Energy Analysis of Closed Systems

1. **Moving Boundary Work**

   - Polytropic Process

2. **Energy Balance for Closed Systems**

3. **Specific Heat**

4. **Internal Energy, Enthalpy, and Specific Heats of Ideal Gases**

   - Specific Heat Relations of Ideal Gases

5. **Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids**

Objectives

- Examine the moving boundary work or $P\,dV$ work commonly encountered in reciprocating devices such as automotive engines and compressors.

- Identify the first law of thermodynamics as simply a statement of the conservation of energy principle for closed (fixed mass) systems.

- Develop the general energy balance applied to closed systems.

- Define the specific heat at constant volume and the specific heat at constant pressure.

- Relate the specific heats to the calculation of the changes in internal energy and enthalpy of ideal gases.

- Describe incompressible substances and determine the changes in their internal energy and enthalpy.

- Solve energy balance problems for closed (fixed mass) systems that involve heat and work interactions for general pure substances, ideal gases, and incompressible substances.

Moving boundary work (*P dV* work):
The expansion and compression work in a piston-cylinder device.

$$\delta W_b = F\,ds = PA\,ds = P\,dV$$

$$W_b = \int_1^2 P\,dV \qquad (kJ)$$

Quasi-equilibrium process:
A process during which the system remains nearly in equilibrium at all times.

W_b is positive → for expansion
W_b is negative → for compression

FIGURE 4–1
The work associated with a moving boundary is called *boundary work*.

FIGURE 4–2
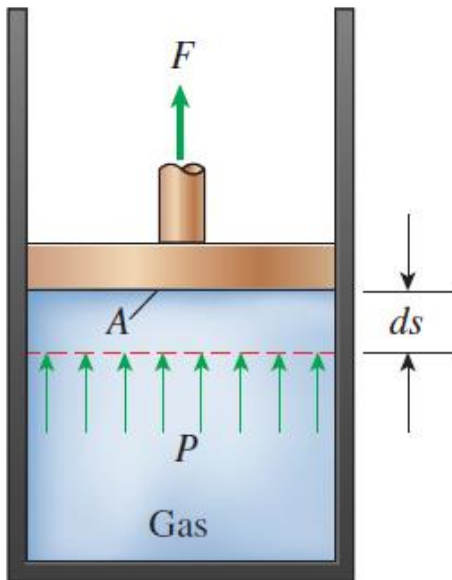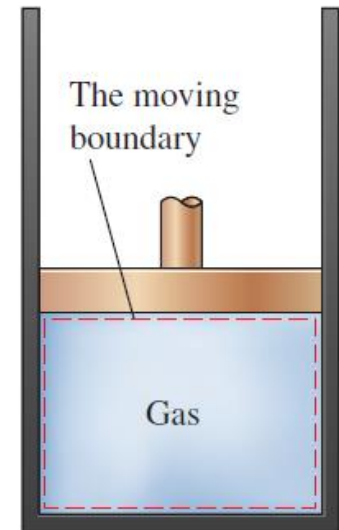A gas does a differential amount of work δW_b as it forces the piston to move by a differential amount ds.
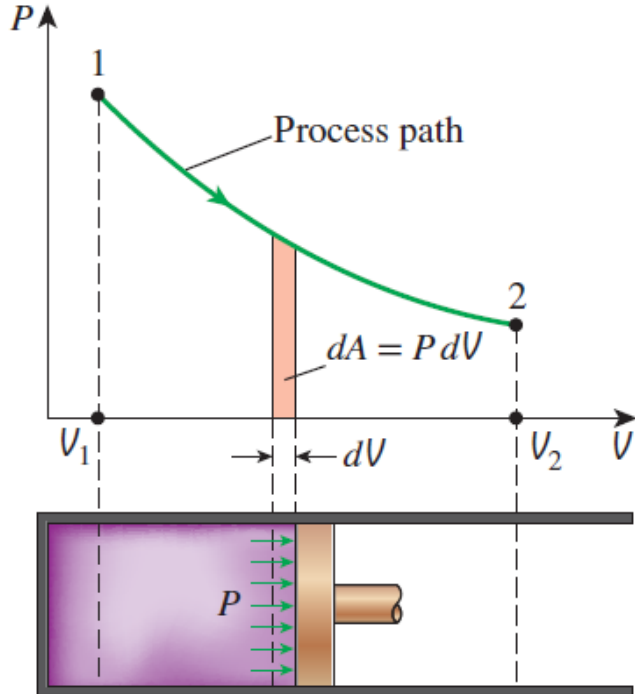
FIGURE 4−3

The area under the process curve on a P-V diagram represents the boundary work.

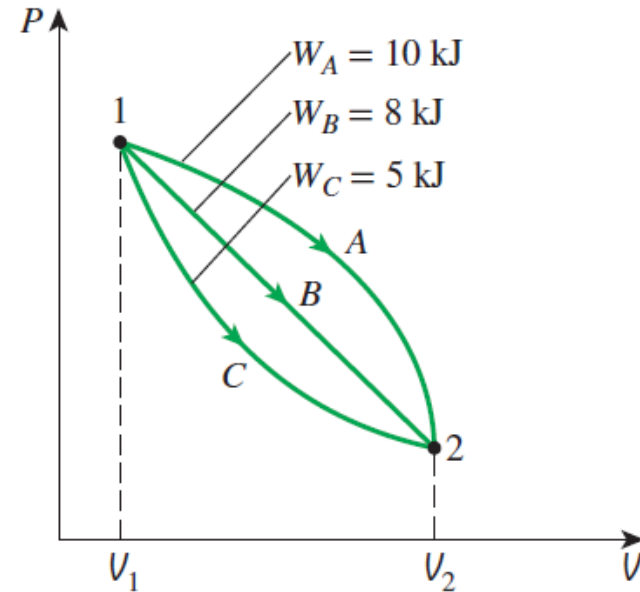$$\text{Area} = A = \int_1^2 dA = \int_1^2 P\, dV$$

FIGURE 4−4

The boundary work done during a process depends on the path followed as well as the end states.

The area under the process curve on a P-V diagram is equal, in magnitude, to the work done during a quasi-equilibrium expansion or compression process of a closed system.
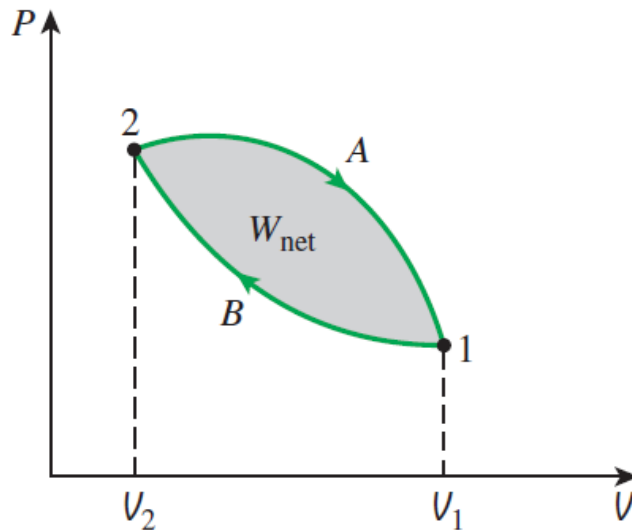
FIGURE 4−5

The net work done during a cycle is
the difference between the work done
by the system and the work done on
the system.

$$W_b = W_{\text{friction}} + W_{\text{atm}} + W_{\text{crank}} = \int_1^2 (F_{\text{friction}} + P_{\text{atm}}A + F_{\text{crank}})\,dx$$

==Generalized boundary
work relation==

$$W_b = \int_1^2 P_i\,dV \qquad \text{(4-4)}$$

P_i is the pressure at the
inner face of the piston.

In a car engine, the boundary work
done by the expanding hot gases is
used to overcome friction between
the piston and the cylinder, to push
atmospheric air out of the way, and
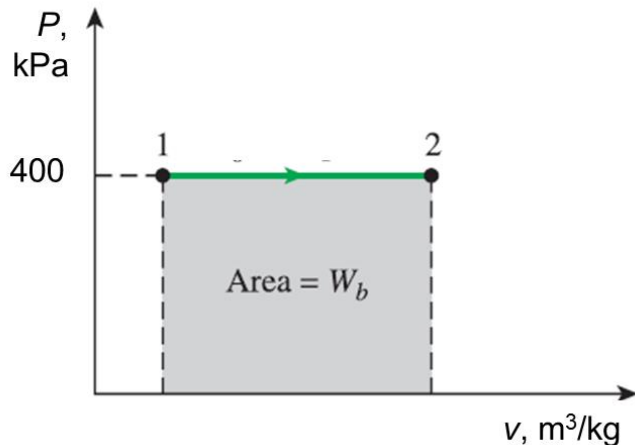to rotate the crankshaft.

Boundary Work for a Constant-Pressure Process

H_2O

← Heat

5 kg
400 kPa

$P,$
kPa

400

1 ——→ 2

Area = W_b

v, m³/kg
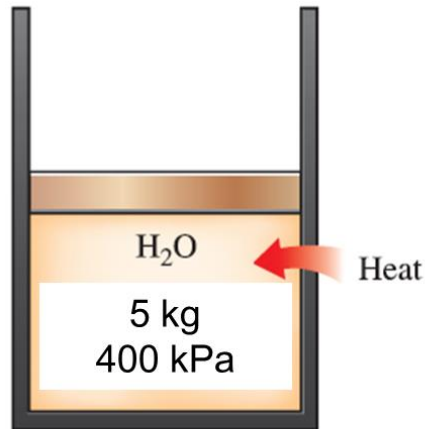
$$W_b = \int_1^2 P \, dV = P_0 \int_1^2 dV = P_0(V_2 - V_1)$$

(4-6)

$$W_b = m P_0(v_2 - v_1)$$

Boundary Work for a Constant-Volume Process

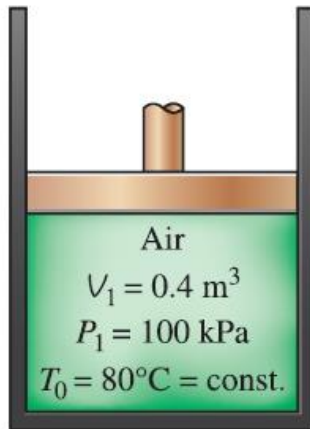Air
$P_1 = 500 \text{ kPa}$
$T_1 = 150°C$

$P_2 = 400 \text{ kPa}$
$T_2 = 65°C$

Heat

$$W_b = \int_1^2 P \, d\cancel{V}^{\;0} = 0$$

P, kPa

500 — — — — • 1

400 — — — — • 2

V
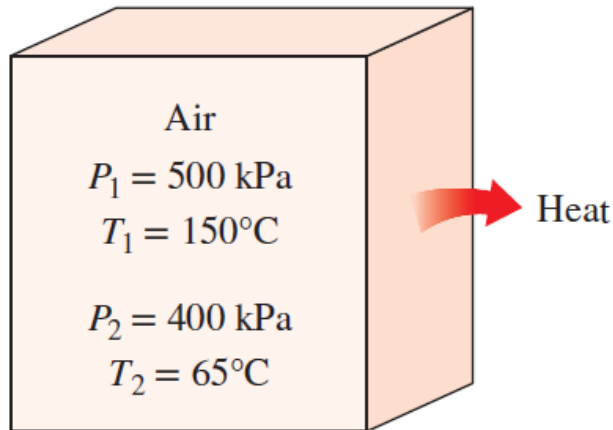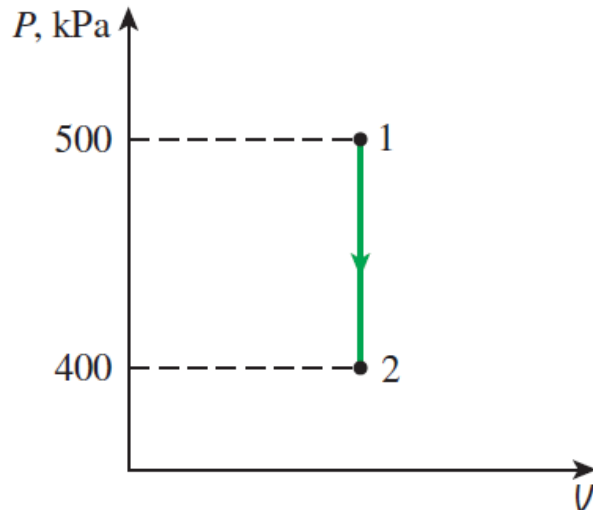
Boundary Work for an <mark>Isothermal Compression Process</mark>

Air
$V_1 = 0.4 \text{ m}^3$
$P_1 = 100 \text{ kPa}$
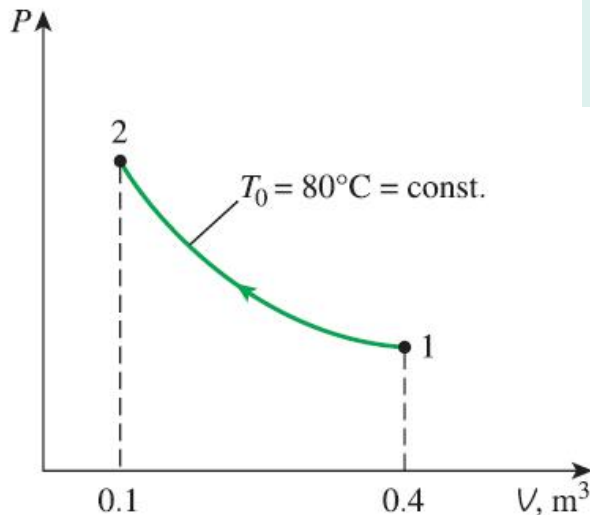$T_0 = 80°C = \text{const.}$

$$W_b = \int_1^2 P\, dV = \int_1^2 CV^{-1}\, dV = PV \ln\left(\frac{V_2}{V_1}\right)$$

$$PV = mRT_0 = C \quad \text{or} \quad P = \frac{C}{V}$$

$$W_b = \int_1^2 P\, dV = \int_1^2 \frac{C}{V}\, dV = C\int_1^2 \frac{dV}{V} = C \ln \frac{V_2}{V_1} = P_1 V_1 \ln \frac{V_2}{V_1}$$

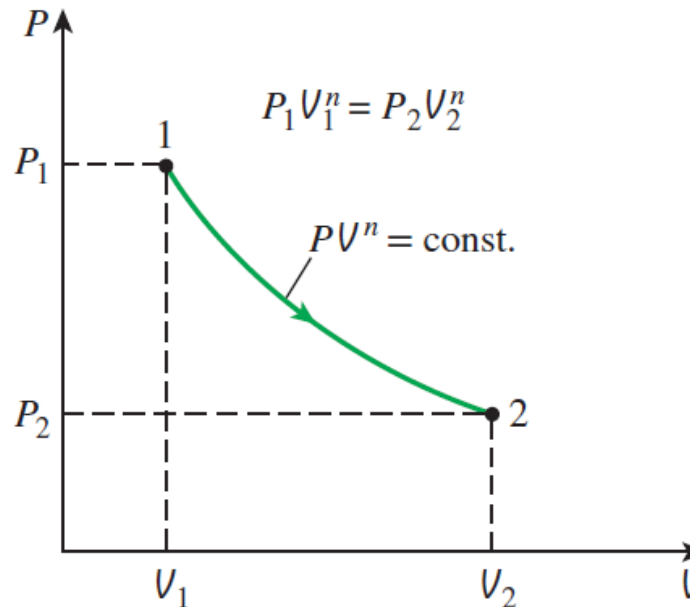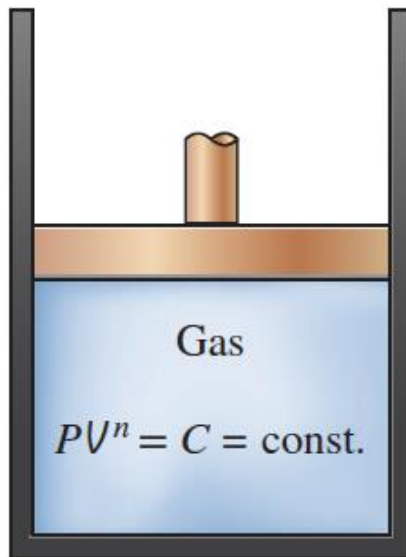(4-7)

$T_0 = 80°C = \text{const.}$

Boundary Work for a Polytropic Process

$$PV^n = \bar{C}, \quad P = CV^{-n}$$

$$W_b = \int_1^2 P\,dV = \int_1^2 CV^{-n}\,dV = C\frac{V_2^{-n+1} - V_1^{-n+1}}{-n+1} = \frac{P_2V_2 - P_1V_1}{1-n} \quad \text{(4-9)}$$

$$W_b = \frac{mR(T_2 - T_1)}{1-n} \qquad n \neq 1 \qquad \text{(kJ)}$$

For ideal gas

$$P_1V_1^n = P_2V_2^n$$

$$PV^n = \text{const.}$$

Gas

$$PV^n = C = \text{const.}$$

Expansion of a Gas against a Spring
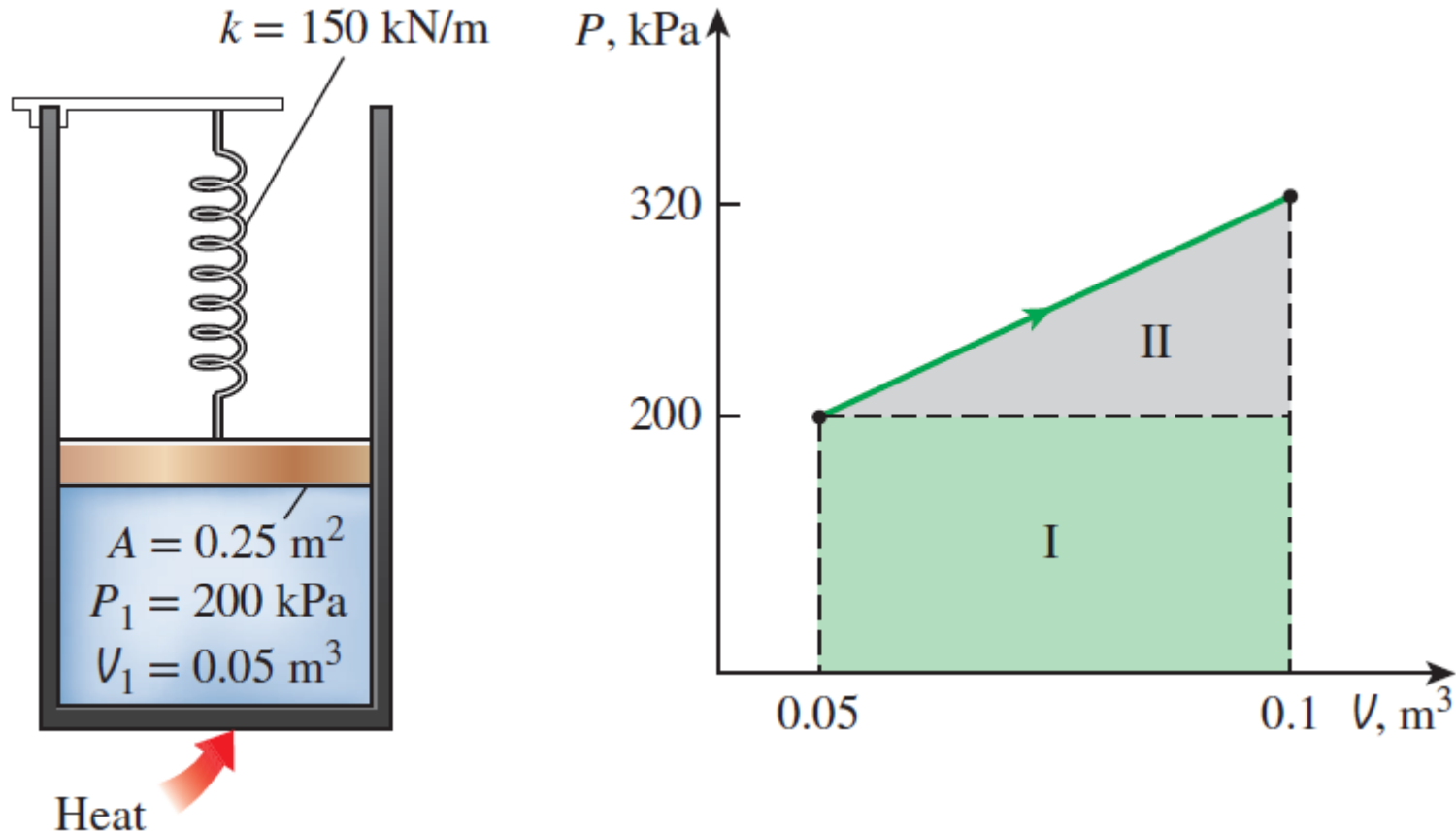
$k = 150 \text{ kN/m}$

$A = 0.25 \text{ m}^2$
$P_1 = 200 \text{ kPa}$
$V_1 = 0.05 \text{ m}^3$

Heat

P, kPa

320

200

II

I

0.05

0.1 V, m^3

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}} \quad (kJ)$$

==Energy balance for any system undergoing any process==

$$\underbrace{\dot{E}_{in} - \dot{E}_{out}}_{\substack{\text{Rate of net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{dE_{system}/dt}_{\substack{\text{Rate of change in internal,} \\ \text{kinetic, potential, etc., energies}}} \quad (kW)$$

Energy balance
in the rate form

==The total quantities== are related to the quantities per unit time

$$Q = \dot{Q}\,\Delta t, \qquad W = \dot{W}\,\Delta t, \qquad \text{and} \qquad \Delta E = (dE/dt)\Delta t \qquad (kJ)$$

$$e_{in} - e_{out} = \Delta e_{system} \qquad (kJ/kg)$$

Energy balance per
unit mass basis

$$\delta E_{in} - \delta E_{out} = dE_{system} \quad \text{or} \quad \delta e_{in} - \delta e_{out} = de_{system}$$

Energy balance in
differential form

$$W_{net,out} = Q_{net,in} \quad \text{or} \quad \dot{W}_{net,out} = \dot{Q}_{net,in}$$

Energy balance
for a cycle

$$W_{net,out} = Q_{net,in} \quad \text{or} \quad \dot{W}_{net,out} = \dot{Q}_{net,in} \quad \text{(for a cycle)}$$
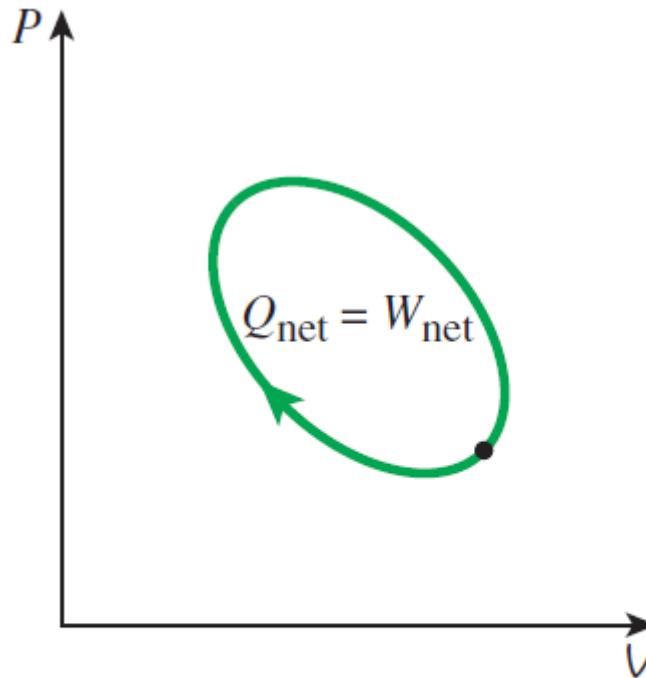
FIGURE 4–11
For a cycle $\Delta E = 0$, thus $Q = W$.

Energy balance when sign convention is used:

- heat input and work output are positive

- heat output and work input are negative

$$Q_{net,in} - W_{net,out} = \Delta E_{system}$$

$$Q - W = \Delta E$$

$$Q = Q_{net,in} = Q_{in} - Q_{out}$$

$$W = W_{net,out} = W_{out} - W_{in}$$

General $Q - W = \Delta E$

Stationary systems $Q - W = \Delta U$

Per unit mass $q - w = \Delta e$
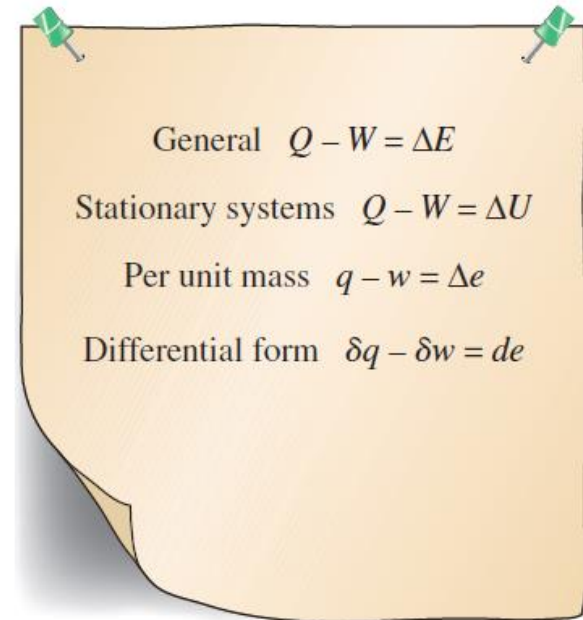
Differential form $\delta q - \delta w = de$

FIGURE 4–12
Various forms of the first-law relation for closed systems.

The first law cannot be proven mathematically, but no process in nature is known to have violated the first law, and this should be taken as sufficient proof.

Energy balance for a constant-pressure expansion or compression process

General analysis for a closed system undergoing a quasi-equilibrium constant-pressure process. *Q* is *to* the system and *W* is *from* the system.

For a constant-pressure expansion or compression process:

$$\Delta U + W_b = \Delta H$$

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

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

$$Q - W_{other} - W_b = U_2 - U_1$$

$$W_b = P_0(V_2 - V_1)$$

$$Q - W_{other} - P_0(V_2 - V_1) = U_2 - U_1$$

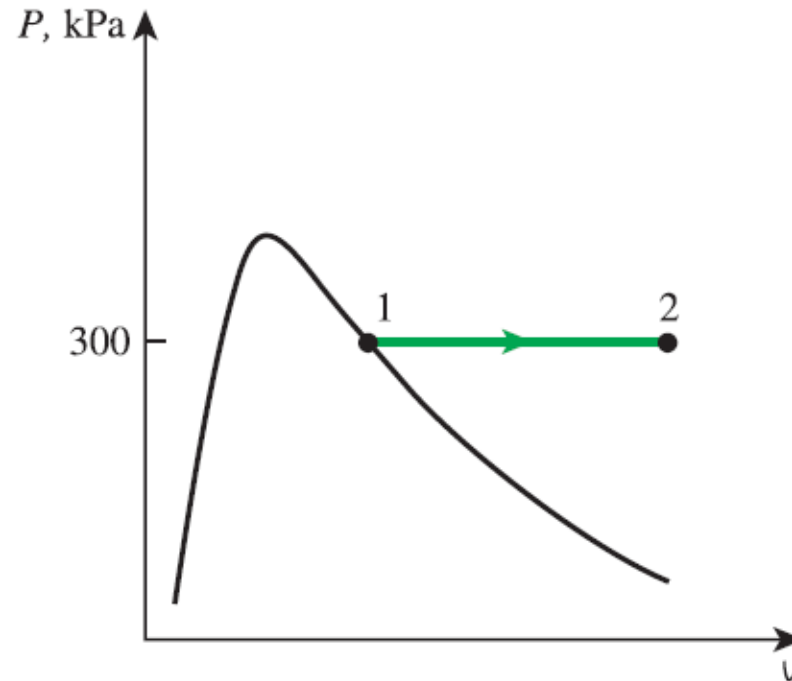$$P_0 = P_2 = P_1 \rightarrow Q - W_{other} = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

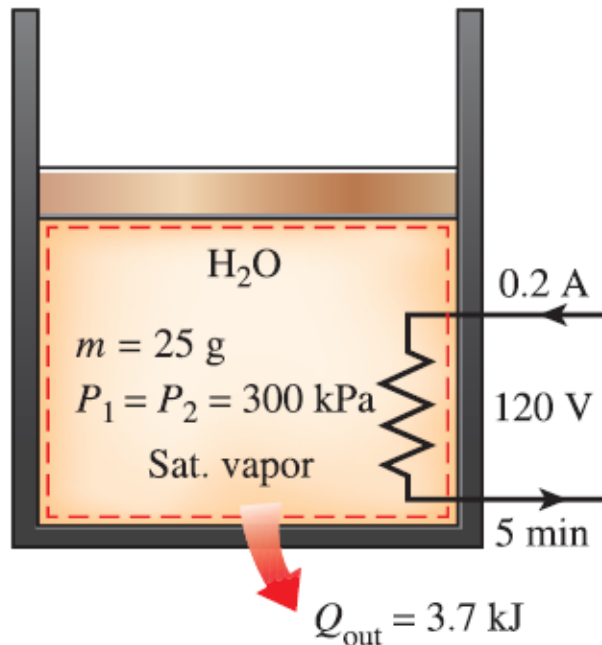$$H = U + PV \qquad Q - W_{other} = H_2 - H_1 \qquad (kJ) \qquad (4\text{-}18)$$

An example of <mark>constant-pressure process</mark>

H_2O
$m = 25$ g
$P_1 = P_2 = 300$ kPa
Sat. vapor

0.2 A
120 V
5 min

$Q_{out} = 3.7$ kJ

$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$

$W_{e,in} - Q_{out} - W_b = \Delta U$

$W_{e,in} - Q_{out} = \underline{\Delta H = m(h_2 - h_1)}$ (since P = constant)

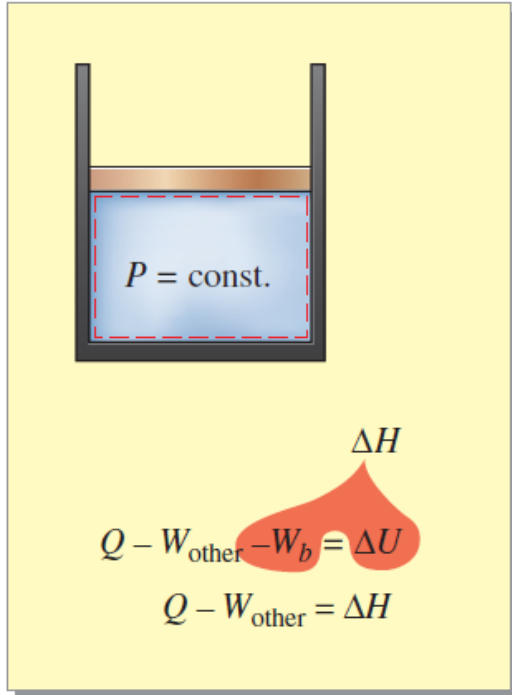$$Q - W_{other} - W_b = \Delta U$$

$$Q - W_{other} = \Delta H$$

FIGURE 4–14

For a closed system undergoing a quasi-equilibrium, P = constant process, $\Delta U + W_b = \Delta H$. Note that this relation is NOT valid for closed systems processes during which pressure DOES NOT remain constant.
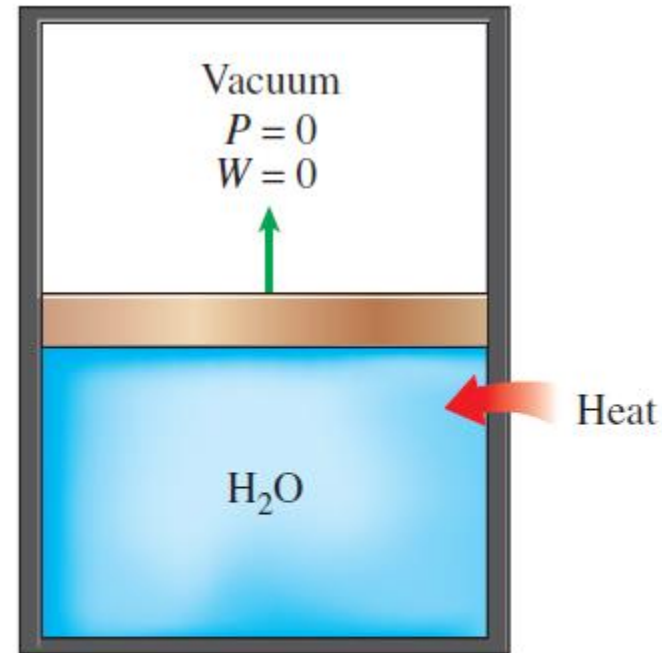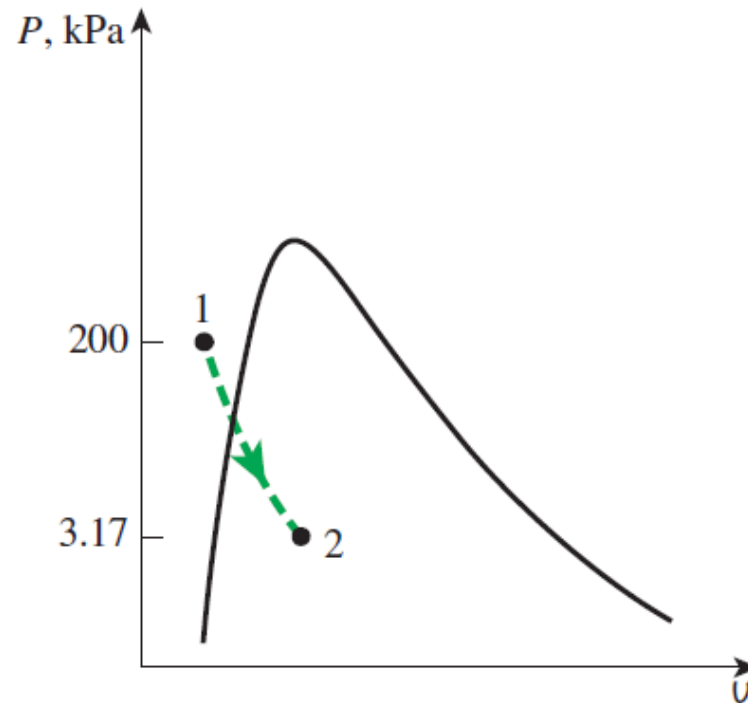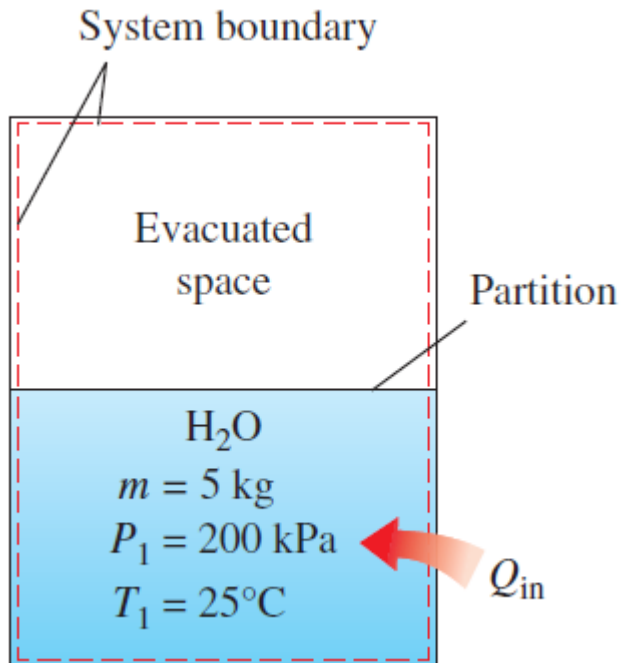

Vacuum
$P = 0$
$W = 0$

Heat

H_2O

FIGURE 4–16

Expansion against a vacuum involves no work and thus no energy transfer.

Unrestrained Expansion of Water

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$Q_{in} = \Delta U = m(u_2 - u_1)$$

System boundary

Evacuated space

Partition

H$_2$O

$m = 5$ kg

$P_1 = 200$ kPa

$T_1 = 25°C$

Q_{in}

P, kPa

200

3.17

1

2

υ

Specific heat <mark>at constant volume, c_v:</mark> The energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant.

Specific heat <mark>at constant pressure, c_p:</mark> The energy required to raise the temperature of the unit mass of a substance by one degree as the pressure is maintained constant.
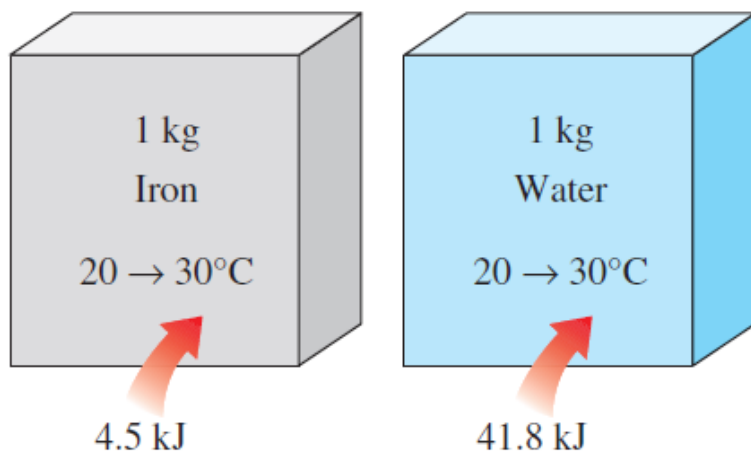
1 kg
Iron
$20 \rightarrow 30°C$

4.5 kJ

1 kg
Water
$20 \rightarrow 30°C$

41.8 kJ

FIGURE 4–17

It takes different amounts of energy to raise the temperature of different substances by the same amount.

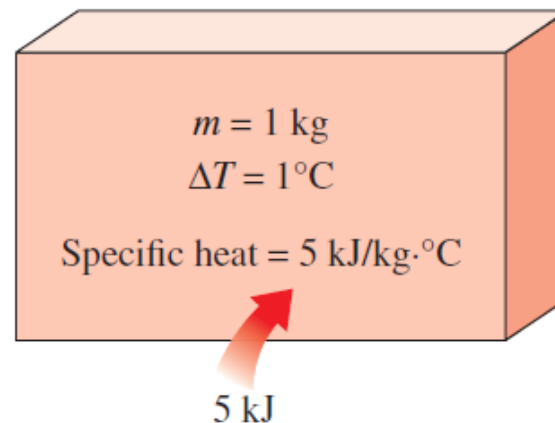$m = 1$ kg
$\Delta T = 1°C$

Specific heat = 5 kJ/kg·°C

5 kJ

FIGURE 4–18

Specific heat is the energy required to raise the temperature of a unit mass of a substance by one degree in a specified way.

FIGURE 4–19
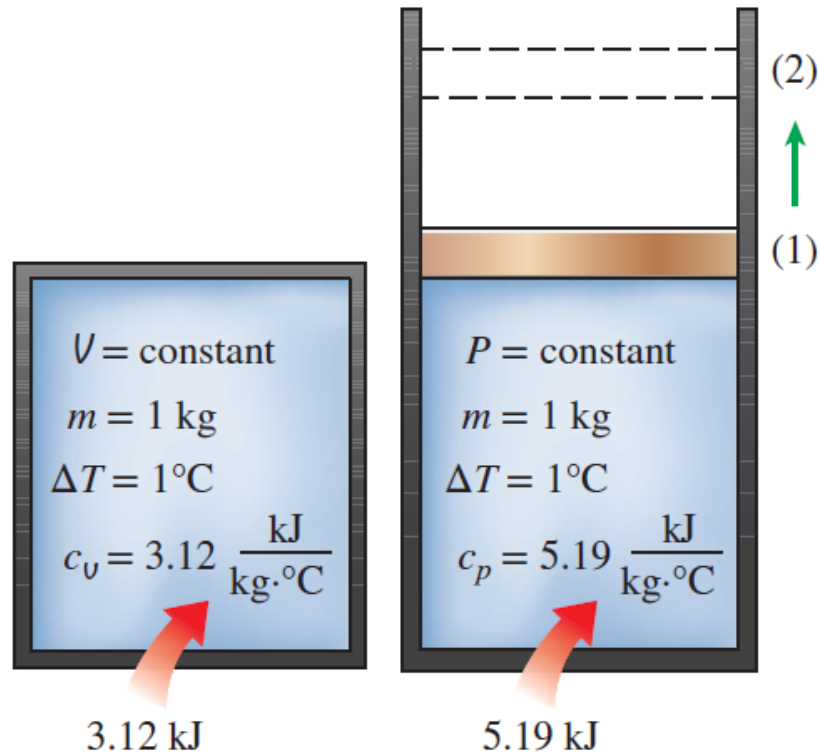
Constant-volume and constant-pressure specific heats c_v and c_p (values given are for helium gas).

Consider a fixed mass in a stationary closed system undergoing a constant-volume process

$$\delta e_{in} - \delta e_{out} = du$$

$$c_v dT = du \qquad \text{at constant volume}$$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \qquad (4\text{-}19)$$

Consider a constant-pressure expansion or compression process

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \qquad (4\text{-}20)$$

The equations are valid for *any* substance undergoing *any* process.

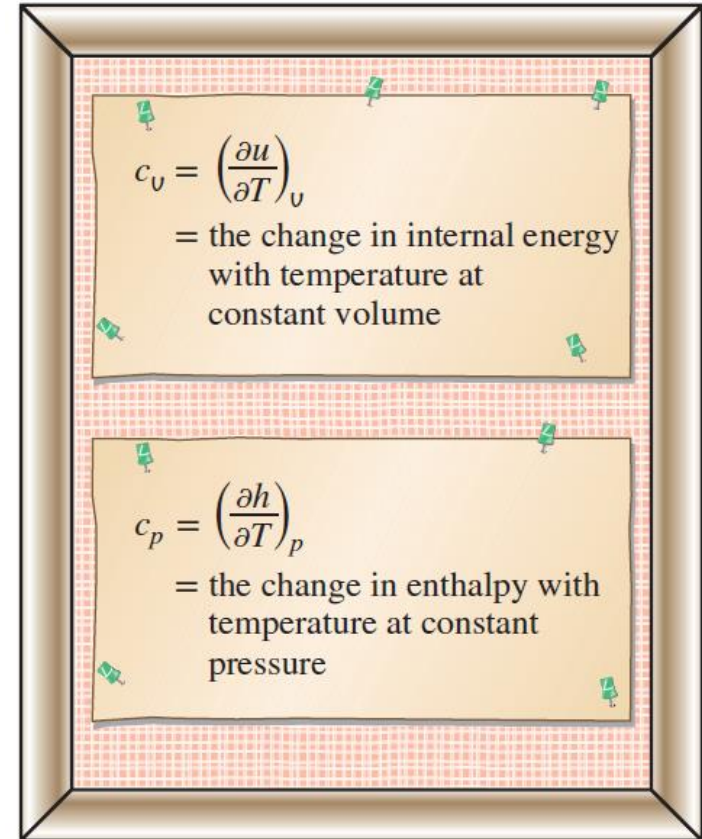c_v is related to the changes in *internal energy* and c_p to the changes in *enthalpy*.

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

= 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

FIGURE 4−20

Formal definitions of c_v and c_p.

Air
m = 1 kg
300 → 301 K

0.718 kJ

Air
m = 1 kg
1000 → 1001 K

0.855 kJ

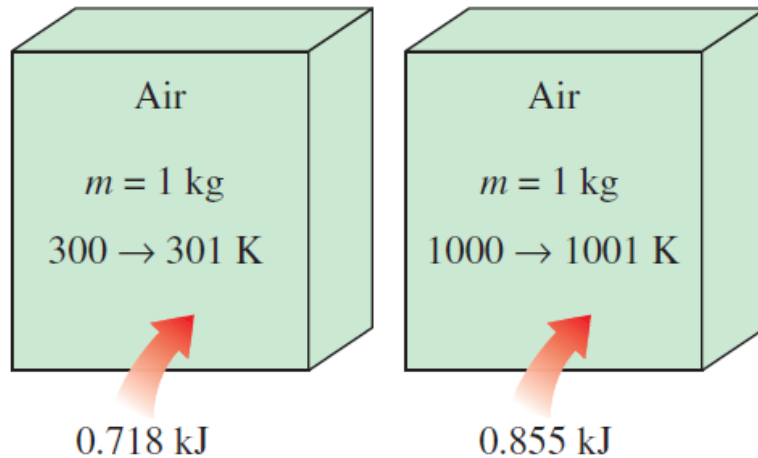**True or False:**
c_p is always greater than c_v

FIGURE 4–21
The specific heat of a substance changes with temperature.

c_v and c_p are properties.

The specific heats of a substance depend on the state.

The energy required to raise the temperature of a substance by one degree is different at different temperatures and pressures.

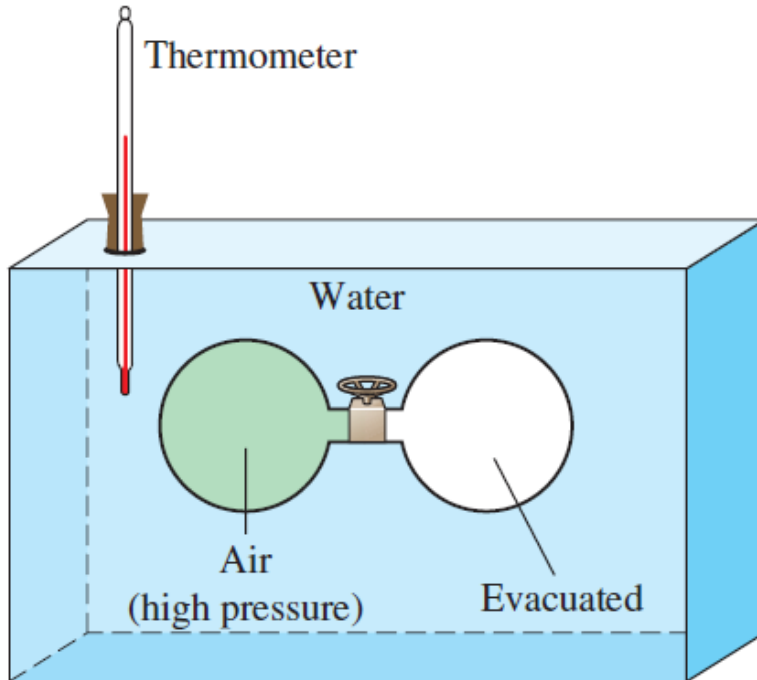A common unit for specific heats is kJ/kg·°C or kJ/kg·K.
Are these units identical?

FIGURE 4−22

Schematic of the experimental apparatus used by Joule.

Joule showed using this experimental apparatus that $u=u(T)$

$$\left.\begin{array}{c} h = u + P\upsilon \\ P\upsilon = RT \end{array}\right\} \quad h = u + RT$$

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

$$du = c_\upsilon(T)dT \qquad \text{(4-23)}$$

$$dh = c_p(T)dT \qquad \text{(4-24)}$$

Internal energy and enthalpy change of an ideal gas

$$\Delta u = u_2 - u_1 = \int_1^2 c_\upsilon(T)\, dT \qquad \text{(kJ/kg)}$$

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T)\, dT \qquad \text{(kJ/kg)}$$

$$u = u(T)$$
$$h = h(T)$$
$$c_v = c_v(T)$$
$$c_p = c_p(T)$$

FIGURE 4−23

For ideal gases, u, h, c_v, and c_p vary with temperature only.
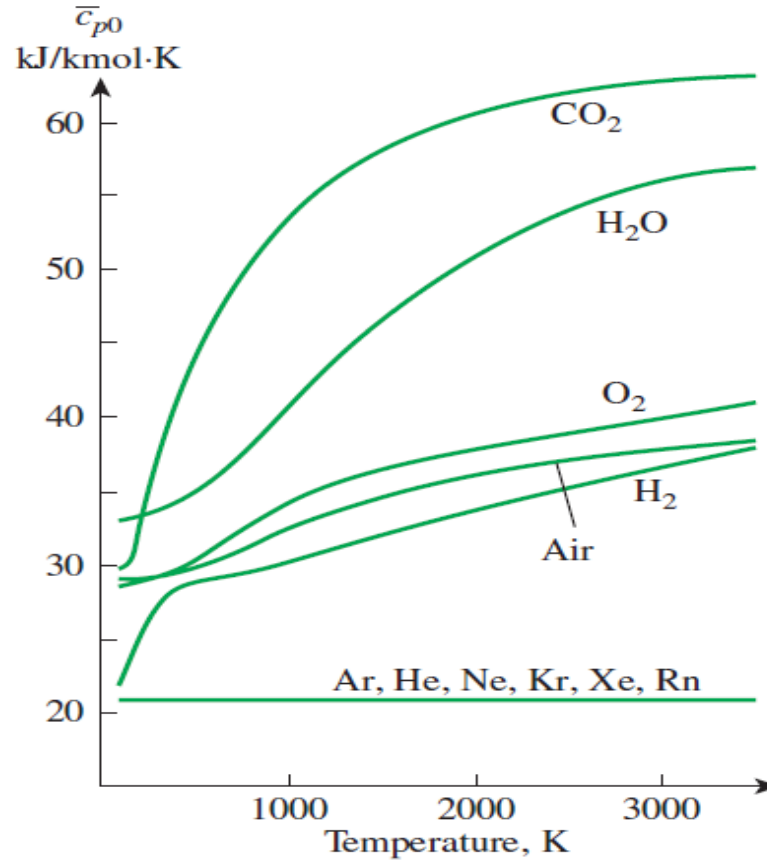
FIGURE 4–24

Ideal-gas constant-pressure specific heats for some gases (see Table A–2c for c_p equations).

At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only.

The specific heats of real gases at low pressures are called *ideal-gas specific heats*, or *zero-pressure specific heats*, and are often denoted c_{p0} and c_{v0}.

u and *h* data for a number of gases have been tabulated.

These tables are obtained by choosing an arbitrary reference point and performing the integrations by treating state 1 as the reference state.

Air

T, K	u, kJ/kg	h, kJ/kg
0	0	0
.	.	.
.	.	.
300	214.07	300.19
310	221.25	310.24
.	.	.
.	.	.

FIGURE 4–25

In the preparation of ideal-gas tables, 0 K is chosen as the reference temperature.

Internal energy and enthalpy change when specific heat is taken constant at an average value

$$u_2 - u_1 = c_{v,\,avg}(T_2 - T_1) \qquad (kJ/kg)$$

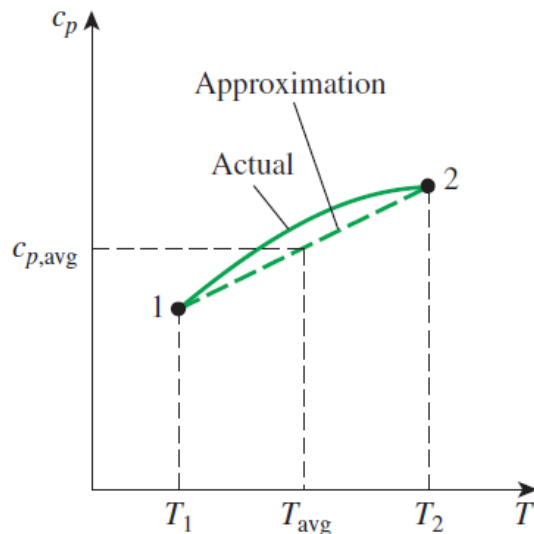$$h_2 - h_1 = c_{p,avg}(T_2 - T_1) \qquad (kJ/kg)$$

FIGURE 4–26

For small temperature intervals, the specific heats may be assumed to vary linearly with temperature.
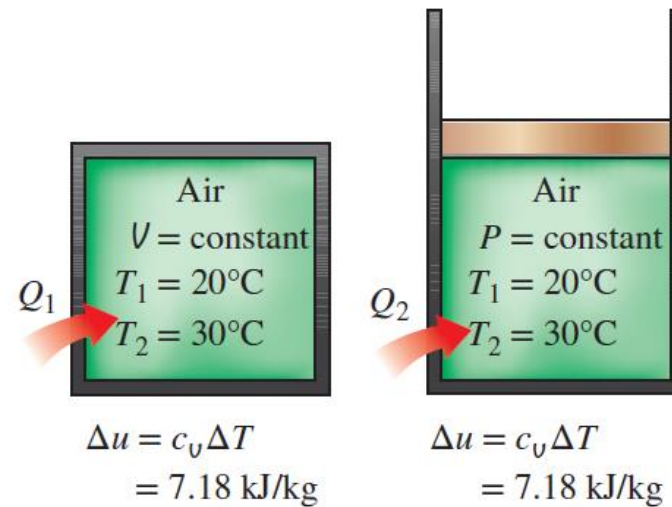

FIGURE 4–27

The relation $\Delta u = c_v \, \Delta T$ is valid for *any* kind of process, constant-volume or not.

Three ways of calculating Δu and Δh

1. By using the tabulated u and h data. This is the easiest and **most accurate** way when tables are readily available.

2. By using the c_v or c_p relations (Table A-2c) as a function of temperature and performing the integrations. This is very inconvenient for hand calculations but quite desirable for computerized calculations. The results obtained are **very accurate**.

3. By using average specific heats. This is very simple and certainly very convenient when property tables are not available. The results obtained are **reasonably accurate** if the temperature interval is not very large.

$$\Delta u = u_2 - u_1 \text{ (table)}$$

$$\Delta u = \int_1^2 c_v(T)\, dT$$

$$\Delta u \cong c_{v,\text{avg}}\, \Delta T$$

Three ways of calculating Δu.

Specific Heat Relations of Ideal Gases

The relationship between c_p, c_v and R

$$h = u + RT,$$

$$dh = du + R\,dT$$

$dh = c_p dT$ and $du = c_v dT$

$$c_p = c_v + R \qquad (\text{kJ/kg·K}) \quad (4\text{-}29)$$

On a molar basis

$$\overline{c}_p = \overline{c}_v + R_u \qquad (\text{kJ/kmol·K}) \quad (4\text{-}30)$$

$$k = \frac{c_p}{c_v} \qquad \text{Specific heat ratio} \quad (4\text{-}31)$$

The specific ratio varies with temperature, but this variation is mild.

For monatomic gases (helium, argon, etc.), its value is essentially constant at 1.667.

Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature.

Air at 300 K

$$\left.\begin{array}{l} c_v = 0.718 \text{ kJ/kg·K} \\ R = 0.287 \text{ kJ/kg·K} \end{array}\right\} c_p = 1.005 \text{ kJ/kg·K}$$

or

$$\left.\begin{array}{l} \bar{c}_v = 20.80 \text{ kJ/kmol·K} \\ R_u = 8.314 \text{ kJ/kmol·K} \end{array}\right\} \bar{c}_p = 29.114 \text{ kJ/kmol·K}$$

FIGURE 4−29

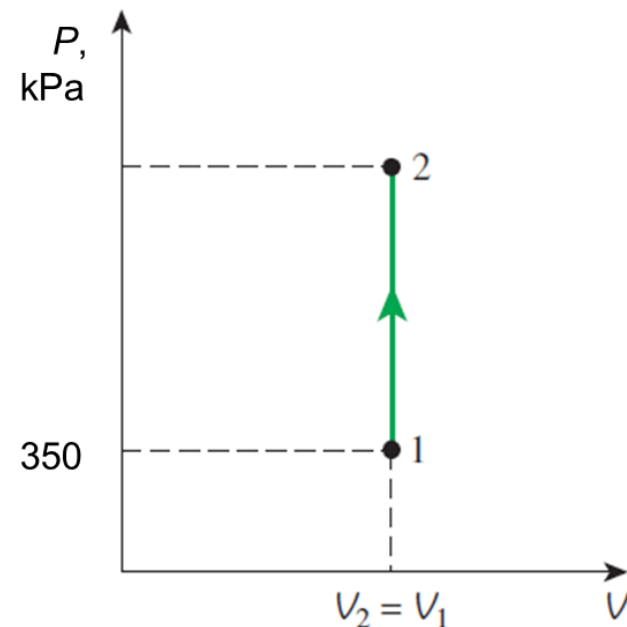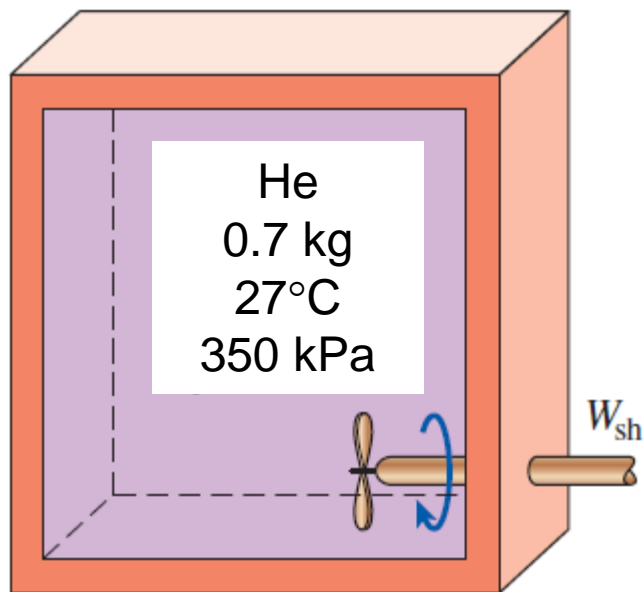The c_p of an ideal gas can be determined from a knowledge of c_v and R.

Heating of a Gas in a Tank by Stirring

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$W_{sh,in} = \Delta U = m(u_2 - u_1) = mc_{v,avg}(T_2 - T_1)$$

He
0.7 kg
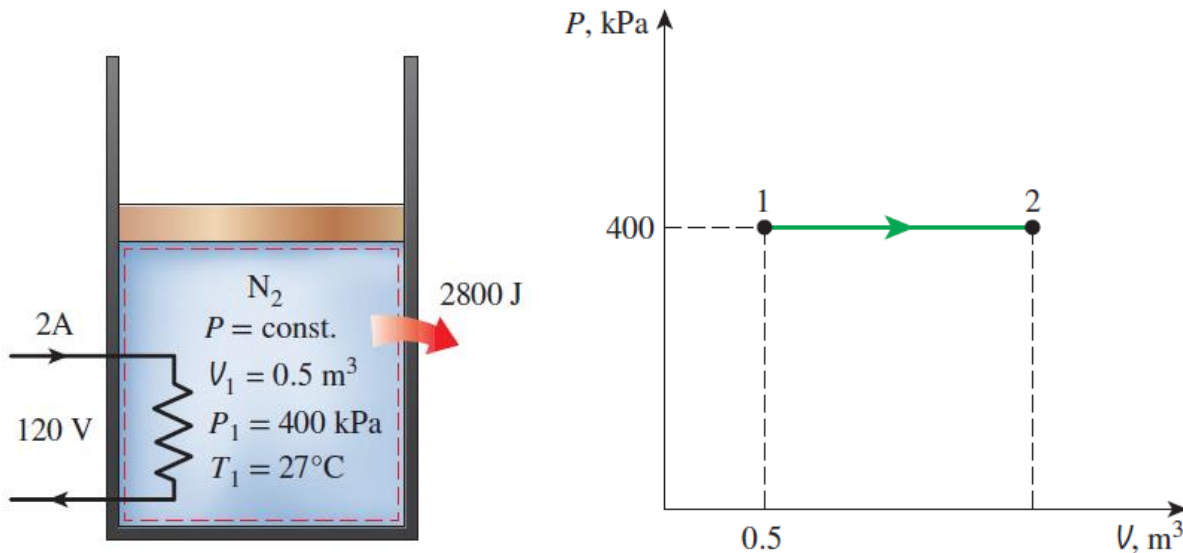27°C
350 kPa

W_{sh}

P, kPa

2

350   1

$V_2 = V_1$ V

Heating of a Gas by a Resistance Heater

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$W_{e,in} - Q_{out} - W_{b,out} = \Delta U$$

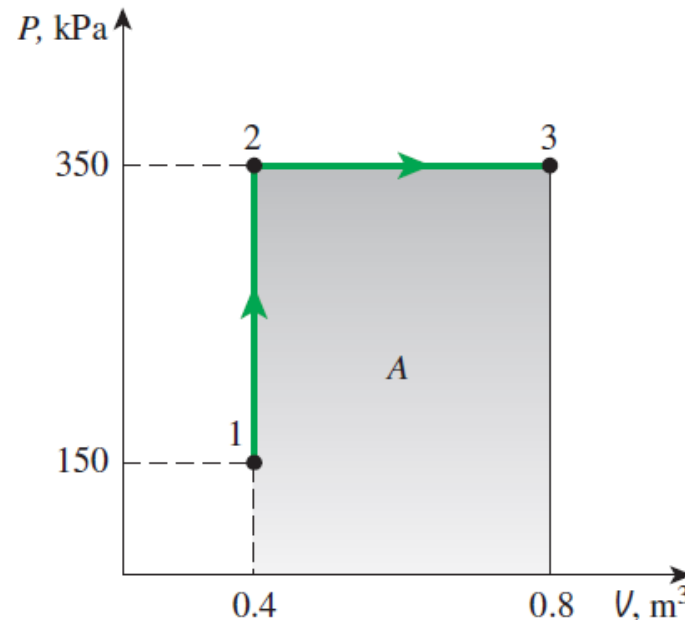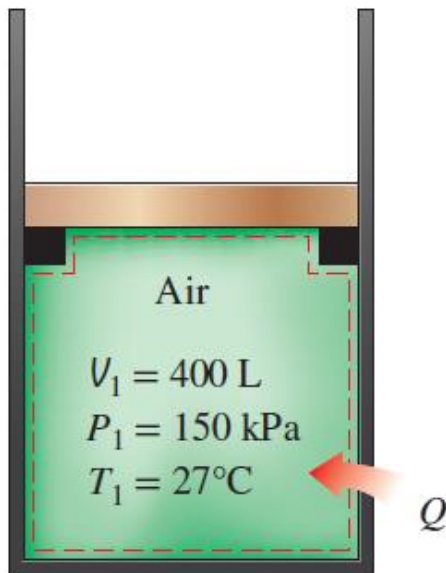$$W_{e,in} - Q_{out} = \Delta H = m(h_2 - h_1) = mc_p(T_2 - T_1)$$

N_2
$P = \text{const.}$
$V_1 = 0.5 \text{ m}^3$
$P_1 = 400 \text{ kPa}$
$T_1 = 27°C$

2A

120 V

2800 J

P, kPa

400

0.5

V, m³

Heating of a Gas at Constant Pressure

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$Q_{in} - W_{b,out} = \Delta U = m(u_3 - u_1)$$

Air
$V_1 = 400 \text{ L}$
$P_1 = 150 \text{ kPa}$
$T_1 = 27°C$

Q

P, kPa

350 — — — 2 ──────▶ 3

A

150 — — — 1

0.4   0.8 V, m^3

Incompressible substance: A substance whose specific volume (or density) is constant.
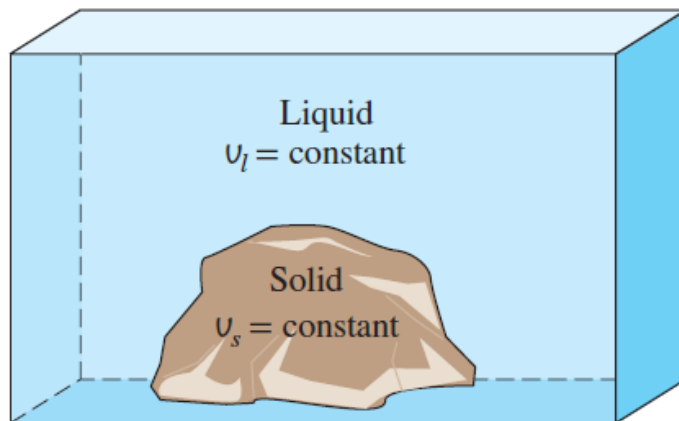
Solids and liquids are incompressible substances.

FIGURE 4–33

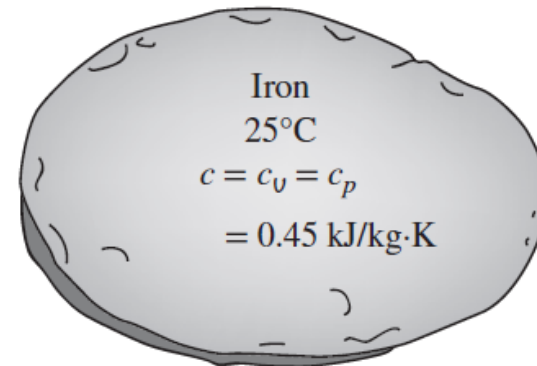The specific volumes of incompressible substances remain constant during a process.

Iron
25°C
$c = c_v = c_p$
$= 0.45 \text{ kJ/kg·K}$

FIGURE 4–34

The c_v and c_p values of incompressible substances are identical and are denoted by c.

Internal Energy Changes

$$du = c_v \, dT = c(T) \, dT$$

$$\Delta u = u_2 - u_1 = \int_1^2 c(T) \, dT \qquad (\text{kJ/kg})$$

$$\Delta u \cong c_{avg}(T_2 - T_1) \qquad (\text{kJ/kg}) \qquad (4\text{-}35)$$

Enthalpy Changes

$$h = u + P\upsilon$$

$$dh = du + \upsilon\, dP + P\, d\upsilon \overset{\nearrow 0}{=} du + \upsilon\, dP$$

$$\Delta h = \Delta u + \upsilon\, \Delta P \cong c_{avg}\, \Delta T + \upsilon\, \Delta P \qquad (kJ/kg)$$

For *solids*, the term $\upsilon\, \Delta P$ is insignificant, and thus $\Delta h \cong \Delta u \cong c_{avg}\Delta T$. For *liquids*, two special cases are commonly encountered:

1. *Constant-pressure processes,* as in heaters ($\Delta P = 0$): $\Delta h = \Delta u \cong c_{avg}\Delta T$
2. *Constant-temperature processes,* as in pumps ($\Delta T = 0$): $\Delta h = \upsilon\, \Delta P$

The enthalpy of a compressed liquid

$$h_{@P,\, T} \cong h_{f\,@\,T} + \upsilon_{f\,@\,T}(P - P_{sat\,@\,T})$$

Usually amore accurate relation than
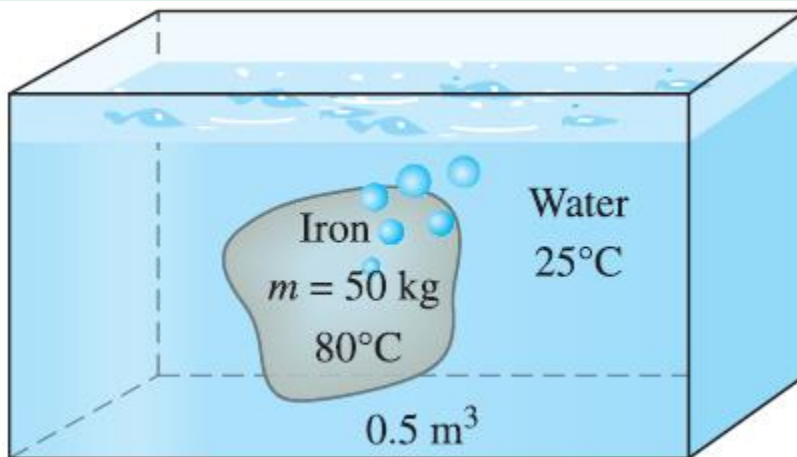
$$h_{@\ P,T} \cong h_{f\ @\ T}$$

Cooling of an Iron Block by Water

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$0 = \Delta U$$

$$\Delta U_{sys} = \Delta U_{iron} + \Delta U_{water} = 0$$

$$[mc(T_2 - T_1)]_{iron} + [mc(T_2 - T_1)]_{water} = 0$$

Iron
$m = 50$ kg
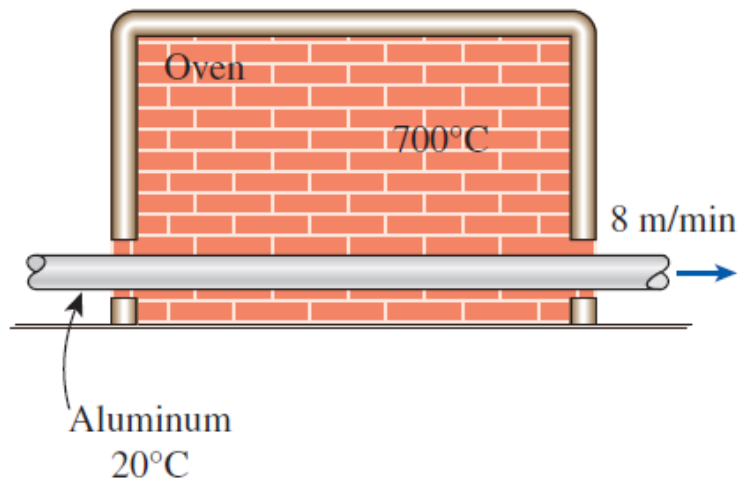$80°C$

Water
$25°C$

0.5 m^3

Heating of Aluminum Rods in a Furnace

$$\underbrace{E_{in} - E_{out}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{system}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$Q_{in} = \Delta U_{rod} = m(u_2 - u_1)$$

$$Q_{in} = mc(T_2 - T_1)$$

$$\dot{Q}_{in} = Q_{in}/\Delta t$$

Oven

700°C

8 m/min

Aluminum
20°C

Summary

Moving boundary work

Energy balance for closed systems

Specific heats

Internal energy, enthalpy, and specific heats of ideal gases

Internal energy, enthalpy, and specific heats of incompressible substances (solids and liquids)