat transfer from the surroundings. The final equilibrium temperature is 42°C. Using the ideal gas model with constant c_v , determine (a) the final equilibrium pressure, in bar, (b) the heat transfer for the process, in kJ.

SOLUTION

Known: Two tanks containing different amounts of carbon monoxide gas at initially different states are connected by a valve. The valve is opened and the gas allowed to mix while receiving energy by heat transfer. The final equilibrium temperature is known.

Find: Determine the final pressure and the heat transfer for the process.

Schematic and Given Data:

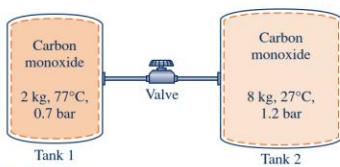


Fig. E3.10

Analysis:

(a) The final equilibrium pressure p_f can be determined from the ideal gas equation of state

$$p_f = \frac{mRT_f}{V}$$

where m is the sum of the initial amounts of mass present in the two tanks, V is the total volume of the two tanks, and T_f is the final equilibrium temperature. Thus,

$$p_f = \frac{(m_1 + m_2)RT_f}{V_1 + V_2}$$

Engineering Model:

1. The total amount of carbon monoxide gas is a closed system.
2. The gas is modeled as an ideal gas with constant c_v .
3. The gas initially in each tank is in equilibrium. The final state is an equilibrium state.
4. No energy is transferred to, or from, the gas by work.
5. There is no change in kinetic or potential energy.

Denoting the initial temperature and pressure in tank 1 as T_1 and p_1 , respectively, $V_1 = m_1RT_1/p_1$. Similarly, if the initial temperature and pressure in tank 2 are T_2 and p_2 , $V_2 = m_2RT_2/p_2$. Thus, the final pressure is

$$p_f = \frac{(m_1 + m_2)RT_f}{\left(\frac{m_1RT_1}{p_1}\right) + \left(\frac{m_2RT_2}{p_2}\right)} = \frac{(m_1 + m_2)T_f}{\left(\frac{m_1T_1}{p_1}\right) + \left(\frac{m_2T_2}{p_2}\right)}$$

Inserting values

$$p_f = \frac{(10 \text{ kg})(315 \text{ K})}{\frac{(2 \text{ kg})(350 \text{ K})}{0.7 \text{ bar}} + \frac{(8 \text{ kg})(300 \text{ K})}{1.2 \text{ bar}}} = 1.05 \text{ bar}$$

(b) The heat transfer can be found from an energy balance, which reduces with assumptions 4 and 5 to give

$$\Delta U = Q - W^0$$

or

$$Q = U_f - U_i$$

U_i is the initial internal energy, given by

$$U_i = m_1u(T_1) + m_2u(T_2)$$

where T_1 and T_2 are the initial temperatures of the CO in tanks 1 and 2, respectively. The final internal energy is U_f

$$U_f = (m_1 + m_2)u(T_f)$$

Introducing these expressions for internal energy, the energy balance becomes

$$Q = m_1[u(T_f) - u(T_1)] + m_2[u(T_f) - u(T_2)]$$

Since the specific heat c_v is constant (assumption 2)

$$Q = m_1c_v(T_f - T_1) + m_2c_v(T_f - T_2)$$

Evaluating c_v as the average of the values listed in Table A-20 at 300 K and 350 K, $c_v = 0.745 \text{ kJ/kg} \cdot \text{K}$. Hence,

$$Q = (2 \text{ kg})\left(0.745 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}\right)(315 \text{ K} - 350 \text{ K}) + (8 \text{ kg})\left(0.745 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}\right)(315 \text{ K} - 300 \text{ K}) \\ = +37.25 \text{ kJ}$$

The plus sign indicates that the heat transfer is into the system.

- ① By referring to a generalized compressibility chart, it can be verified that the ideal gas equation of state is appropriate for CO in this range of temperature and pressure. Since the specific heat c_v of CO varies little over the temperature interval from 300 to 350 K (Table A-20), it can be treated as constant with acceptable accuracy.

Skills Developed

- Ability to...
- ❑ define a closed system and identify interactions on its boundary.
- ❑ apply the energy balance using the ideal gas model when the specific heat c_v is constant.

Polytropic Process Relations

polytropic process

$$pV^n = \text{constant}$$

For a polytropic process between two states

$$p_1 V_1^n = p_2 V_2^n$$

The exponent n may take on any value from $-\infty$ to $+\infty$ depending on the particular process. When $n = 0$, the process is an **isobaric (constant-pressure) process**, and when $n = \pm\infty$ the process is an **isometric (constant-volume) process**.

For a polytropic process, for any exponent n except $n = 1$

$$\int_1^2 p \, dV = \frac{p_2 V_2 - p_1 V_1}{1 - n} \quad (n \neq 1) \quad (3.54)$$

When $n=1$,

$$\int_1^2 p \, dV = p_1 V_1 \ln \frac{V_2}{V_1} \quad (n = 1) \quad (3.55)$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{(n-1)/n} = \left(\frac{V_1}{V_2} \right)^{n-1} \quad (\text{ideal gas}) \quad (3.56)$$

$$\int_1^2 p \, dV = \frac{mR(T_2 - T_1)}{1 - n} \quad (\text{ideal gas, } n \neq 1) \quad (3.57)$$

$$\int_1^2 p \, dV = mRT \ln \frac{V_2}{V_1} \quad (\text{ideal gas, } n = 1) \quad (3.58)$$

EXAMPLE 3–11 The Use of Generalized Charts

Determine the specific volume of refrigerant-134a at 1 MPa and 50°C, using (a) the ideal-gas equation of state and (b) the generalized compressibility chart. Compare the values obtained to the actual value of 0.021796 m³/kg and determine the error involved in each case.

SOLUTION The specific volume of refrigerant-134a is to be determined assuming ideal- and nonideal-gas behavior.

Analysis The gas constant, the critical pressure, and the critical temperature of refrigerant-134a are determined from Table A–1 to be

$$R = 0.0815 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K}$$

$$P_{\text{cr}} = 4.059 \text{ MPa}$$

$$T_{\text{cr}} = 374.2 \text{ K}$$

(a) The specific volume of refrigerant-134a under the ideal-gas assumption is

$$v = \frac{RT}{P} = \frac{(0.0815 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(323 \text{ K})}{1000 \text{ kPa}} = \mathbf{0.026325 \text{ m}^3/\text{kg}}$$

Therefore, treating the refrigerant-134a vapor as an ideal gas would result in an error of $(0.026325 - 0.021796)/0.021796 = 0.208$, or 20.8 percent in this case.

(b) To determine the correction factor Z from the compressibility chart, we first need to calculate the reduced pressure and temperature:

$$\left. \begin{aligned} P_R &= \frac{P}{P_{\text{cr}}} = \frac{1 \text{ MPa}}{4.059 \text{ MPa}} = 0.246 \\ T_R &= \frac{T}{T_{\text{cr}}} = \frac{323 \text{ K}}{374.2 \text{ K}} = 0.863 \end{aligned} \right\} Z = 0.84$$

Thus

$$v = Z v_{\text{ideal}} = (0.84)(0.026325 \text{ m}^3/\text{kg}) = \mathbf{0.022113 \text{ m}^3/\text{kg}}$$

Discussion The error in this result is less than **2 percent**. Therefore, in the absence of tabulated data, the generalized compressibility chart can be used with confidence.

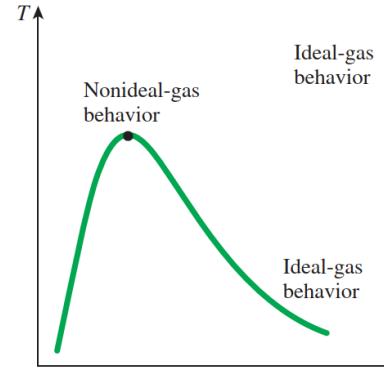


FIGURE 3–50

Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

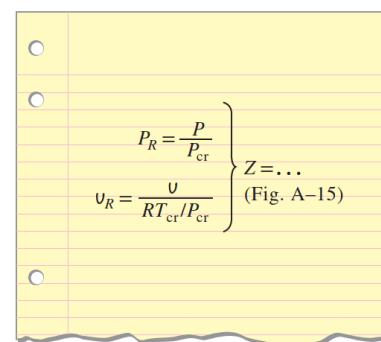


FIGURE 3–51

The compressibility factor can also be determined from a knowledge of P_R and v_R .

► KEY EQUATIONS

$$x = \frac{m_{\text{vapor}}}{m_{\text{liquid}} + m_{\text{vapor}}}$$

$$v = (1 - x)v_f + xv_g = v_f + x(v_g - v_f)$$

$$u = (1 - x)u_f + xu_g = u_f + x(u_g - u_f)$$

$$h = (1 - x)h_f + xh_g = h_f + x(h_g - h_f)$$

$$v(T, p) \approx v_f(T)$$

$$u(T, p) \approx u_f(T)$$

$$h(T, p) \approx h_f(T)$$

Quality, x , of a two-phase, liquid–vapor mixture.

Specific volume, internal energy and enthalpy of a two-phase liquid–vapor mixture.

Specific volume, internal energy, and enthalpy of liquids, approximated by saturated liquid values, respectively.

$$pv = RT$$

$$u = u(T)$$

$$h = h(T) = u(T) + RT$$

Ideal gas model.

$$u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v(T) dT$$

$$u(T_2) - u(T_1) = c_v(T_2 - T_1)$$

Change in specific internal energy.

For constant c_v .

$$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T) dT$$

$$h(T_2) - h(T_1) = c_p(T_2 - T_1)$$

Change in specific enthalpy.

For constant c_p .