Thermodynamics

Chapter 4

ENERGY ANALYSIS OF CLOSED SYSTEMS

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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

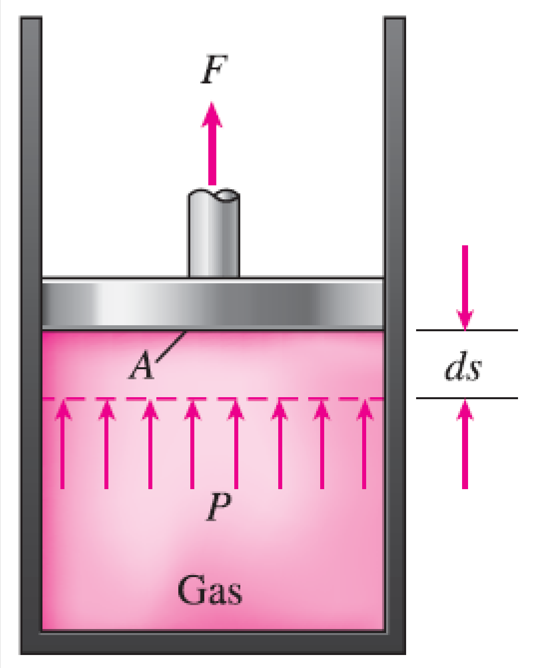
Moving boundary work (*P dV* work): The expansion and compression work in a piston-cylinder device.

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

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

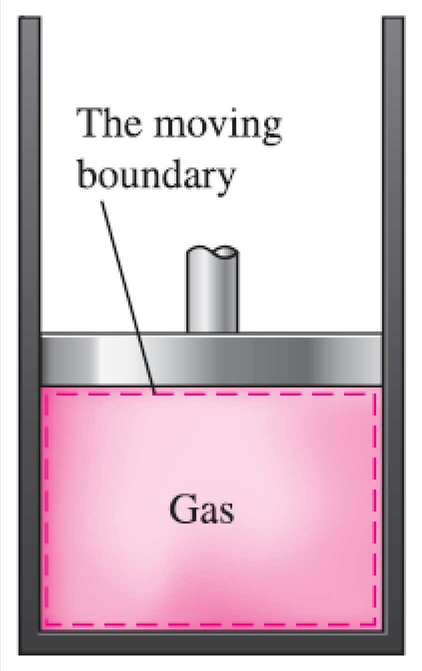
Quasi-equilibrium process: A process during which the system remains nearly in equilibrium at all times.

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



A gas does a differential amount of work δW_b as it forces the piston to move by a differential amount *ds*.

The work associated with a moving boundary is called *boundary work.*



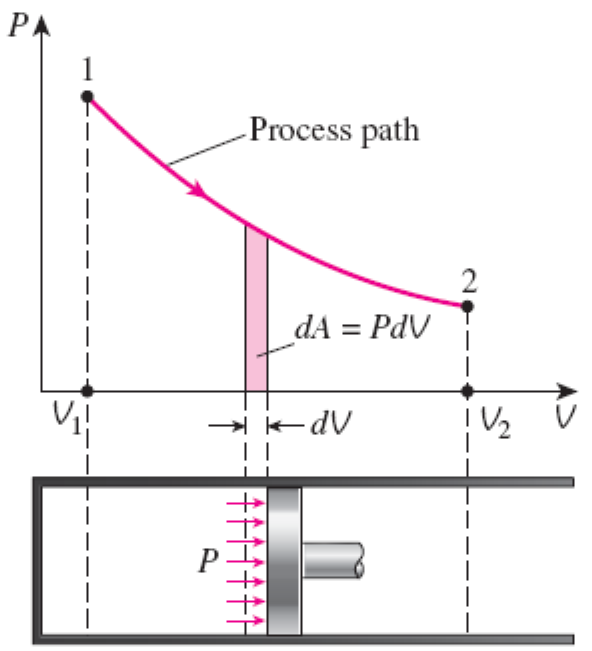


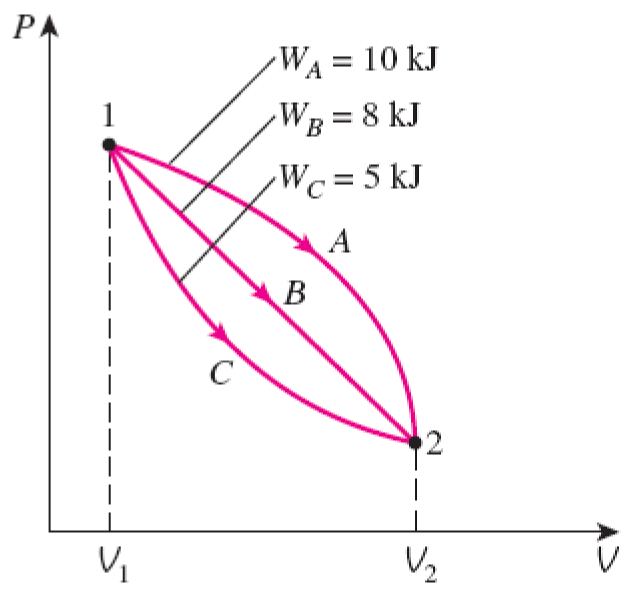
FIGURE 4–3

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

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

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.

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



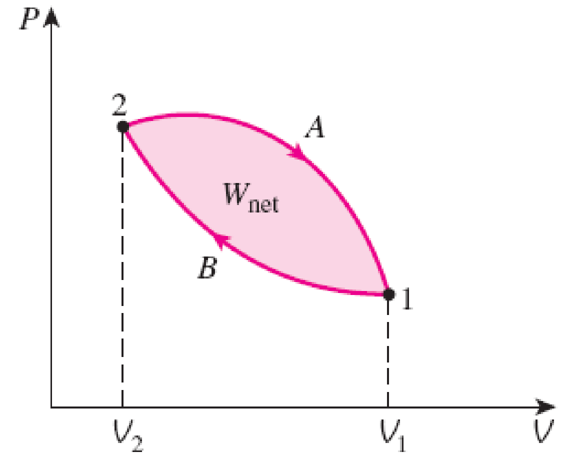


FIGURE 4–5

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

Polytropic, Isothermal, and Isobaric processes

$P = CV^{-n}$ Polytropic process: *C*, *n* (polytropic exponent) constants

$$W_b = \int_1^2 P\,dV = \int_1^2 CV^{-n}\,dV = C\frac{V_2^{-n+1} - V_1^{-n+1}}{-n+1} = \frac{P_2V_2 - P_1V_1}{1-n}$$

Polytropic process

$$W_b = \frac{mR(T_2 - T_1)}{1-n}$$

Polytropic and for ideal gas

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

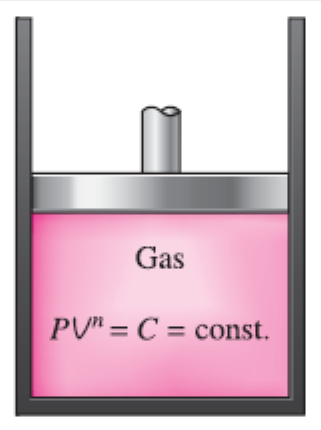
When *n* = 1 (isothermal process)

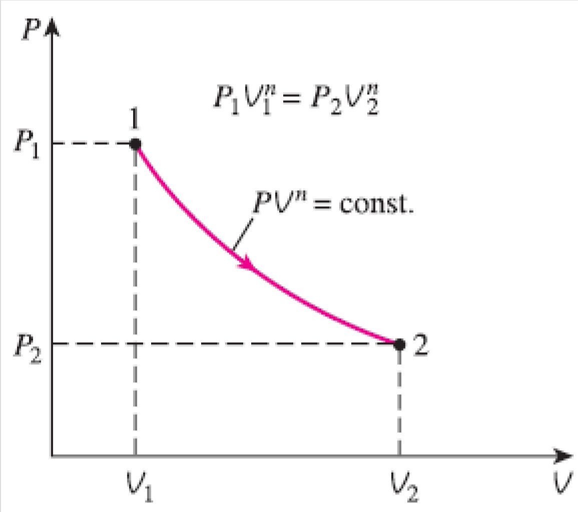
$$W_b = \int_1^2 P\,dV = P_0\int_1^2 dV = P_0(V_2 - V_1)$$

Constant pressure process

What is the boundary work for a constant-volume process?

Schematic and *P-V* diagram for a polytropic process.





ENERGY BALANCE FOR CLOSED SYSTEMS

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

Energy balance for any system undergoing any process

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

Energy balance in the rate form

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

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

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

Energy balance per unit mass basis

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

Energy balance in differential form

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

Energy balance for a cycle

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta E_{\text{system}} \quad \text{or} \quad Q - W = \Delta E$$

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

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

Energy balance when sign convention is used: (i.e., heat input and work output are positive; heat output and work input are negative).

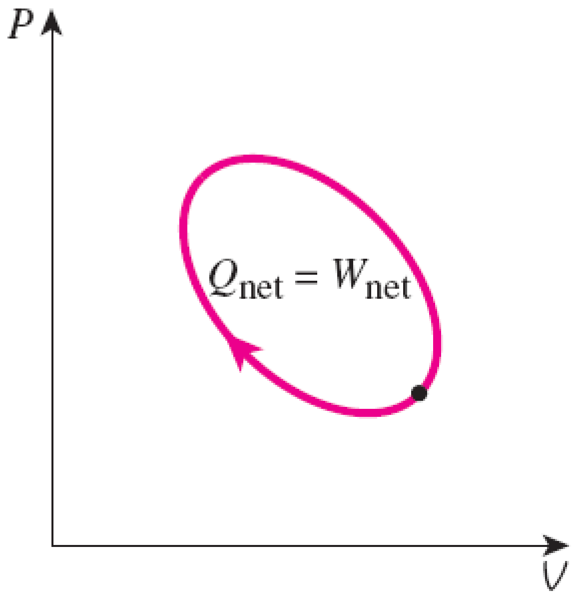
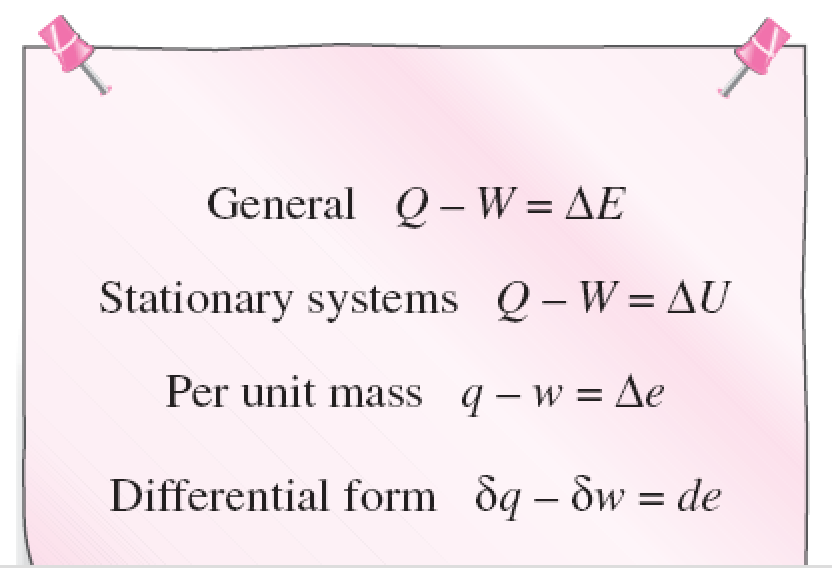


FIGURE 4–11

For a cycle $\Delta E = 0$, thus $Q = W$.



General $Q - W = \Delta E$

Stationary systems $Q - W = \Delta U$

Per unit mass $q - w = \Delta e$

Differential form $\delta q - \delta w = de$

Various forms of the first-law relation for closed systems when sign convention is used.

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.

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

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

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

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

$$Q - W_{\text{other}} = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$H = U + PV$$

$$Q - W_{\text{other}} = H_2 - H_1$$

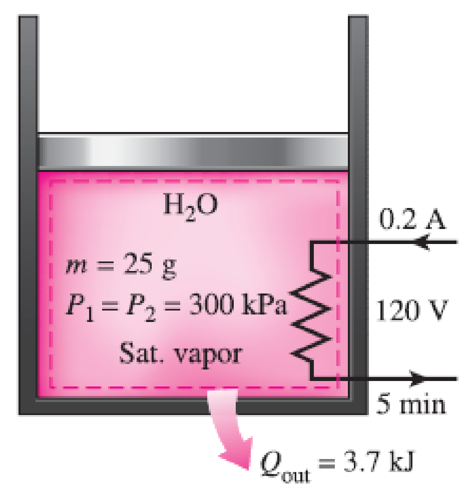
For a constant-pressure expansion or compression process:

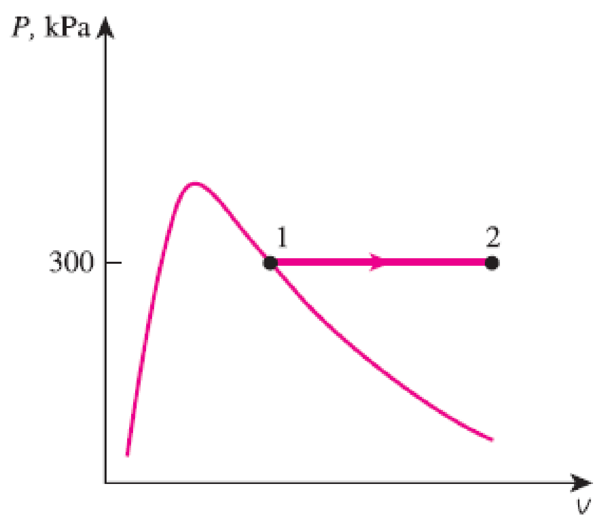
$$\Delta U + W_b = \Delta H$$

An example of constant-pressure process

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

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





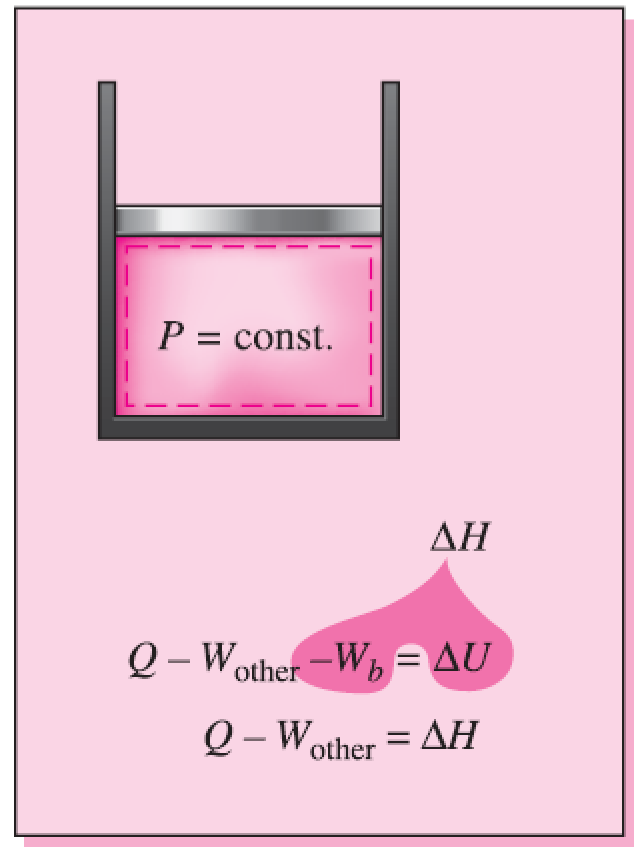


FIGURE 4–14

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.

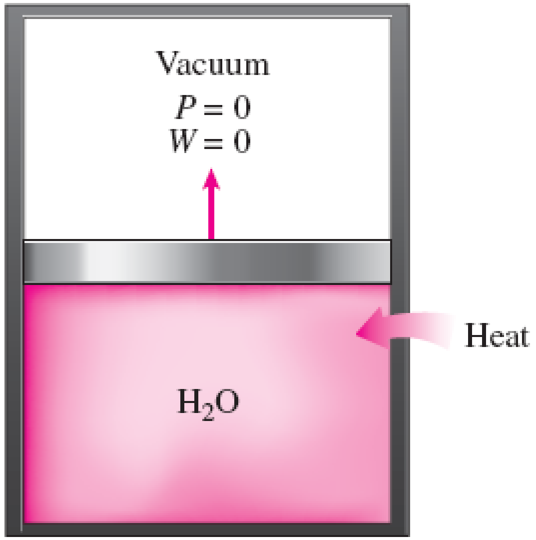


FIGURE 4–16

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

SPECIFIC HEATS

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

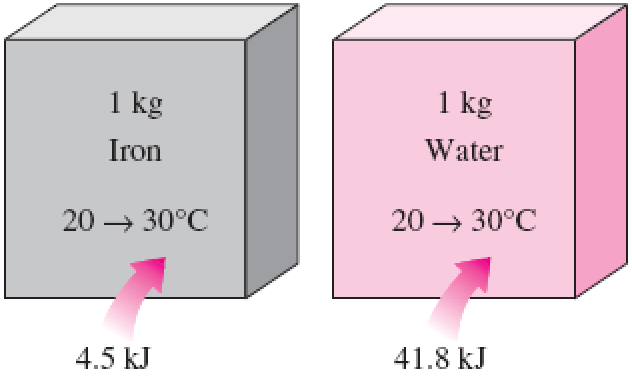


FIGURE 4–17
It takes different amounts of energy to raise the temperature of different substances by the same amount.

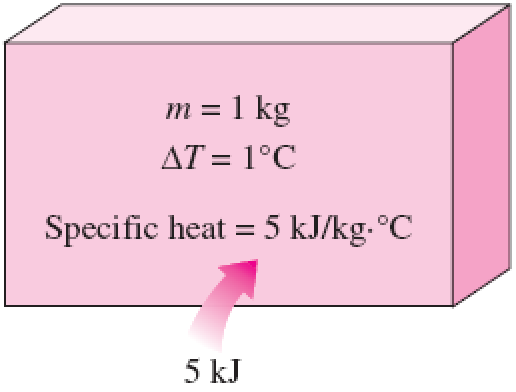
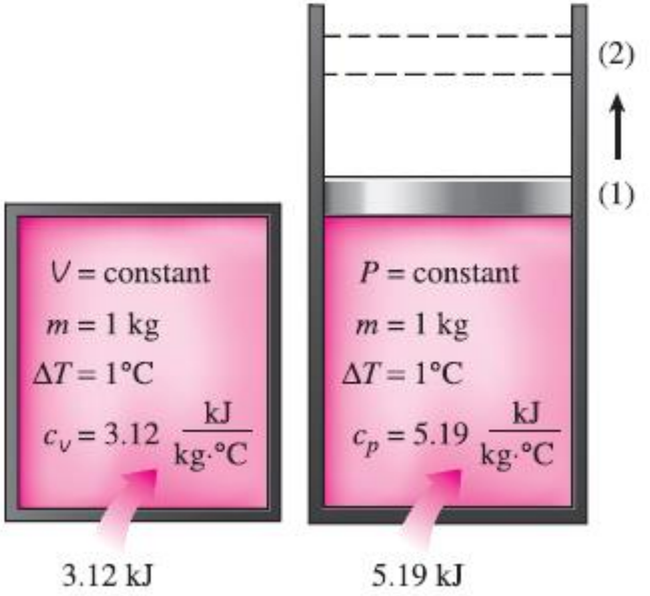


FIGURE 4–18
Specific heat is the energy required to raise the temperature of a unit mass of a substance by one degree in a specified way.



Constant-volume and constant-pressure specific heats c_v and c_p (values are for helium gas).

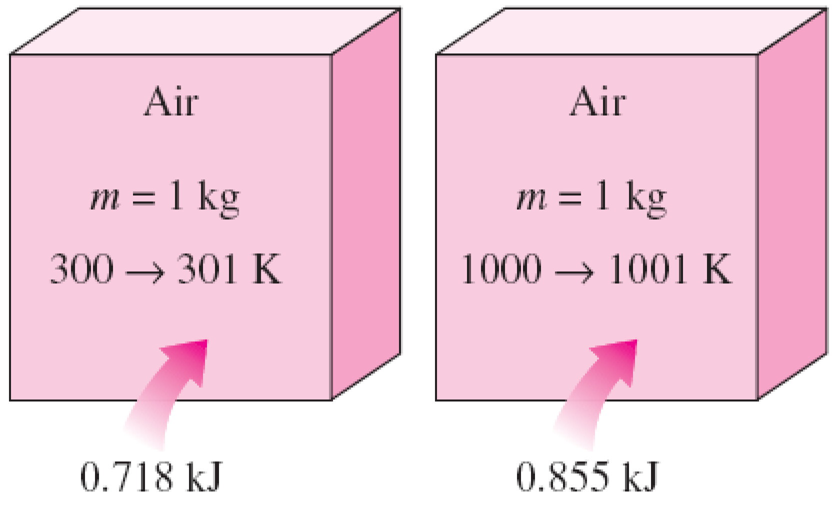


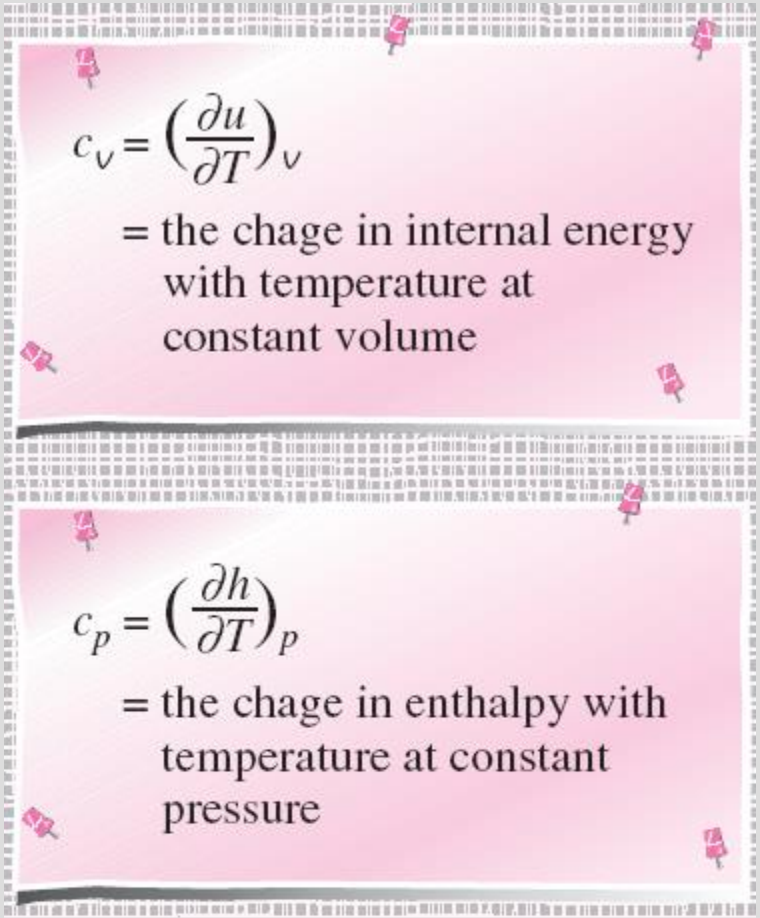
FIGURE 4–21

The specific heat of a substance changes with temperature.

- The equations in the figure are valid for *any* substance undergoing *any* process.
- c_v and c_p are properties.
- c_v is related to the changes in *internal energy* and c_p to the changes in *enthalpy*.
- A common unit for specific heats is kJ/kg·°C or kJ/kg·K. **Are these units identical?**

True or False?

c_p is always greater than c_v



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

= the chage in internal energy with temperature at constant volume

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

= the chage in enthalpy with temperature at constant pressure

Formal definitions of c_v and c_p.

INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEATS OF IDEAL GASES

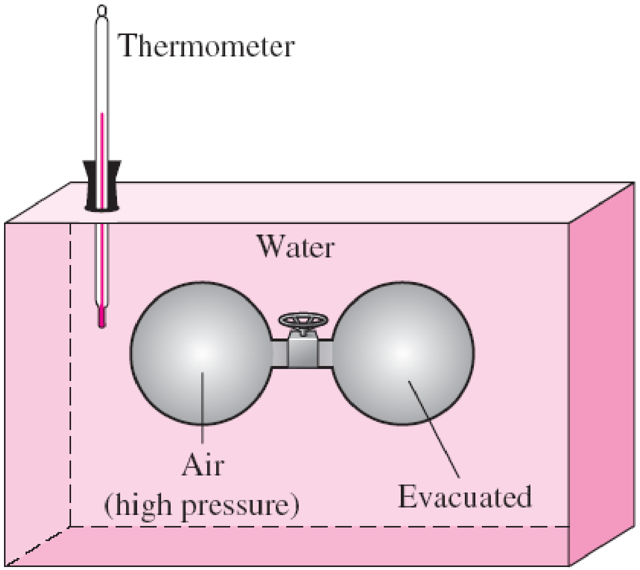


FIGURE 4–22
Schematic of the experimental apparatus used by Joule.

$$\left.\begin{aligned} h &= u + Pv \\ Pv &= RT \end{aligned}\right\} \quad h = u + RT$$

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

$$du = c_v(T)\,dT \qquad dh = c_p(T)\,dT$$

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T)\,dT$$

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T)\,dT$$

Internal energy and enthalpy change of an ideal gas

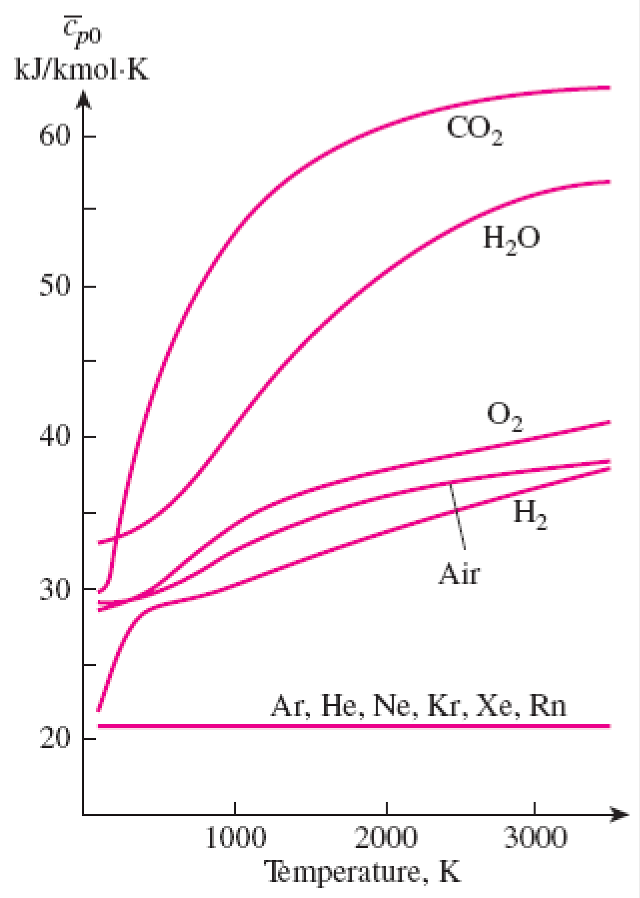
Joule showed using this experimental apparatus that $u=u(T)$

$$\boxed{\begin{aligned} u &= u(T) \\ h &= h(T) \\ c_v &= c_v(T) \\ c_p &= c_p(T) \end{aligned}}$$

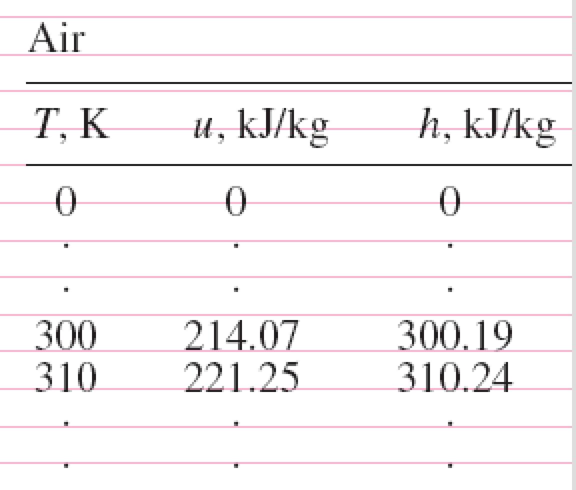
For ideal gases, u, h, c_v, and c_p vary with temperature only.

- 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.



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



Air

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

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

$$u_2 - u_1 = c_{v,\text{avg}}(T_2 - T_1)$$

$$h_2 - h_1 = c_{p,\text{avg}}(T_2 - T_1)$$

(kJ/kg)

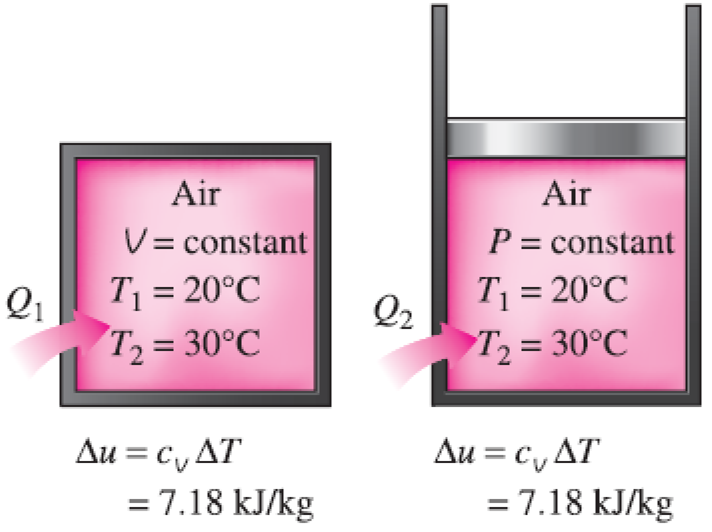


FIGURE 4–27

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

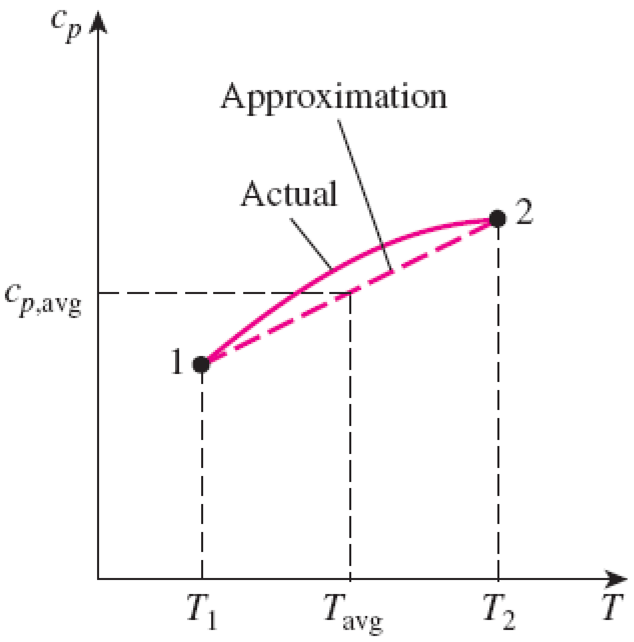
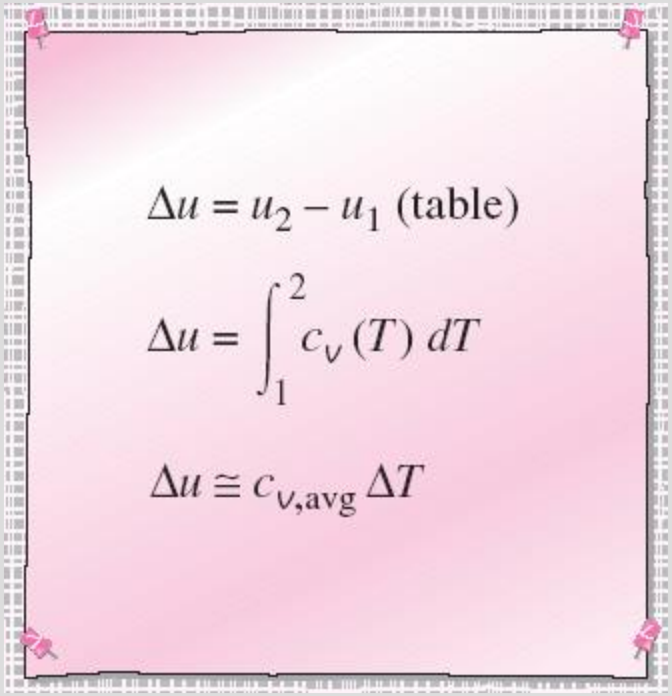


FIGURE 4–26

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

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

$$h = u + RT$$

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

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

$$\left.\begin{array}{l} h = u + RT \\ dh = du + R\,dT \\ dh = c_p dT \text{ and } du = c_v dT \end{array}\right\} \longrightarrow c_p = c_v + R$$

The relationship between c_p, c_v and R

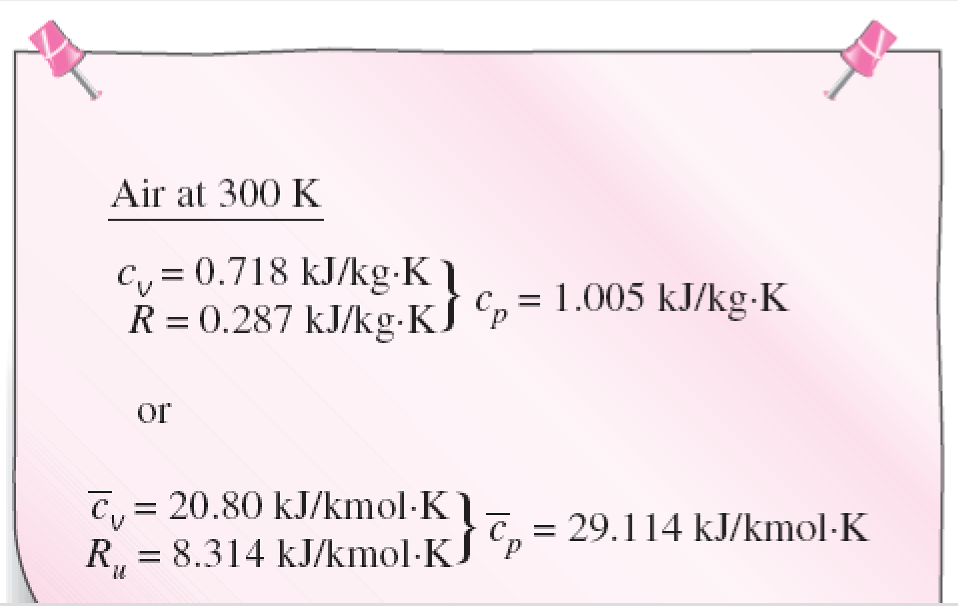
$$c_p = c_v + R \qquad (\text{kJ/kg}\cdot\text{K})$$

On a molar basis

$$\bar{c}_p = \bar{c}_v + R_u \qquad (\text{kJ/kmol}\cdot\text{K})$$

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

Specific heat ratio



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

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

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

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

INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEATS OF SOLIDS AND LIQUIDS

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

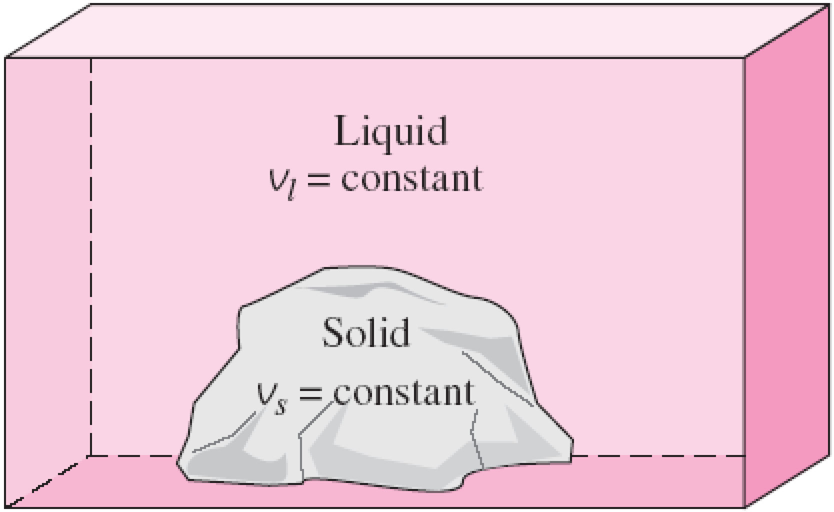


FIGURE 4–33
The specific volumes of incompressible substances remain constant during a process.

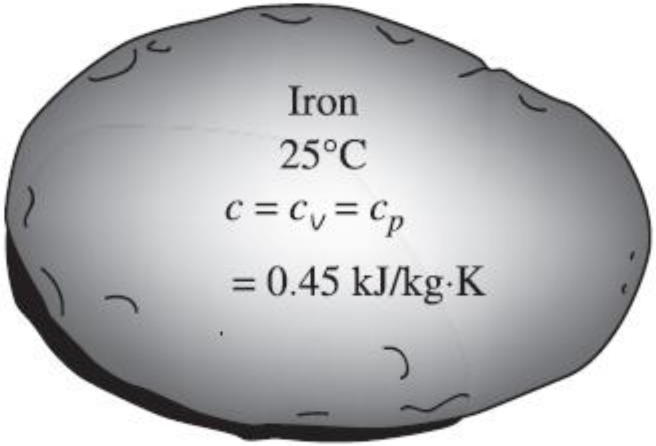


FIGURE 4–34
The c_v and c_p values of incompressible substances are identical and are denoted by c.

Internal Energy Changes

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

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

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

Enthalpy Changes

$$h = u + Pv$$

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

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

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

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

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

The enthalpy of a compressed liquid

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

Summary

- Moving boundary work
  - ✓ W_b for an isothermal process
  - ✓ W_b for a constant-pressure process
  - ✓ W_b for a polytropic process
- Energy balance for closed systems
  - ✓ Energy balance for a constant-pressure expansion or compression process
- Specific heats
  - ✓ Constant-pressure specific heat, c_p
  - ✓ Constant-volume specific heat, c_v
- Internal energy, enthalpy, and specific heats of ideal gases
  - ✓ Specific heat relations of ideal gases
- Internal energy, enthalpy, and specific heats of incompressible substances (solids and liquids)