

EQUILIBRIUM IN CHEMICAL REACTIONS

CHAPTER 12

Thermodynamic Processes and Thermochemistry

CHAPTER 13

Spontaneous Processes and Thermodynamic Equilibrium

CHAPTER 14

Chemical Equilibrium

CHAPTER 15

Acid-Base Equilibrium

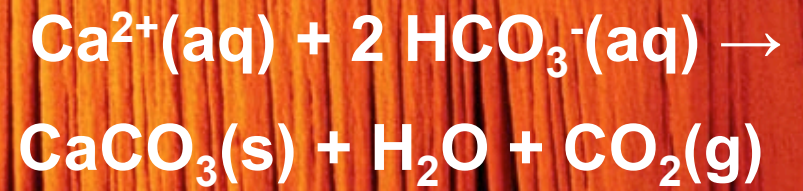
CHAPTER 16

Solubility and Precipitation Equilibria

CHAPTER 17

Electrochemistry

Stalactites (top) and stalagmites (bottom)



12

CHAPTER

THERMODYNAMIC PROCESSES AND THERMOCHEMISTRY

- 12.1** Systems, States, and Processes
- 12.2** The First Law of Thermodynamics:
Internal Energy, Work, and Heat
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- 12.4** The First Law and Ideal Gas Processes
- 12.5** Molecular Contributions to Internal Energy and
Heat Capacity
- 12.6** Thermochemistry
- 12.7** Reversible Processes in Ideal Gases

Steam locomotive

thermal \rightarrow mechanical



Diesel locomotive

chemical \rightarrow

electrical \rightarrow mechanical



Thermodynamics

- ✓ **Thermodynamics**: Gr. θερμη *therme*, meaning **heat**, and δυναμις *dynamis*, meaning **power**
- ✓ Study of transformation of energy from one form to another
- ✓ Phenomenological (*Macroscopic*)
- ✓ Cannot be derived or proved but summary of observations and experimentation ~ *operational*
- ✓ Universal
- ✓ Equilibrium thermodynamics → no change in time

▶ First law of thermodynamics:

Energy conservation

~ Black, Davy, Rumford, Mayer(1842),
Joule, Helmholtz

▶ Second law of thermodynamics:

Irreversibility or *Spontaneity*

~ Carnot, Clausius, Thomson (Lord Kelvin),
Boltzmann

▶ **Third law of thermodynamics:**

Unavailability of 0 K

~ Nernst, Planck

▶ **Zeroth law of thermodynamics:**

Concept of temperature

~ *Thermal equilibrium at contact*
(A,B,C)



➤ **A perpetual motion machine of 1st kind**

제1종 영구기관

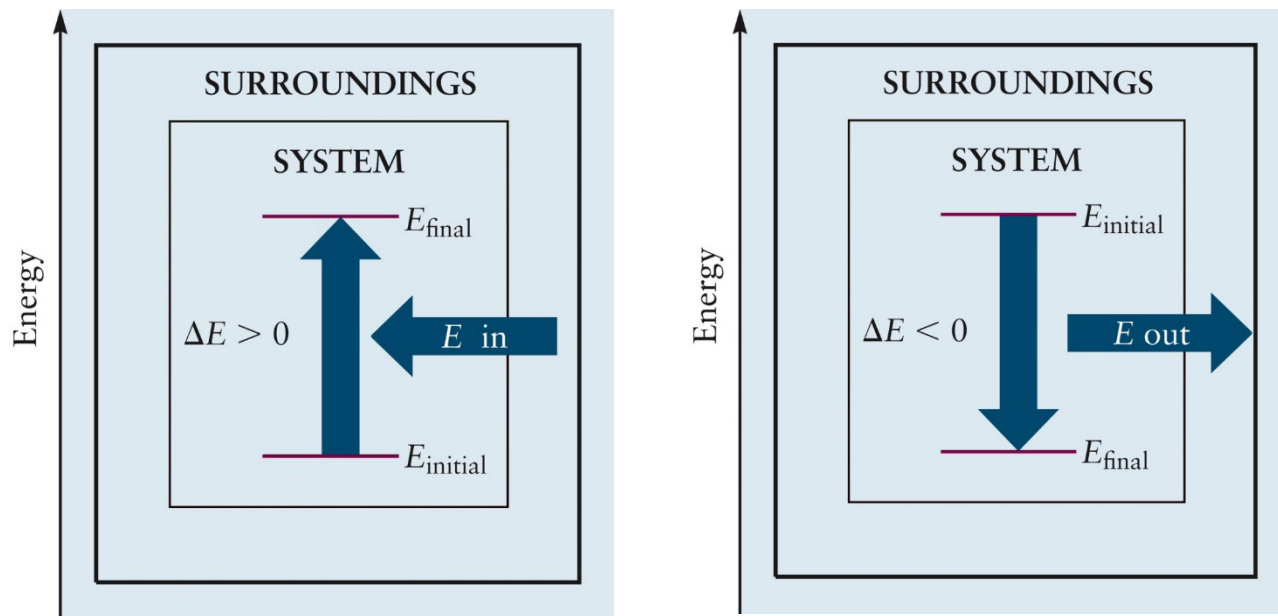
“Waterfall” (1961)

**by Maurice C. Escher
(1898-1972)
Dutch artist**



12.1 SYSTEMS, STATES, AND PROCESSES

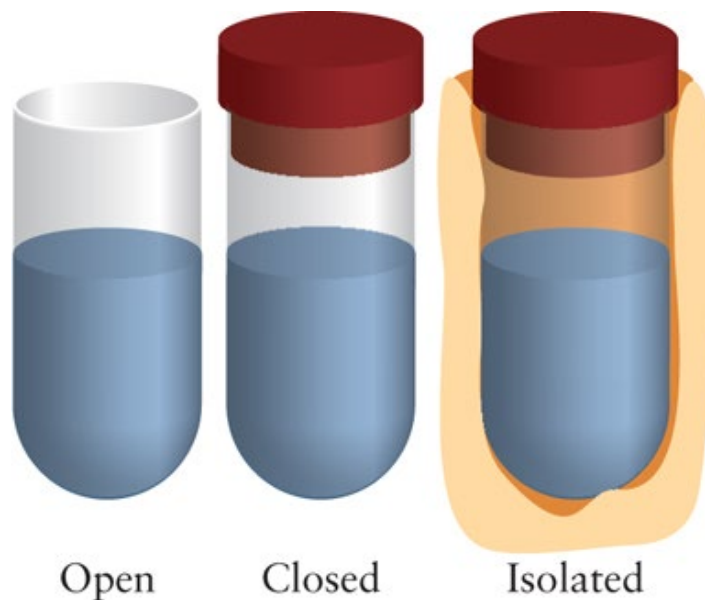
- ▶ **System** : Anything of our interest
- ▶ **Surroundings**: Everything else
- ▶ **Universe** = system + boundary + surroundings



The system gains energy from the surroundings.

The system loses energy to the surroundings.

- ▷ **Open system** : Exchange of both matter and heat with the surroundings
- ▷ **Closed system**: Exchange only heat
- ▷ **Isolated system**: Exchange nothing



7.1 Identify the following systems as open, closed, or isolated:

- (a) Coffee in a very high quality thermos bottle
- (b) Coolant in a refrigerator coil
- (c) A bomb calorimeter in which benzene is burned
- (d) Gasoline burning in an automobile engine
- (e) Mercury in a thermometer
- (f) A living plant

7.1 (a) isolated; (b) closed; (c) isolated; (d) open; (e) closed;
(f) open

◆ **Thermodynamic state** ~ A macroscopic condition of a system
 Properties uniquely determined at fixed values independent
 of time → Equilibrium state

◆ **Thermodynamic process**

~ leads to a change in the
 thermodynamic state along
 a *path* (physical and chemical
 processes)

- **Isotherm:** constant temperature
- **Isochore:** constant volume

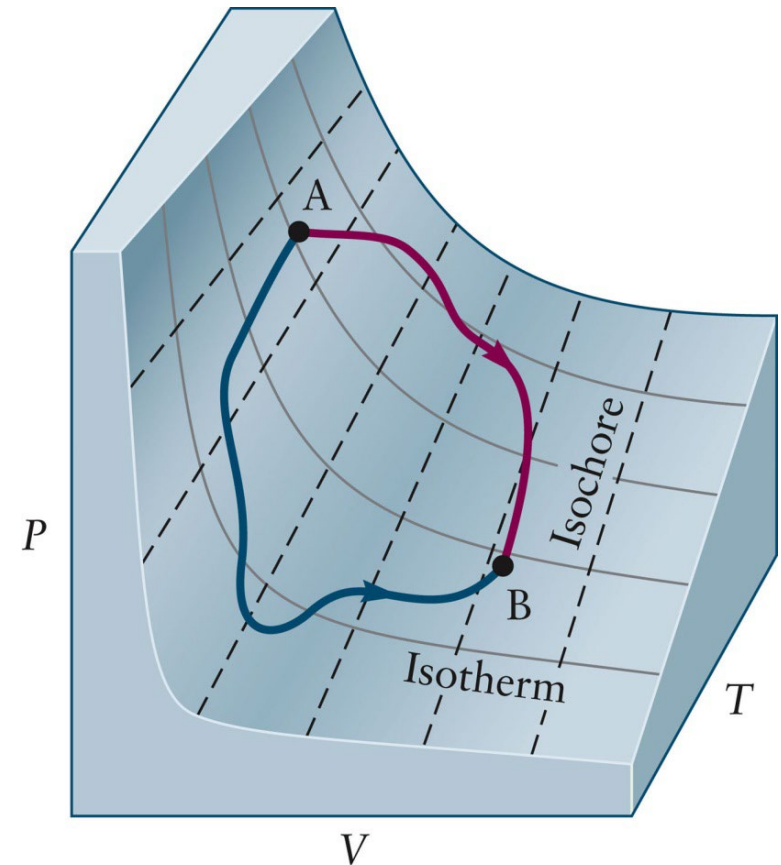


Fig. 12.1 P-V-T surface of 1 mol of ideal gas

◆ Reversible process

- ~ infinitesimal change in external conditions
- ~ a path on the equation-of-state surface → unique
- ~ a path along ideal equilibrium states
- ~ ideal, infinitesimally slow

◆ Irreversible process

- ~ abrupt, finite, real changes in external conditions
- ~ many irreversible paths between thermodynamic states

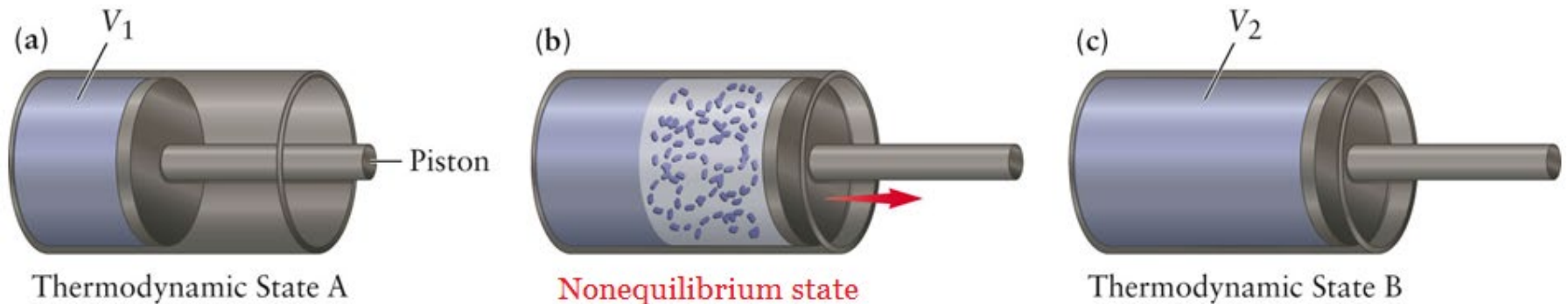


Fig. 12.2. Stages in an irreversible expansion of a gas from an initial state (a) of volume V_1 to a final state (c) with volume V_2 . In the intermediate stage (b)

Ge the system is not in equilibrium.



- Extensive property : m, V

→ A property that does depend on the size (extent) of the sample. *Additive property*: $m_{\text{tot}} = m_1 + m_2$

- Intensive property : P, T

→ A property that does not depend on the size of the sample.

★ State function : E, P, V, T, d, m, \dots

→ A property that depends only on the current state of the system and is independent of how that state was prepared.

★ Path function : w, q, \dots

→ A property that depends on the paths leading to the current state.

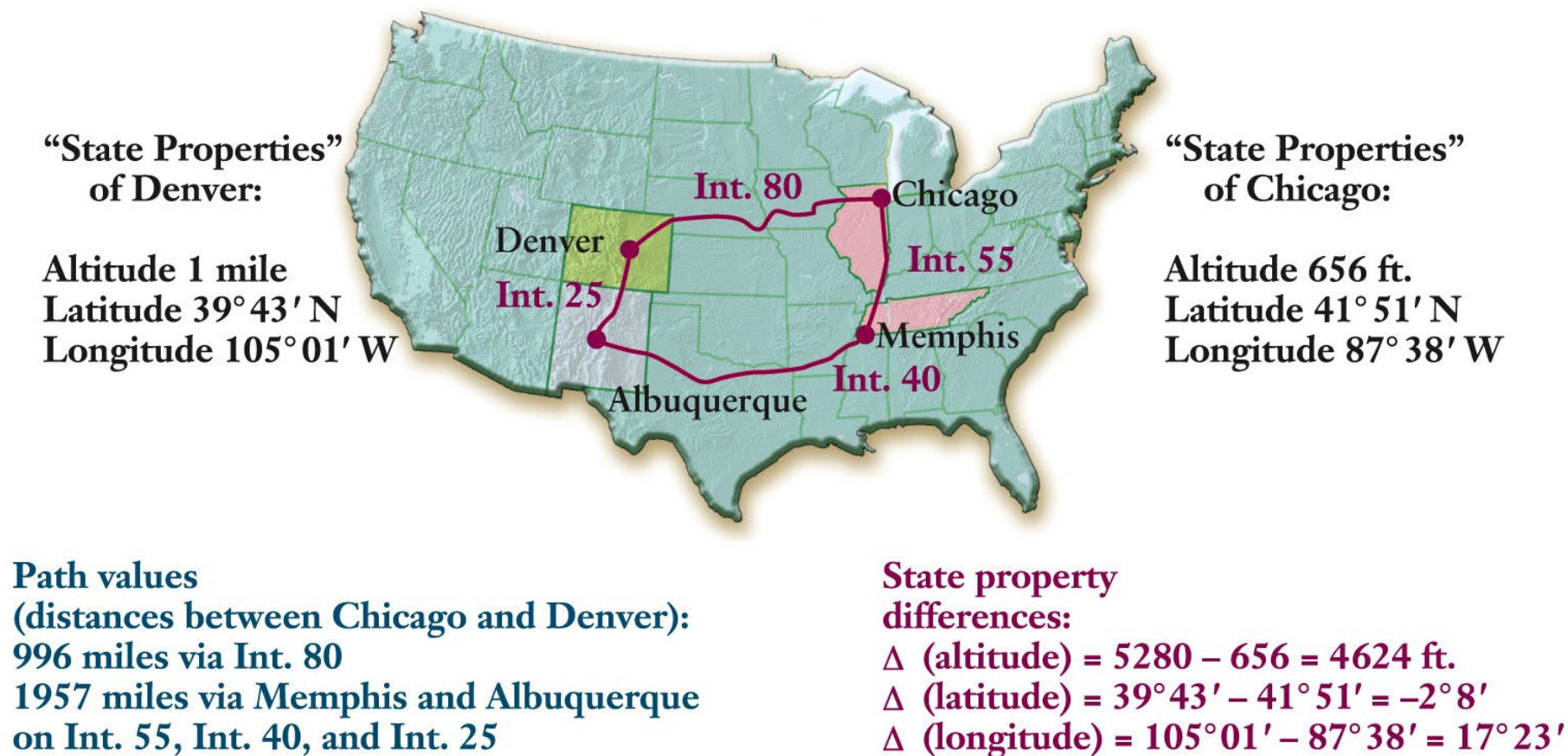


Fig. 12.3. Differences in state properties are independent of the path followed.

12.2 THE FIRST LAW OF THERMODYNAMICS: INTERNAL ENERGY, WORK, AND HEAT

◆ Work

➤ Mechanical work

$$w = F(r_f - r_i) \quad (\text{force along direction of path})$$

$$= Ma(r_f - r_i) = M \left(\frac{v_f - v_i}{t} \right) \left(\frac{v_i + v_f}{2} \right) t$$

$$= \frac{M}{2} v_f^2 - \frac{M}{2} v_i^2 = \Delta E_{kin} \quad (\text{Change in KE})$$

$$w = Mg(h_f - h_i) = Mg\Delta h = \Delta E_{pot} \quad (\text{Change in PE})$$

➤ Pressure-Volume Work (PV-work)

$$w = -F_{\text{ext}}(h_f - h_i) = -P_{\text{ext}} A\Delta h$$

$$w = -P_{\text{ex}} \Delta V$$

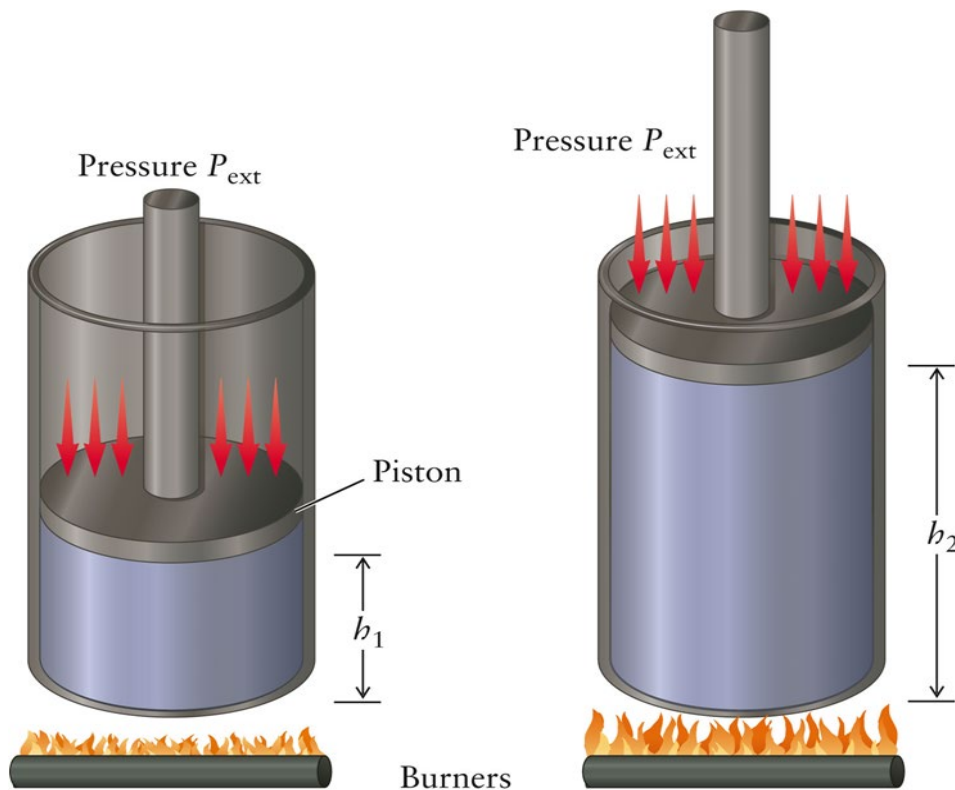


Fig. 12.4. As the gas inside is heated, it expands, pushing the piston against the pressure P_{ext} exerted by the gas outside.

Expansion: $\Delta V > 0 \rightarrow w < 0$ (system does work)

Compression: $\Delta V < 0 \rightarrow w > 0$ (work is done on the system)

7.3 Air in a bicycle pump is compressed by pushing in the handle. If the inner diameter of the pump is 3.0 cm and the pump is depressed 20 cm with a pressure of 2.00 atm,

- (a) how much work is done in the compression?
 (b) Is the work positive or negative with respect to the air in the pump?

7.3 (a) Work is given by $w = -P_{\text{ext}} \Delta V$. The applied external pressure is known, but we must calculate the change in volume given the physical dimensions of the pump and the distance, d , the piston in the pump moves:

$$\Delta V = -\pi r^2 d = \pi(1.5 \text{ cm})^2 (20. \text{ cm}) \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right) = -0.14 \text{ L}$$

ΔV is negative because the air in the pump is compressed to a smaller volume; work is then:

$$w = -(2.00 \text{ atm})(-0.14 \text{ L}) \left(\frac{101.325 \text{ L}}{\text{L} \cdot \text{atm}} \right) = 28 \text{ J}$$

(b) Work on the air is positive by convention as work is done on the air, it is compressed.

◆ Internal energy, U

~ Sum of KE, PE, bond energies of molecules in a system

◆ Heat (or thermal energy), q

~ Amount of energy transferred between two substances at different temperature

~ Changes the internal energy of a system

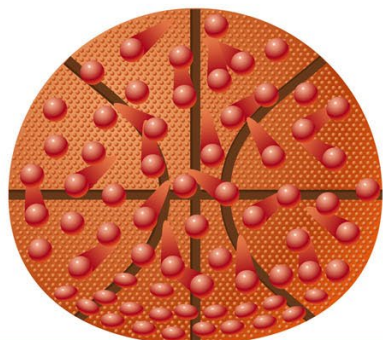
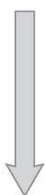
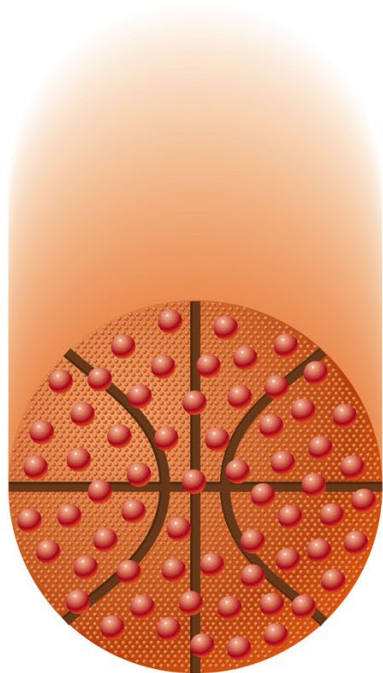


Fig. 12.5. Internal energy of a dropped ball increased. After the impact, the potential energy between the molecules is increased. As the ball bounces, the kinetic energy of the molecules increases.

◆ Measurement of amount of heat

➤ Ice calorimeter

~ Amount of heat transfer vs.
volume change of the bath
(ice-water)

System → Bath
decreases bath volume
Bath → System
increases bath volume

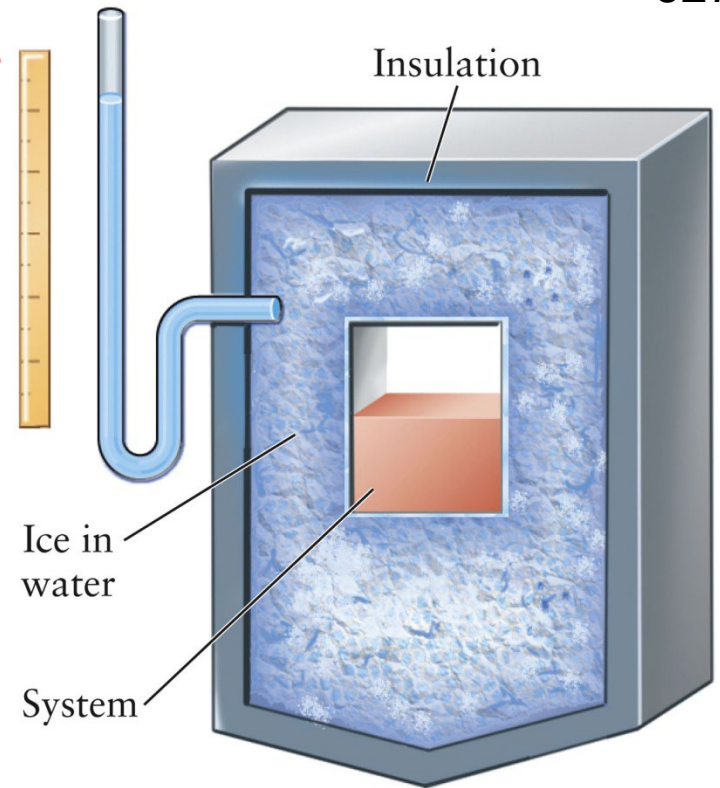


Fig. 12.6. Ice calorimeter

◆ Specific heat capacity, c_s

Amount of heat in raising temperature of 1 g of material by 1 °C

$$q = Mc_s \Delta T, \quad c_s = 1.00 \text{ cal K}^{-1} \text{ g}^{-1} \text{ for water at } 15 \text{ }^\circ\text{C}$$

◆ Equivalence of heat and work

➤ Thompson (later Count Rumford)

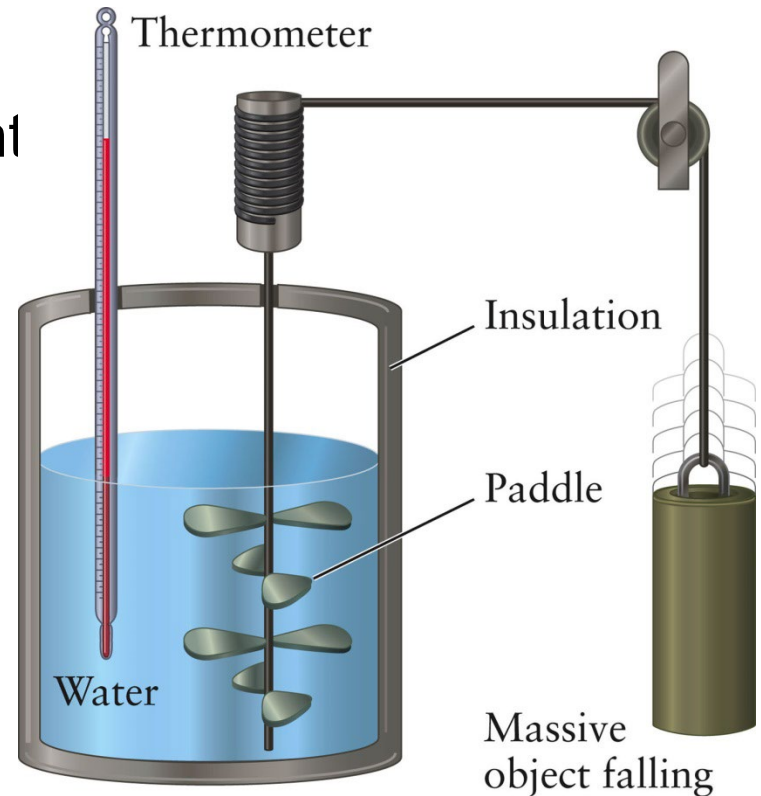
~ Cannon barrel

➤ Mayer and Joule

A paddle driven by a falling weight

$$1 \text{ cal} = 4.184 \text{ J}$$

Fig. 12.7. The falling weight turns a paddle, doing work on the system, increasing T .



Work (or Heat) is a transient form of energy

Work induces a concerted motion

Heat induces a random motion

◆ The First Law of Thermodynamics

➤ Principle of conservation of energy

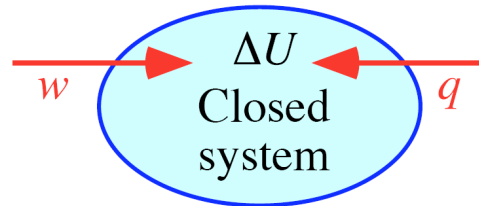
$$\Delta U = q + w$$

q , w : path functions, ΔU : state function

➤ **The first law of thermodynamics (closed system)**

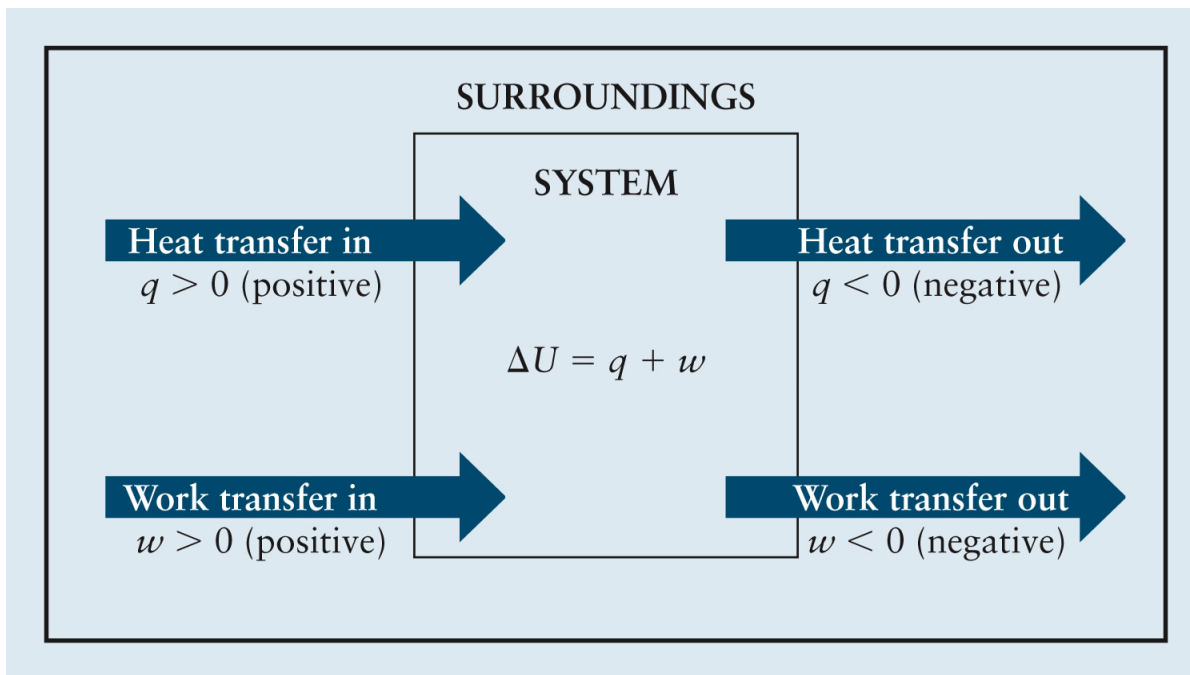
applicable to any process that begins and ends in equilibrium states

$$\Delta U = q + w$$



All the energies received turned into the energy of the system: **Energy conservation**

The total energy of an isolated system is constant.



Change in internal energy in a process is the sum of the heat transfer and the work transfer.

$$\begin{aligned}\Delta U_{\text{univ}} &= \Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0 \\ &= (q_{\text{sys}} + w_{\text{sys}}) + (q_{\text{surr}} + w_{\text{surr}}) \\ &= (q_{\text{sys}} + w_{\text{sys}}) + (-q_{\text{sys}} - w_{\text{sys}}) = 0\end{aligned}$$

7.5 A gas sample in a cylinder is supplied with 524 kJ of energy as heat. At the same time, a piston compresses the gas, doing 340 kJ of work. What is the change in internal energy of the gas during this process?

7.5 The change in internal energy ΔU is given simply by summing the two energy terms involved in this process. We must be careful, however, that the signs on the energy changes are appropriate. In this case, internal energy will be added to the gas sample by heating and through compression. Therefore the change in internal energy is:

$$\Delta U = 524 \text{ kJ} + 340 \text{ kJ} = 864 \text{ kJ}$$

12.3 HEAT CAPACITY, CALORIMETRY, AND ENTHALPY

◆ Heat Capacity and Specific Heat Capacity

➤ Heat capacity, C

Amount of energy to increase the temperature of the system by 1 K (Units of J K^{-1})

$$q = C\Delta T$$

➤ Molar heat capacity at constant volume, c_v

$$q_v = n c_v \Delta T$$

➤ Molar heat capacity at constant pressure, c_p

$$q_p = n c_p \Delta T$$

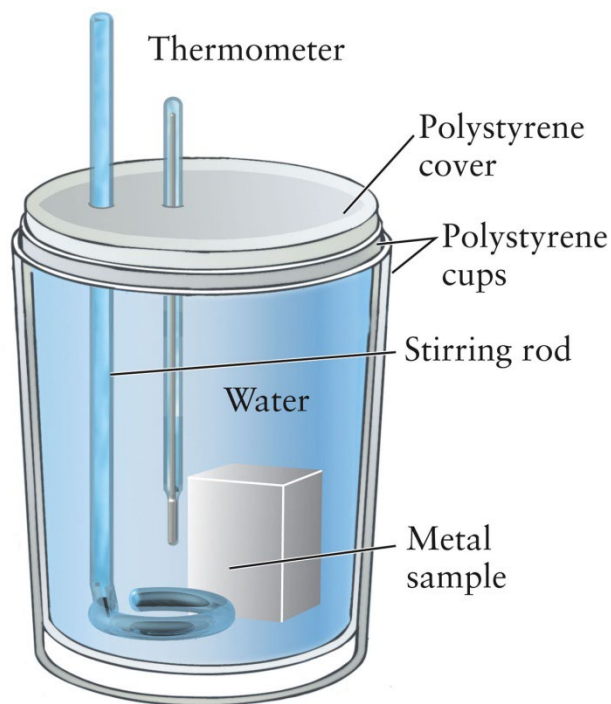


Fig. 12.8. A styrofoam cup calorimeter.

T A B L E 12.1

**Specific Heat Capacities at
Constant Pressure (at 25°C)**

Substance	Specific Heat Capacity ($\text{J K}^{-1} \text{g}^{-1}$)
$\text{Hg}(\ell)$	0.140
$\text{Cu}(s)$	0.385
$\text{Fe}(s)$	0.449
$\text{SiO}_2(s)$	0.739
$\text{CaCO}_3(s)$	0.818
$\text{O}_2(g)$	0.917
$\text{H}_2\text{O}(\ell)$	4.18

- If C_V and C_P do not change with temperature,

$$q_V = nC_{V,m} \Delta T$$

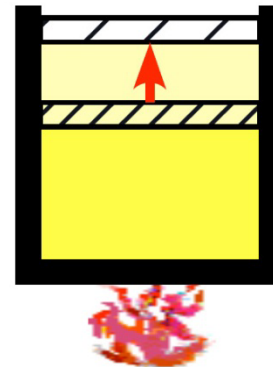
$$q_P = nC_{P,m} \Delta T$$

Constant volume



$$q_V = nC_{V,m} \Delta T$$

$$q_V < q_P$$



Constant pressure

$$q_P = nC_{P,m} \Delta T$$

◆ Heat Transfer at
Constant Volume:
Internal Energy

$$q_V = \Delta U \quad (\text{constant } V)$$

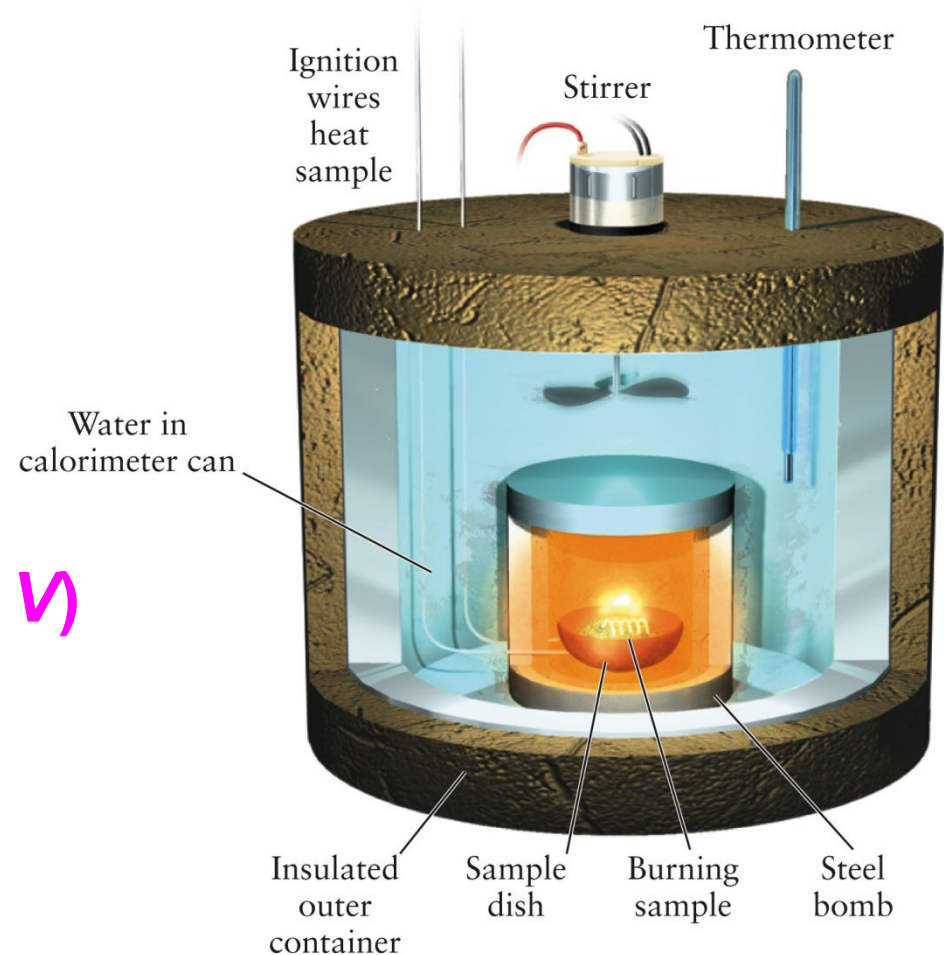


Fig. 12.9. The combustion calorimeter, called a “bomb calorimeter”.

◆ Heat Transfer at Constant Pressure: Enthalpy

$$\Delta U (= q_V) = q_P + w = q_P - P_{\text{ext}} \Delta V$$

Assume that $P_{\text{ext}} = P$ (internal pressure)

$$\Delta U = q_P - P \Delta V$$

$$q_P = \Delta U + P \Delta V = \Delta(U + PV) \equiv \Delta H$$

Enthalpy, H $H = U + PV$

$$\Delta H = q_P = \Delta U + P \Delta V \quad (\text{at constant } P)$$

$$\Delta H = \Delta U + \Delta(PV) \quad (\text{in general})$$

12.4 THE FIRST LAW AND IDEAL GAS PROCESSES

◆ Heat Capacities of Ideal Gases

Kinetic energy of an n mol of ideal gas

$$E_{\text{kin}} = (3/2) nRT \rightarrow \Delta U = (3/2)nR \Delta T \quad (1)$$

At constant volume, $w = -P\Delta V = 0$.

$$\Delta U = q_V = nc_V \Delta T \quad (\text{ideal gas}) \quad (2)$$

Compare (1) and (2).

$$c_V = (3/2)R \quad (\text{monatomic ideal gas})$$

9.5 THE KINETIC THEORY OF GASES

➤ **mean-square speed** $PV = \frac{1}{3}Nm\overline{u^2}$ $P = \frac{Nm\overline{u^2}}{3V}$

$$PV = \frac{1}{3}Nm\overline{u^2} = nRT \qquad \frac{1}{3}N_A m\overline{u^2} = RT$$

- Kinetic energy of N_A molecules, $\overline{E} = \frac{1}{2}N_A m\overline{u^2} = \frac{3}{2} \times \left(\frac{1}{3}N_A m\overline{u^2}\right) = \frac{3}{2}RT$

- **average kinetic energy per molecule**, $\overline{\epsilon} = \frac{3}{2}k_B T$ $k_B = R/N_A$

- **root-mean-square speed** $\overline{u^2} = \frac{3RT}{M}$ $u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$

$M = \text{molar mass} = N_A m$

At constant pressure,

$$\Delta U = q_p + w$$

$$[\Delta U = nc_V \Delta T, q_p = nc_p \Delta T, w = -P\Delta V]$$

$$nc_V \Delta T = nc_p \Delta T - P(V_2 - V_1)$$

$$nc_V \Delta T = nc_p \Delta T - nR \Delta T \quad (PV_i = nRT_i)$$

$$c_p = c_V + R \quad (\text{any ideal gas})$$

$$\Delta U = nc_V \Delta T \quad (\text{any ideal gas})$$

$$\Delta H = nc_p \Delta T \quad (\text{ideal gas})$$

◆ Heat and Work for Ideal Gases

Along the path $A \rightarrow C \rightarrow B$,

$$w_{AC} = -P_{\text{ext}}\Delta V = -P_A(V_B - V_A)$$

$$w_{CB} = 0$$

$$\begin{aligned} w_{ACB} &= w_{AC} + w_{CB} = -P_A(V_B - V_A) \\ &= -40.0 \text{ L atm} = -4050 \text{ J} \end{aligned}$$

$$\begin{aligned} q_{AC} &= q_p = nc_p\Delta T = (5/2)nR(T_C - T_A) \\ &= (5/2)(P_C V_C - P_A V_A) \end{aligned}$$

$$\begin{aligned} q_{CB} &= q_v = nc_v\Delta T = (3/2)nR(T_B - T_C) \\ &= (3/2)(P_B V_B - P_C V_C) \end{aligned}$$

$$\begin{aligned} q_{ACB} &= q_{AC} + q_{CB} \\ &= (5/2)(P_C V_C - P_A V_A) + (3/2)(P_B V_B - P_C V_C) \\ &= 5570 \text{ J} \end{aligned}$$

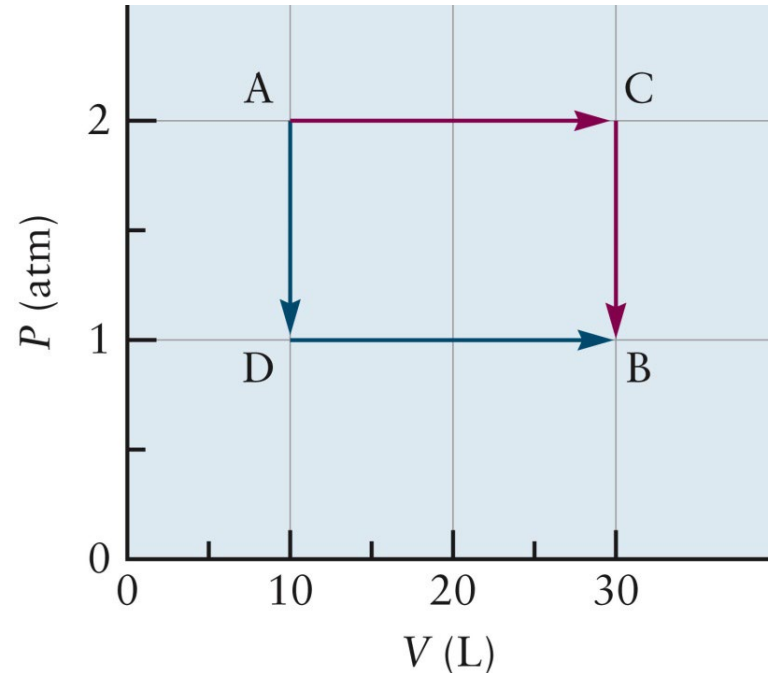


Fig. 12.10. Two different processes between the states A and B.

$$\Delta U = w_{ACB} + q_{ACB} = (-4050 + 5570) \text{ J} \\ = 1520 \text{ J}$$

State function ΔU is independent of paths

Similarly, along the path $A \rightarrow D \rightarrow B$,

$$w_{ADB} = -2030 \text{ J}$$

$$q_{ADB} = 3550 \text{ J}$$

$$\Delta U = w_{ADB} + q_{ADB} = (-2030 + 3550) \text{ J} \\ = 1520 \text{ J}$$

$$1 \text{ L atm} = 101.3 \text{ J (exact)}$$

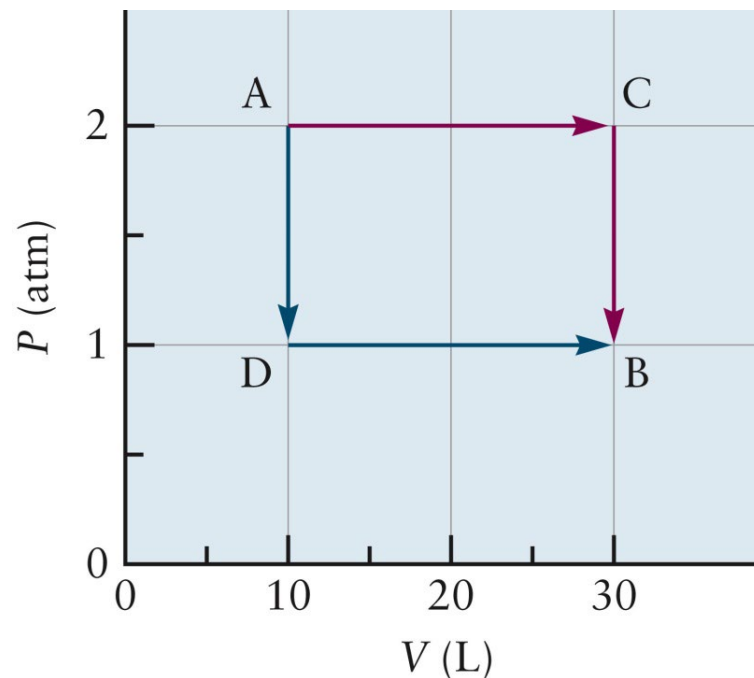


Fig. 12.10. Two different processes between the states A and B.

12.5 MOLECULAR CONTRIBUTIONS TO INTERNAL ENERGY AND HEAT CAPACITY

◆ Kinetic theory of matter

→ Bridge between thermodynamics and mechanics of molecules

➤ Total kinetic energy in n moles of an ideal gas:

$$E_{\text{kin}} = \left(\frac{3}{2}\right)nRT$$

→ Internal energy of a monatomic gas

➤ Molar heat capacity of a monatomic ideal gas

$$c_p = c_v + R = \frac{3}{2}R + R = \frac{5}{2}R = 20.785 \text{ J mol}^{-1}\text{K}^{-1}$$

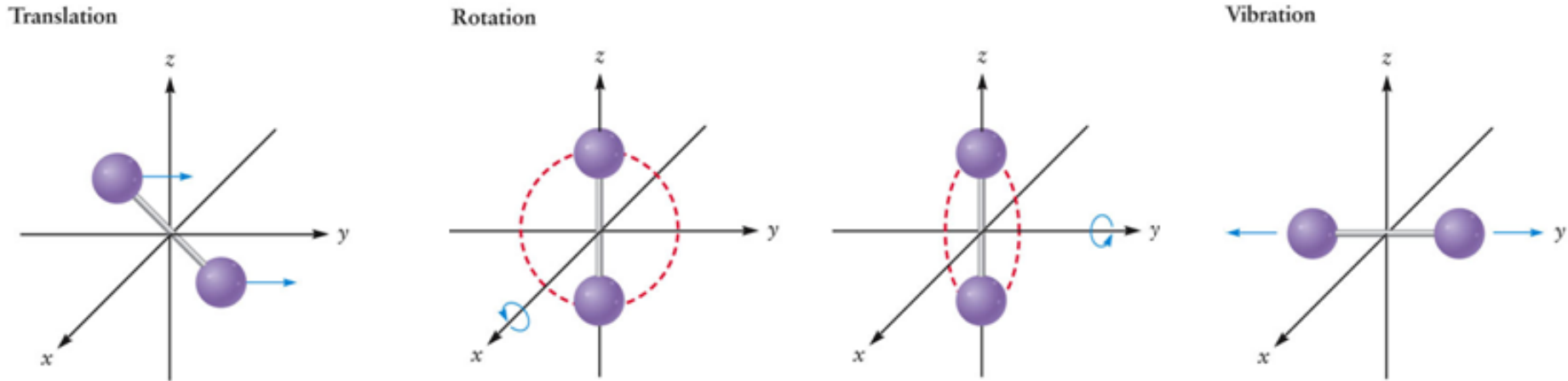
→ Good agreement with experiments!

TABLE 12.2

Measured Values of c_p
for Selected Gases at 298 K
and 1 atm Pressure

Gas	c_p (J mol ⁻¹ K ⁻¹)
He	20.79
Ne	20.79
Ar	20.79
H ₂	28.81
O ₂	29.36
F ₂	31.30
H ₂ O	33.54

➤ Diatomic molecules



⊙ 3 translational degrees of freedom: x -, y -, z -directions, $E_{\text{trans}} = \frac{1}{2} M v^2$

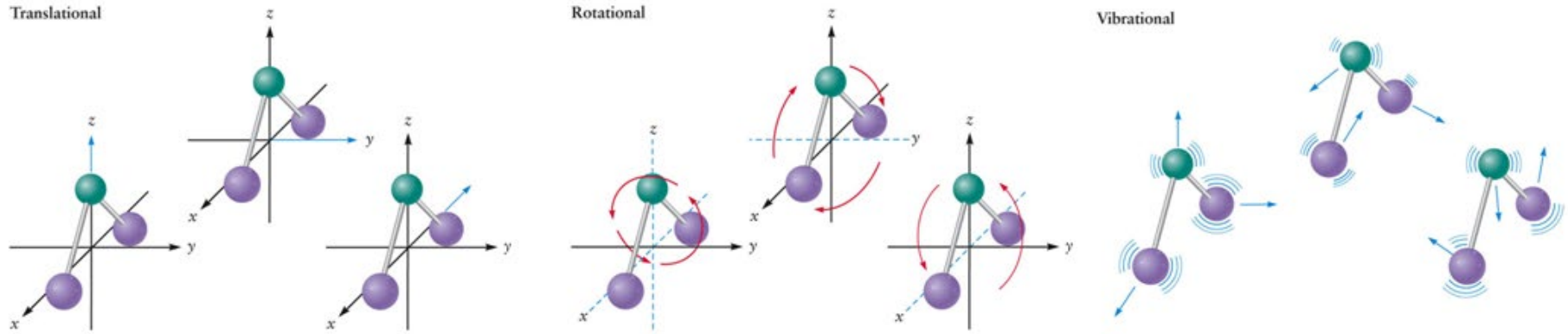
⊙ 2 rotational degrees of freedom: z - y , z - x planes, $E_{\text{rot}} = \frac{1}{2} I \omega^2$

I : moment of inertia, ω : angular velocity

⊙ 1 vibrational degree of freedom: Along y -axis,

$$(PE)_{\text{vib}} = \frac{1}{2} k (R_{\text{AB}} - R_e)^2 \text{ and } (KE)_{\text{vib}} = \frac{1}{2} \left(\frac{dR_{\text{AB}}}{dt} \right)^2, R_e: \text{equilibrium bond length}$$

➤ Polyatomic molecules



$$K_N = K_{\text{trans}} + K_{\text{rot}} + K_{\text{vib}}$$

- ⊙ Translational degrees of freedom: **3** (motion of the center of mass)
- ⊙ Rotational degrees of freedom: **3 (nonlinear-)**, **2 (linear-)** molecule
- ⊙ Vibrational degrees of freedom: **$3N - 6$ (nonlinear)** or **$3N - 5$ (linear)**

Total degrees of freedom of N atoms of a molecule: **$3N$**

Subtract the degrees of freedom for translation (**3**) and rotation (**3** or **2**)

◆ **Equipartition theorem** ← classical concept

Each quadratic term that appears in the energy of a molecule contributes $RT/2$ to the average energy calculated from the Maxwell-Boltzmann distribution.

➤ Contributions to internal energy of a molecule:

Each translational degree of freedom: $RT/2$

Each rotational degree of freedom: $RT/2$

Each vibrational degree of freedom: (only for high T)

$$RT \leftarrow KE\left(\frac{1}{2}mv^2\right) + PE\left(\frac{1}{2}kx^2\right)$$

➤ Contribution of each mode to the heat capacities

$$c_v \text{ and } c_p (= c_v + R) \rightarrow \text{Table 12.3}$$

T A B L E 12.3

Contributions to Heat Capacity Estimated by the Equipartition Theorem

Molecule	Degrees of Freedom				Equipartition Values (R)		Values of c_p ($J mol^{-1} K^{-1}$)	
	f_{tot}	f_{tran}	f_{rot}	f_{vib}	c_V	c_p	Calculated	Measured
Ar	3	3	0	0	$3/2$	$5/2$	20.79	20.79
H ₂	6	3	2	1	$7/2$	$9/2$	37.41	28.81
N ₂	6	3	2	1	$7/2$	$9/2$	37.41	29.12
O ₂	6	3	2	1	$7/2$	$9/2$	37.41	29.36
F ₂	6	3	2	1	$7/2$	$9/2$	37.41	31.30
Cl ₂	6	3	2	1	$7/2$	$9/2$	37.41	33.91
Br ₂	6	3	2	1	$7/2$	$9/2$	37.41	36.02
CO	6	3	2	1	$7/2$	$9/2$	37.41	29.12
CO ₂	9	3	2	4	$13/2$	$15/2$	62.37	37.13
H ₂ O	9	3	3	3	$12/2$	$14/2$	58.18	33.54
CH ₄	15	3	3	9	$24/2$	$26/2$	108.08	35.31
C ₂ H ₄	18	3	3	12	$30/2$	$32/2$	133.02	43.56
Si	3	0	0	3	$6/2$	$\sim 6/2$	24.94	20.0
Al	3	0	0	3	$6/2$	$\sim 6/2$	24.94	24.35

➤ Temperature dependence of contributions of each modes to c_p

□ Translation:

$5R/2$ at all temperatures above 0 K

□ Rotation for H_2 :

Begins at low temperature

Reaches its equipartition value R

at room temperature

□ Translation + Rotation for H_2 : $7R/2$

□ Vibration in H_2 , N_2 , O_2 :

Contributes only above room temp.

□ Equipartition value for T+R+V, $9R/2$

(= $37.41 \text{ J mol}^{-1} \text{ K}^{-1}$) reached at high T .

Equipartition values do not agree with measured values at low temperature.
→ Quantum mechanical effect

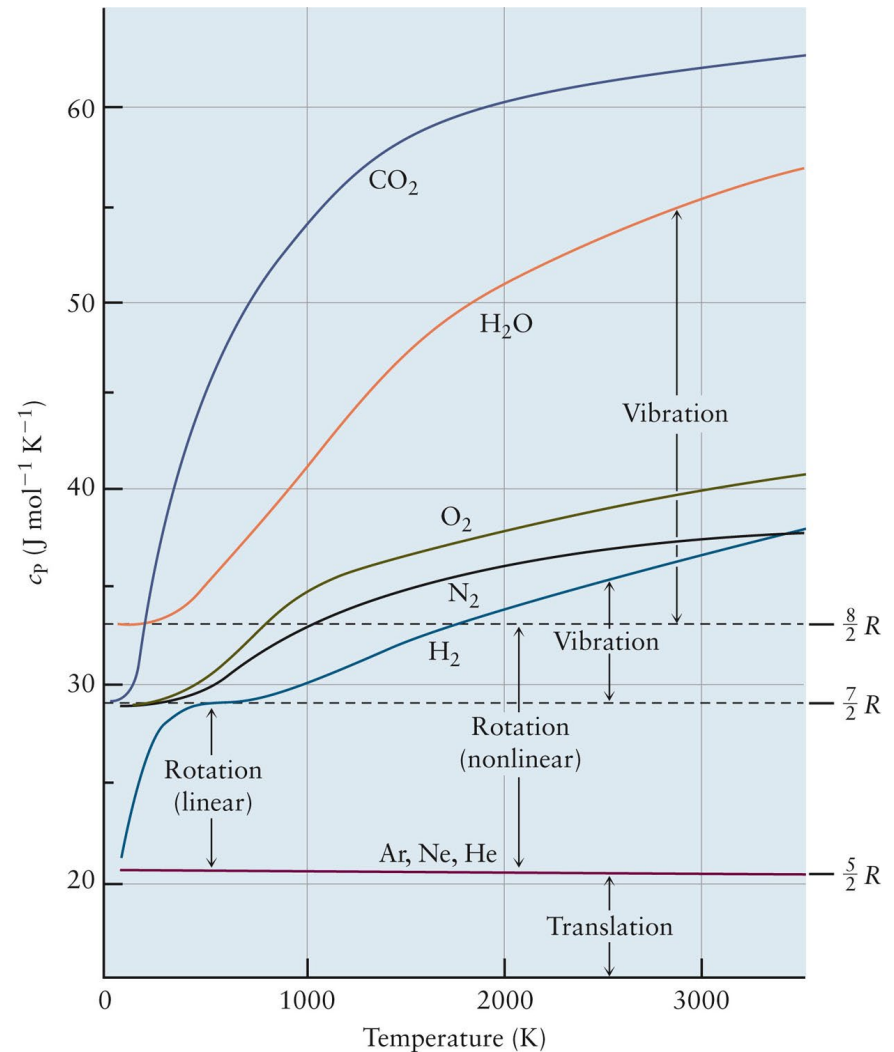


Fig. 12.12. Temperature dependence of c_p for several gases.

◆ Heat capacities for solids

➤ Dulong-Petit's law (1820):

$c_v = 3R$ ($= 24.9 \text{ J K}^{-1}$) for elemental solids at room temp

Classical 3D spring model for atoms in solid

→ 3 vibrational modes for each atom → 6 quadratic terms in PE & KE

→ $6R/2 = 3R$ to c_v

Low values for c_v at low temperatures → QM effect!

⊙ Einstein (1907) ~ Planck's hypothesis for harmonic oscillators

→ Predicted low values of c_v at low temperature

⊙ Debye (1912) ~ Modified Einstein's theory, better agreement with

experiment, c_v approaches 0 as a T^3 -power law

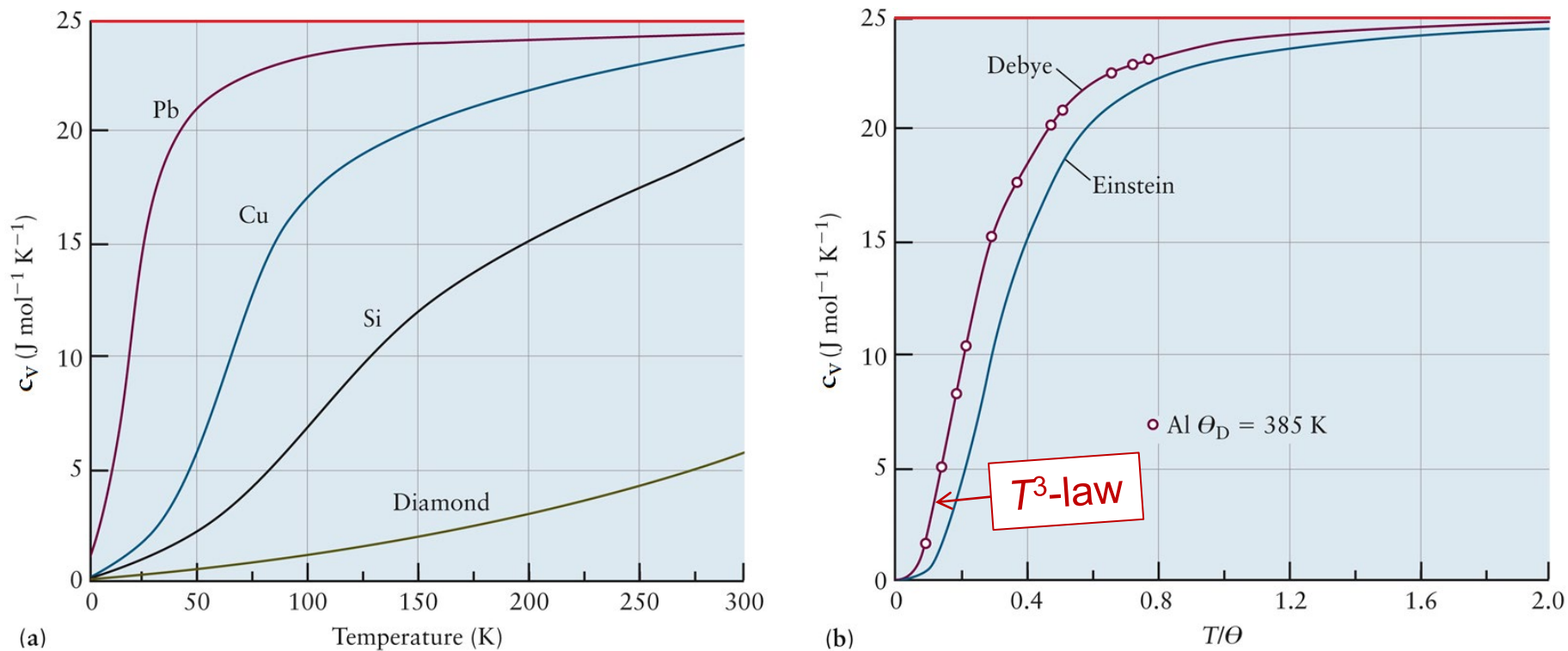


Fig. 12.13. Temperature dependence of c_v for solids. (a) Measured values for elemental solids. (b) Debye and Einstein models for c_v for Al.

7.25 Which molecular substance do you expect to have the higher molar heat capacity, NO or NO₂? Why?

7.25 NO₂. The heat capacity increases with molecular complexity—as more atoms are present in the molecule, there are more possible bond vibrations that can absorb added energy.

12.6 THERMOCHEMISTRY

◆ Thermochemistry

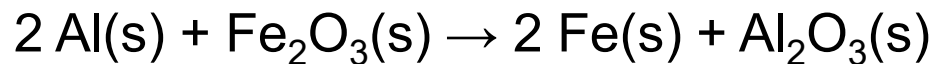
- ~ Study effects of **Heat** given off or taken up during a chemical reaction
- ~ Usually at constant pressure (1 atm)
 - Heat (or Enthalpy) of reaction, $q_P = \Delta H$

$$q_P = \Delta H = H_f - H_i = H_{\text{products}} - H_{\text{reactants}} = \Delta H_{\text{reaction}}$$

Exothermic: $\Delta H_{\text{reaction}} < 0$

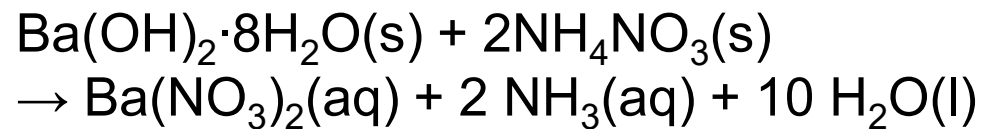
Endothermic: $\Delta H_{\text{reaction}} > 0$

◆ Exothermic Reaction



Ge
(b)

◆ Endothermic Reaction



(b)

◆ Hess's Law

When chemical equations are added, the corresponding enthalpies are also added.

← *Enthalpy is an extensive quantity and a state function.*

Ex. Calculate the heat of reaction that is difficult to measure.

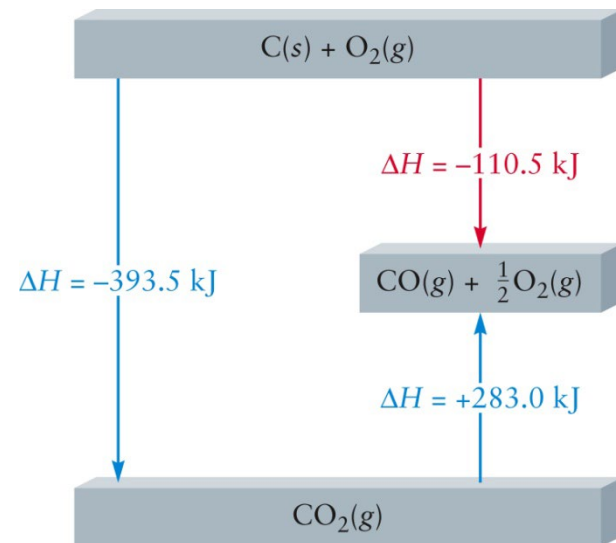
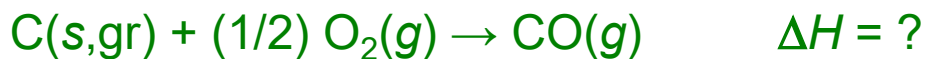
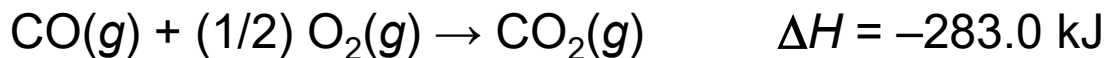
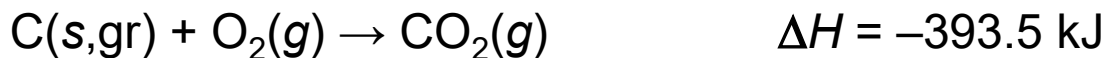
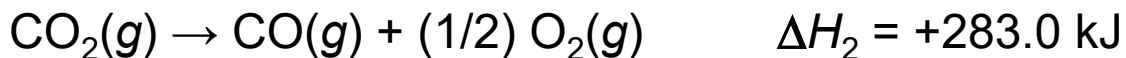
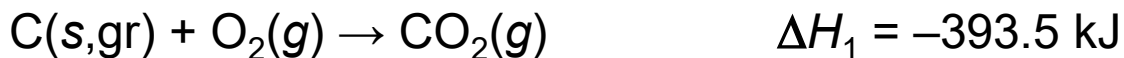
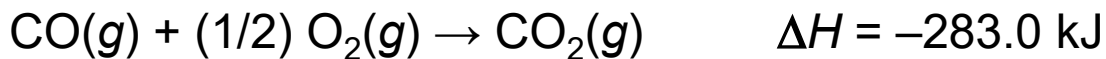
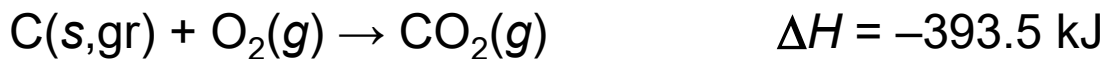
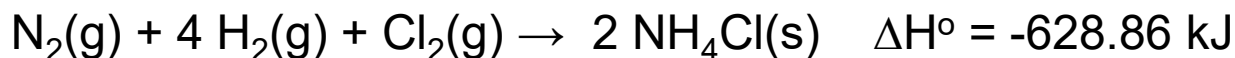
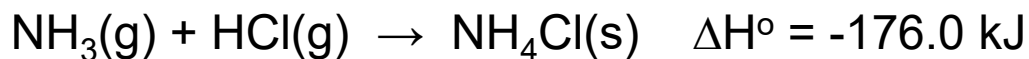


Fig. 12.17 Hess's law.



7.67 Calculate the reaction enthalpy for the synthesis of hydrogen chloride gas, $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$, from the following data:



◆ Enthalpy of phase change at constant T & P



T A B L E 12.4

Enthalpy Changes of Fusion and Vaporization[†]

Substance	ΔH_{fus} (kJ mol ⁻¹)	ΔH_{vap} (kJ mol ⁻¹)
NH ₃	5.650	23.35
HCl	1.992	16.15
CO	0.836	6.04
CCl ₄	2.500	30.00
H ₂ O	6.007	40.66
NaCl	28.800	170.00

†The enthalpy changes are measured at the normal melting point and the normal boiling point, respectively.

7.37 How much heat is needed to convert 80.0 g of ice at 0.0 °C into liquid water at 20.0 °C?

7.37 This process is composed of two steps: melting the ice at 0°C and then raising the temperature of the liquid water from 0°C to 25°C :

$$\text{Step 1: } \Delta H = \left(\frac{80.0 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} \right) (6.01 \text{ kJ} \cdot \text{mol}^{-1}) = 26.7 \text{ kJ}$$

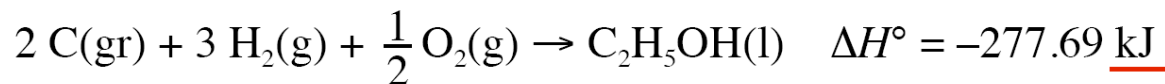
$$\text{Step 2: } \Delta H = (80.0 \text{ g})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(20.0\text{°C} - 0.0\text{°C}) = 6.69 \text{ kJ}$$

$$\text{Total heat required} = 26.7 \text{ kJ} + 6.69 \text{ kJ} = 33.4 \text{ kJ}$$

◆ Standard-State Enthalpies

- **Standard states** at a specified temperature (usually at 25°C)
 - liquids, solids ~ thermodynamically stable states at 1 atm
 - gases ~ at 1 atm, exhibiting ideal gas behavior
 - dissolved species ~ 1 M at 1 atm, exhibiting ideal solution behavior
- **Standard enthalpy of formation ΔH_f°** of a compound (Appendix D)
 - ~ Enthalpy change of the formation reaction from its **elements** in their **stable states** at **25 °C, 1 atm, per mole**





$$\Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH}(\text{l})) = -277.69 \text{ kJ/mol}$$



$$\Delta H_f^\circ(\text{C}(\text{gr})) = 0 \text{ kJ/mol}; \quad \text{most stable element}$$

$$\Delta H_f^\circ(\text{C}(\text{dia})) = +1.9 \text{ kJ/mol}$$

- Standard Enthalpies of Formation at 25 °C (kJ·mol⁻¹) (Appendix D)

Substance	Formula	ΔH_f°	Substance	Formula	ΔH_f°
Inorganic compounds			Organic compounds		
ammonia	NH ₃ (g)	-46.11	benzene	C ₆ H ₆ (l)	+49.0
carbon dioxide	CO ₂ (g)	-393.51	ethanol	C ₂ H ₅ OH(l)	-277.69
carbon monoxide	CO(g)	-110.53	ethyne	C ₂ H ₂ (g)	+226.73
dinitrogen tetroxide	N ₂ O ₄ (g)	+9.16	(acetylene)		
hydrogen chloride	HCl(g)	-92.31	glucose	C ₆ H ₁₂ O ₆ (s)	-1268
hydrogen fluoride	HF(g)	-271.1	methane	CH ₄ (g)	-74.81
nitrogen dioxide	NO ₂ (g)	+33.18			
nitric oxide	NO(g)	+90.25			
sodium chloride	NaCl(s)	-411.15			
water	H ₂ O(l)	-285.83			
	H ₂ O(g)	-241.82			

◆ Standard enthalpy change of reaction



$$\Delta H^\circ = c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D) - a\Delta H_f^\circ(A) - b\Delta H_f^\circ(B)$$

$$\Delta H^\circ = \sum_{i=1}^{prod} n_i \Delta H_i^\circ - \sum_{j=1}^{react} n_j \Delta H_j^\circ$$

◆ Bond enthalpy

~ Enthalpy when a bond is broken in the **gas** phase

Bond enthalpy of a C—H bond in $\text{CH}_4(g)$ ~ measured

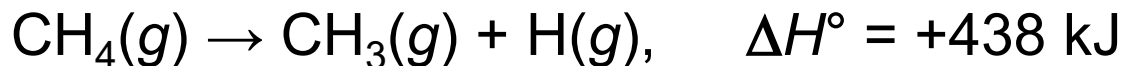


TABLE 12.5

Average Bond Enthalpies

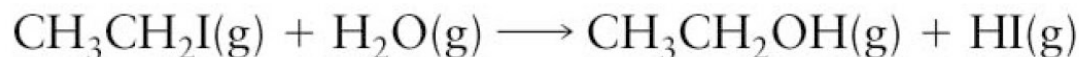
	Molar Enthalpy of Atomization (kJ mol ⁻¹)‡	Bond Enthalpy (kJ mol ⁻¹)†								
		H—	C—	C=	C≡	N—	N=	N≡	O—	O=
H	218.0	436	413			391			463	
C	716.7	413	348	615	812	292	615	891	351	728
N	472.7	391	292	615	891	161	418	945		
O	249.2	463	351	728					139	498
S	278.8	339	259	477						
F	79.0	563	441			270			185	
Cl	121.7	432	328			200			203	
Br	111.9	366	276							
I	106.8	299	240							

†From Appendix D.

‡Data from L. Pauling. *The Nature of the Chemical Bond*, 3rd ed. Ithaca, NY: Cornell University Press, 1960.

EXAMPLE 7.14

Estimate the enthalpy of the reaction between gaseous iodoethane and water vapor:



- Breaking the bonds

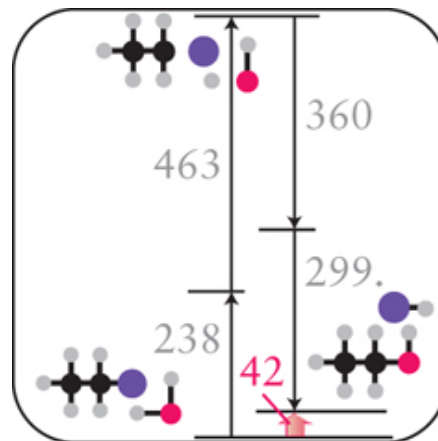
$$\Delta H_{\text{B}}^{\circ}(\text{C-I}) + \Delta H_{\text{B}}^{\circ}(\text{O-H}) = \Delta H^{\circ} = 238 + 463 \text{ kJ} = +701 \text{ kJ}$$

- Forming the bonds

$$\Delta H_{\text{B}}^{\circ}(\text{C-O}) + \Delta H_{\text{B}}^{\circ}(\text{H-I}) = \Delta H^{\circ} = 360 + 299 \text{ kJ} = +659 \text{ kJ}$$

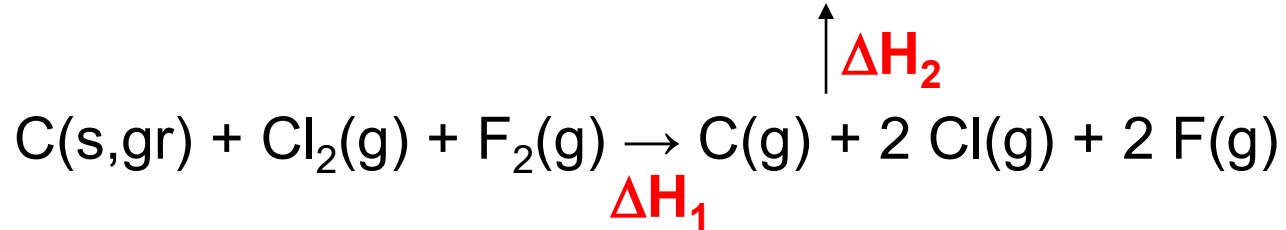
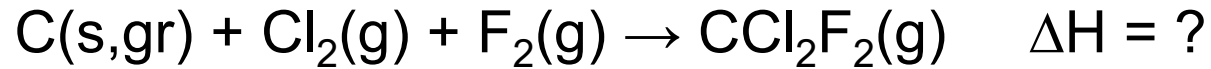
- The overall enthalpy change:

$$\Delta H^{\circ} = 701 + (-659) \text{ kJ} = +42 \text{ kJ}$$



EXAMPLE 12.9

$$\Delta H_f^\circ(\text{CCl}_2\text{F}_2(\text{g})) = ? \quad \text{Freon-12}$$



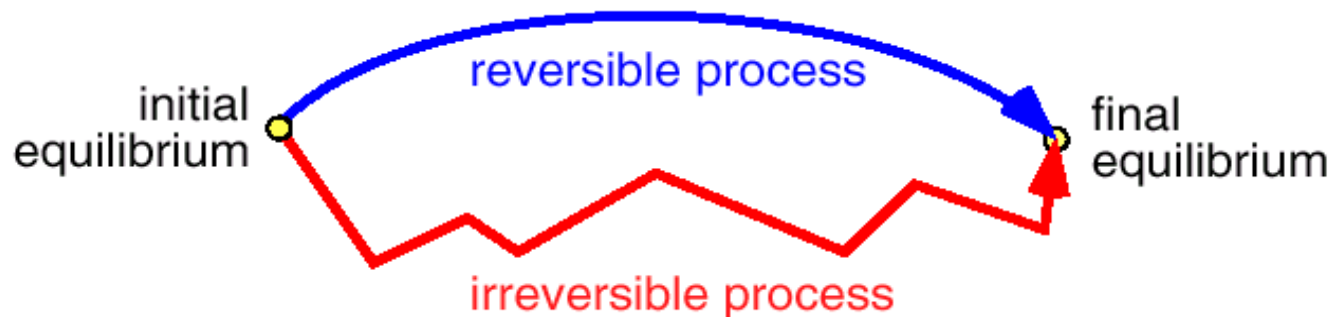
$$\begin{aligned} \Delta H_1 &= \Delta H_f^\circ(\text{C}(\text{g})) + 2 \Delta H_f^\circ(\text{Cl}(\text{g})) + 2 \Delta H_f^\circ(\text{F}(\text{g})) \\ &= 716.7 + 2(121.7) + 2(79.0) = 1118 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H_2 &= - (2 \Delta H_B^\circ(\text{C-Cl}) + 2 \Delta H_B^\circ(\text{C-F})) \\ &= - (2(328) + 2(441)) = -1538 \text{ kJ} \end{aligned}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 1118 - 1538 = -420 \text{ kJ}$$

12.7 REVERSIBLE PROCESSES IN IDEAL GASES

- Isochoric process : constant volume
- Isobaric process : constant pressure
- Isothermal process : constant temperature
- Adiabatic process : $q = 0$
- Reversible process : ideal, proceeds with infinitesimal speed
- Irreversible process : real, proceeds with finite speed



◆ Isothermal Processes

For an ideal gas, $U = (3/2) nRT$

$$\Delta U = 0, \quad w = -q \quad \text{isothermal process}$$

For a reversible process,

$$P_{\text{ext}} = P_{\text{gas}} (\equiv P) = nRT / V$$

P_{ext} changes continuously as V increases.

$$dw = -P_{\text{ext}} dV$$

$$w = - \int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

$$\Delta T = 0, \quad \Delta U = 0, \quad q = -w$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = 0$$

General Chemistry I

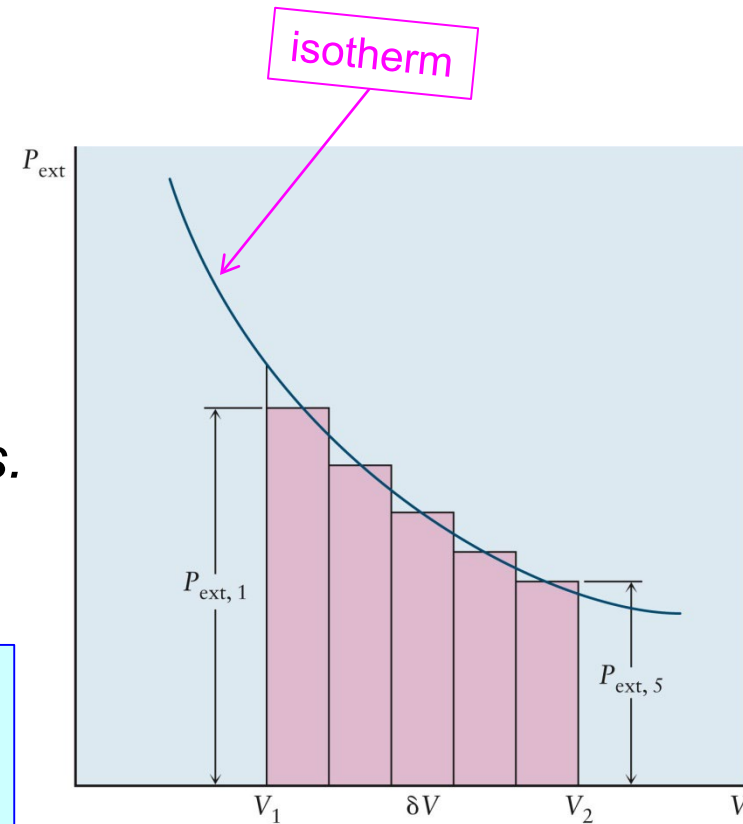


Fig. 12.19 Sum of the rectangles is approximated as the work

EXAMPLE 12.10

Calculate q and w along a process in which 5.00 mol of gas expands reversibly at constant $T = 298\text{ K}$ from $P = 10.00$ to 1.00 atm .

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{10.0\text{ atm}}{1.00\text{ atm}} = 10.0$$

$$w = -nRT \ln \frac{V_2}{V_1} = -nRT \ln(10.0) = -28.5\text{ kJ}$$

$$q = -w = +28.5\text{ kJ}$$

◆ Adiabatic Processes

$$q = 0 \rightarrow \Delta U = w$$

$$dU = nC_v dT = dw = -P_{ext} dV$$

For a reversible process, $P_{ext} = P$.

$$nC_v dT = -P_{ext} dV = -\left(\frac{nRT}{V}\right) dV$$

$$C_v \int_{T_1}^{T_2} \frac{1}{T} dT = -R \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$\Delta U = w = nc_v \Delta T$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$= nc_v \Delta T + nR \Delta T = nc_p \Delta T$$

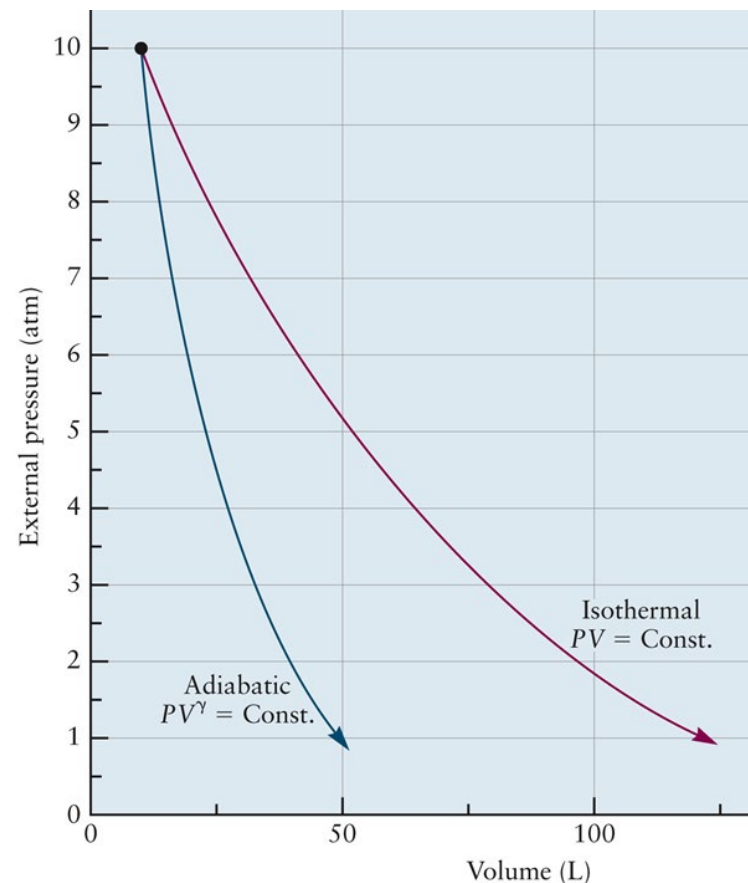


Fig. 12.20. Comparison of reversible isothermal and adiabatic expansions.

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(C_P/C_V)-1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

where $\gamma = C_P/C_V$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\Delta U = w = nc_v \Delta T$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$= nc_v \Delta T + nR \Delta T = nc_p \Delta T$$

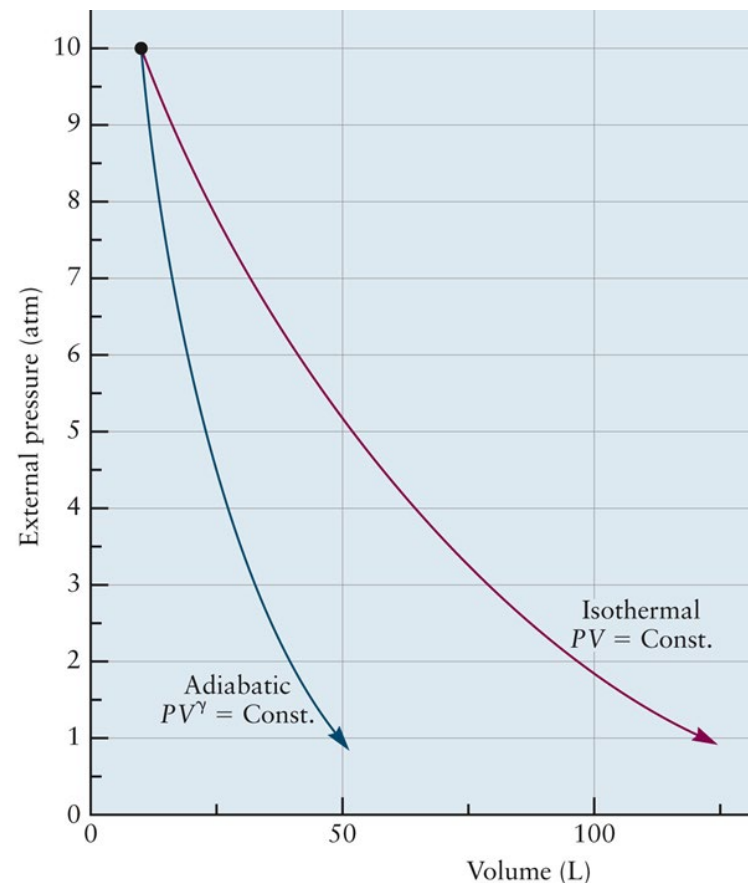


Fig. 12.20. Comparison of reversible isothermal and adiabatic expansions.

EXAMPLE 12.11

Calculate the final V and T , ΔU , ΔH , and w along a process in which 5.00 mol of monatomic gas at an initial $T = 298$ K and $P = 10.0$ atm expands adiabatically and reversibly until $P = 1.00$ atm.

$$V_1 = \frac{nRT_1}{P_1} = 12.2 \text{ L} \quad \gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

$$\frac{P_1}{P_2} V_1^\gamma = V_2^\gamma = V_2^{5/3} \quad V_2 = 48.7 \text{ L} \quad T_2 = \frac{P_2 V_2}{nR} = 119 \text{ K}$$

$$w = \Delta U = nC_V \Delta T = \frac{3}{2} nR \Delta T = -11,200 \text{ J}$$

$$\Delta H = nC_p \Delta T = \frac{5}{2} nR \Delta T = -18,600 \text{ J}$$