UNIT IV

EQUILIBRIUM IN CHEMICAL REACTIONS

CHAPTER 12
Thermodynamic Processes and Thermochemistry

CHAPTER 13
Spontaneous Processes and Thermodynamic Equilibrium

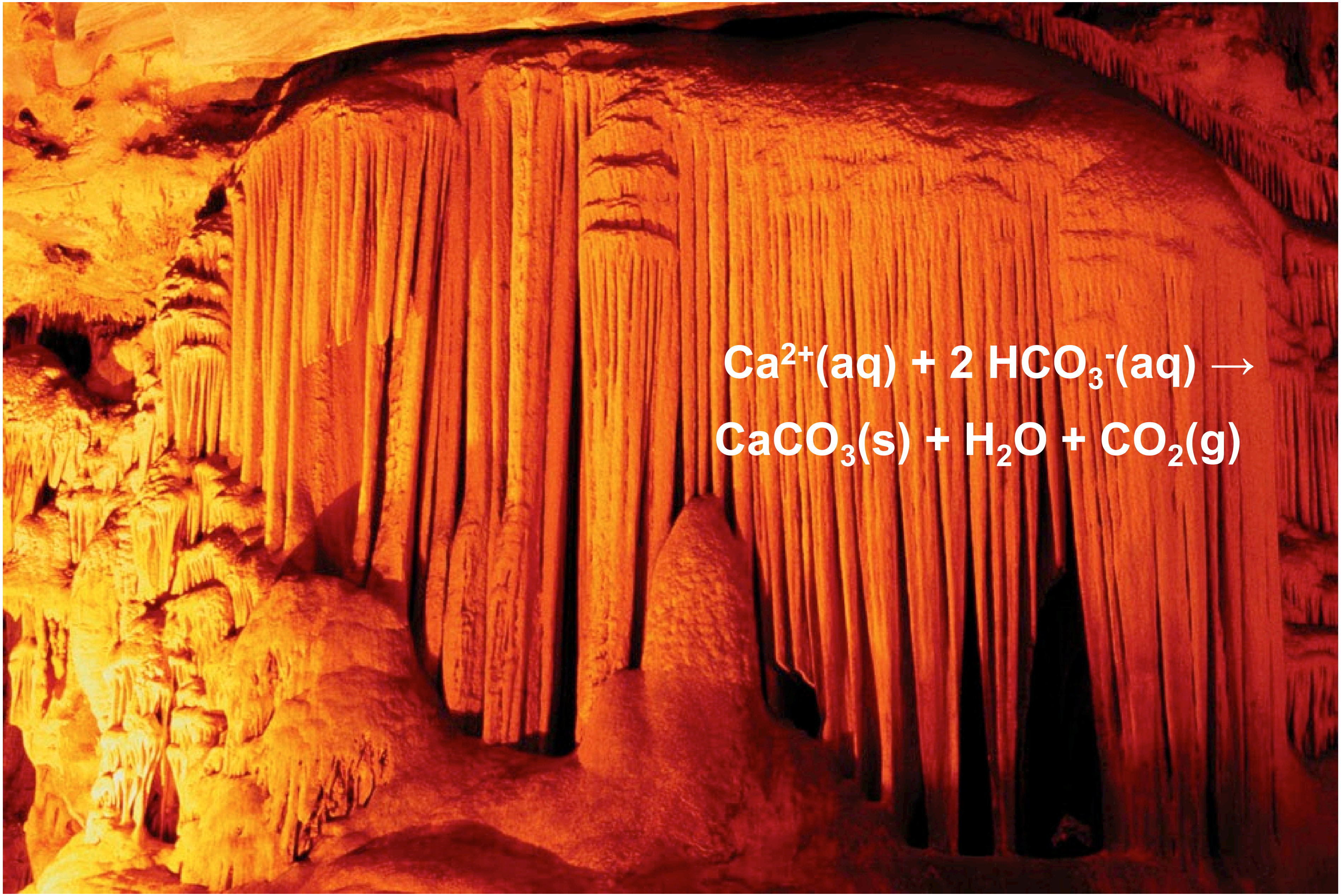
CHAPTER 14
Chemical Equilibrium

CHAPTER 15
Acid-Base Equilibrium

CHAPTER 16
Solubility and Precipitation Equilibria

CHAPTER 17
Electrochemistry

Stalactites (top) and stalagmites (bottom)



$$Ca^{2+}(aq) + 2\ HCO_3^-(aq) \rightarrow CaCO_3(s) + H_2O + CO_2(g)$$

12

CHAPTER

THERMODYNAMIC PROCESSES AND THERMOCHEMISTRY

→ Heat is the most important factor influencing the extent of chemical reactions.

→ Thermodynamics describes the meaning of heat and gives procedures for measuring heat transfer quantitatively.

Steam locomotive

thermal → mechanical

Diesel locomotive

chemical →
electrical → mechanical

Thermodynamics

√ **Thermodynamics**: Gr. θέρμη *therme*, meaning heat, and δύναμις *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

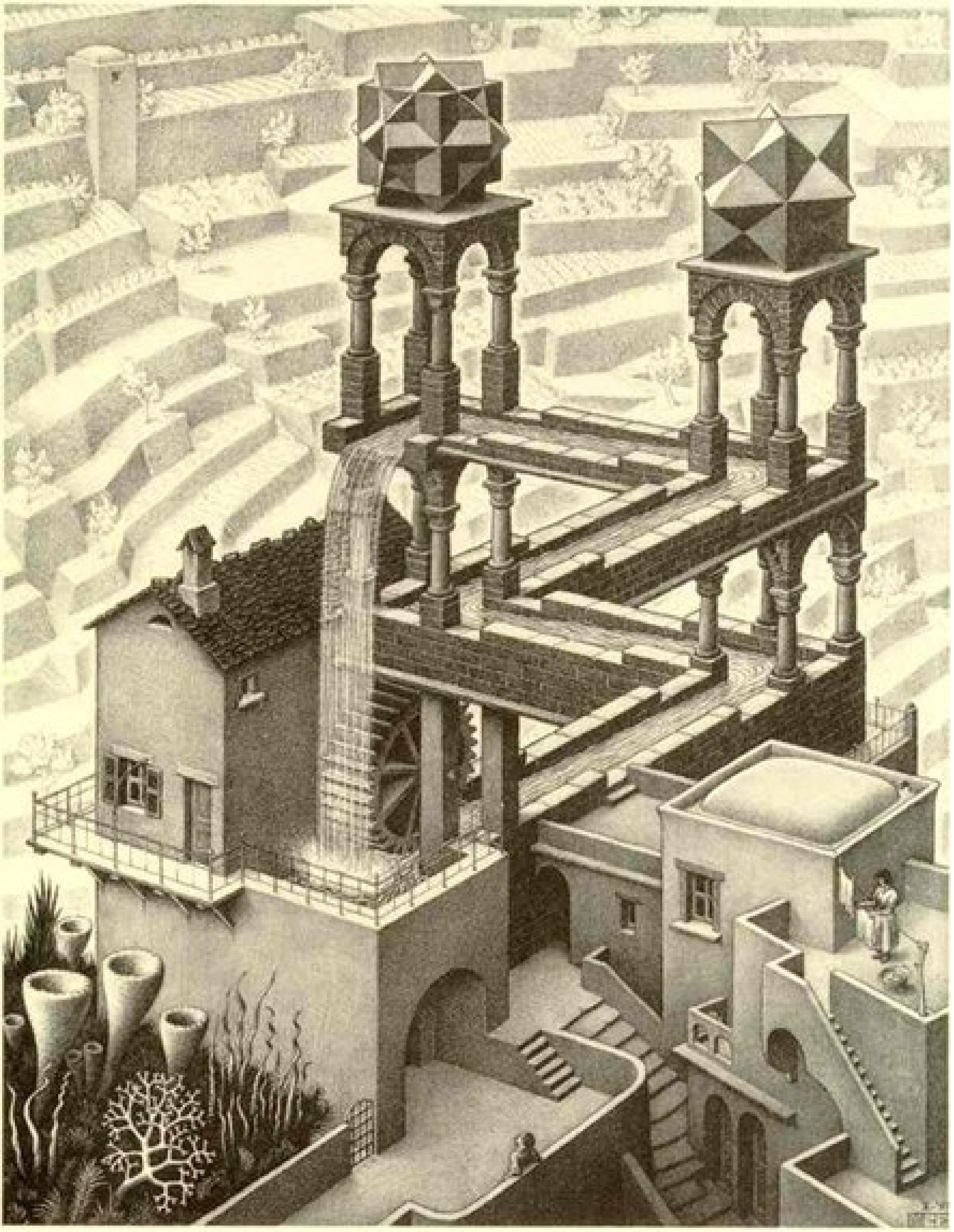
~ Nernst, Planck

▶ Zeroth law of thermodynamics:

Concept of temperature

~ *Thermal equilibrium at contact*

(A,B,C)



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

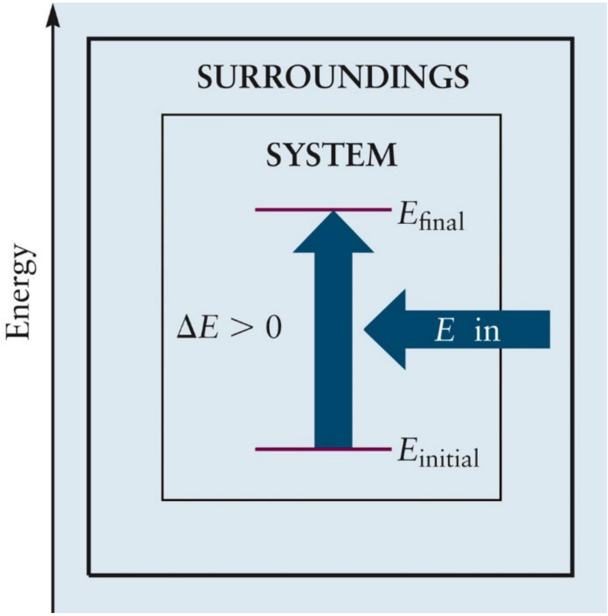
"Waterfall"(1961)

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

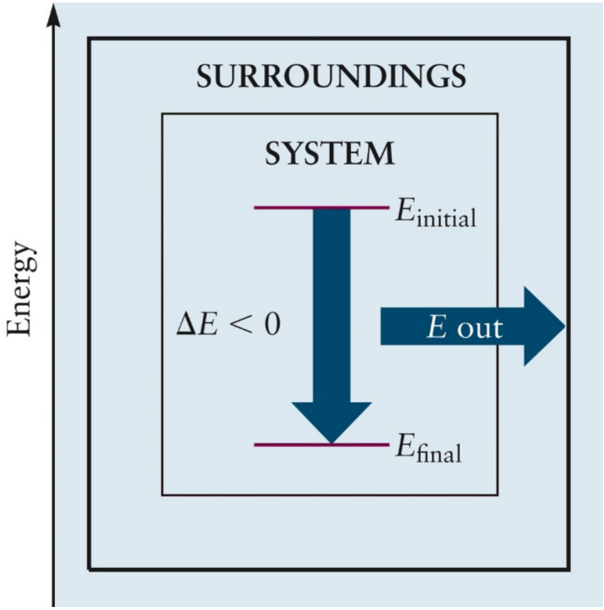
→ The language of thermodynamics

12.1 SYSTEMS, STATES, AND PROCESSES

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

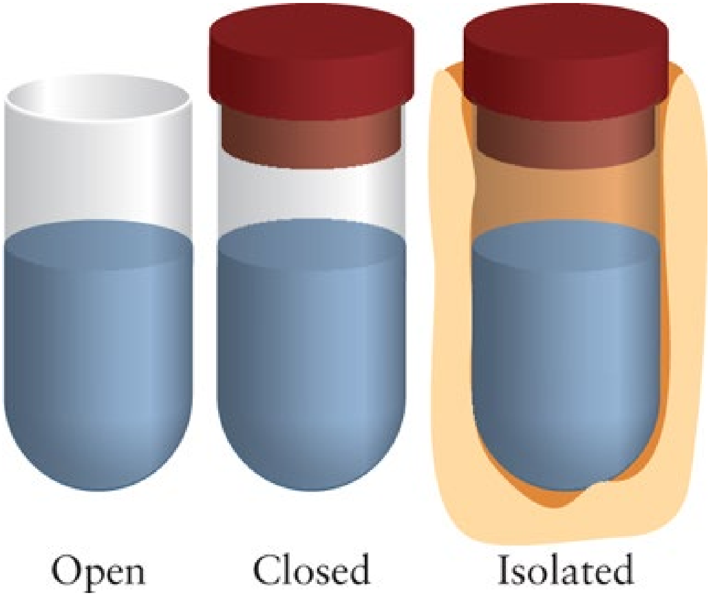


The system gains energy from the surroundings.



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

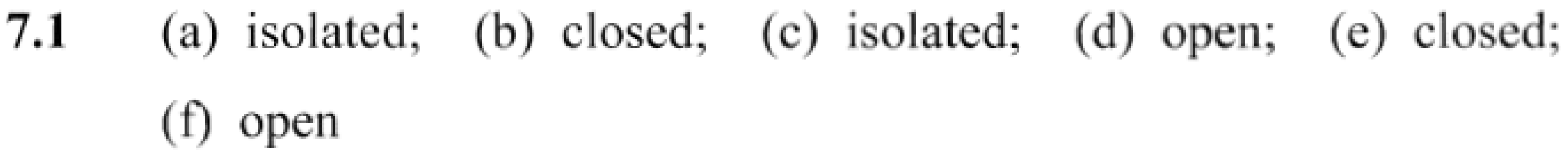
(b) Coolant in a refrigerator coil

(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

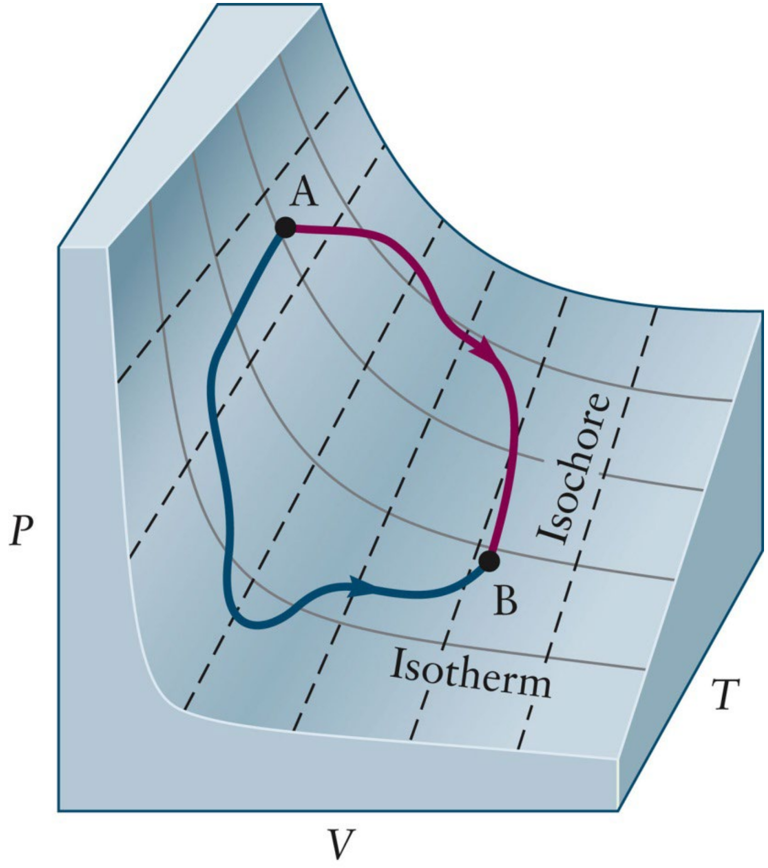


Fig. 12.1 P-V-T surface of 1 mol of ideal gas

◆ 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

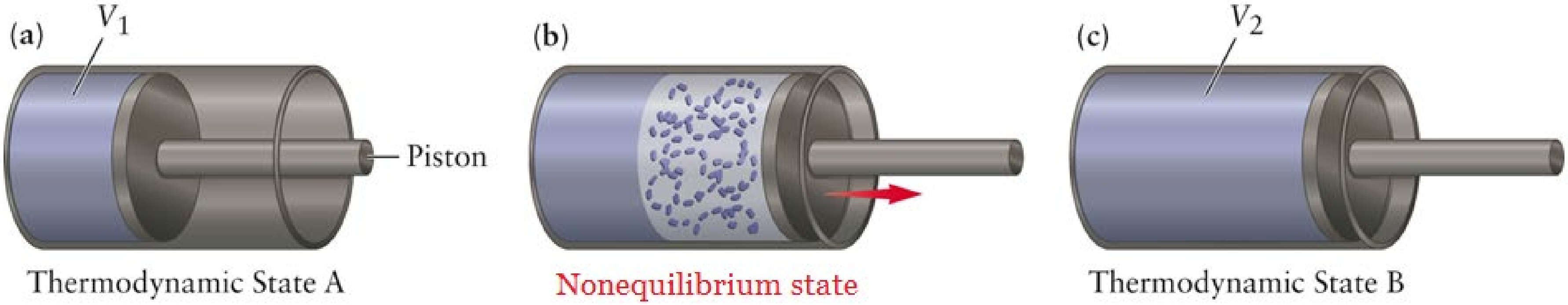


Fig. 12.2. Stages in an irreversible expansion of a gas from an initial state (a) of volume V_1 to a final state (c) with volume V_2. In the intermediate stage (b) the system is not in equilibrium.

- **Extensive property** : *m*, *V*

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

- **Intensive property** : *P*, *T*

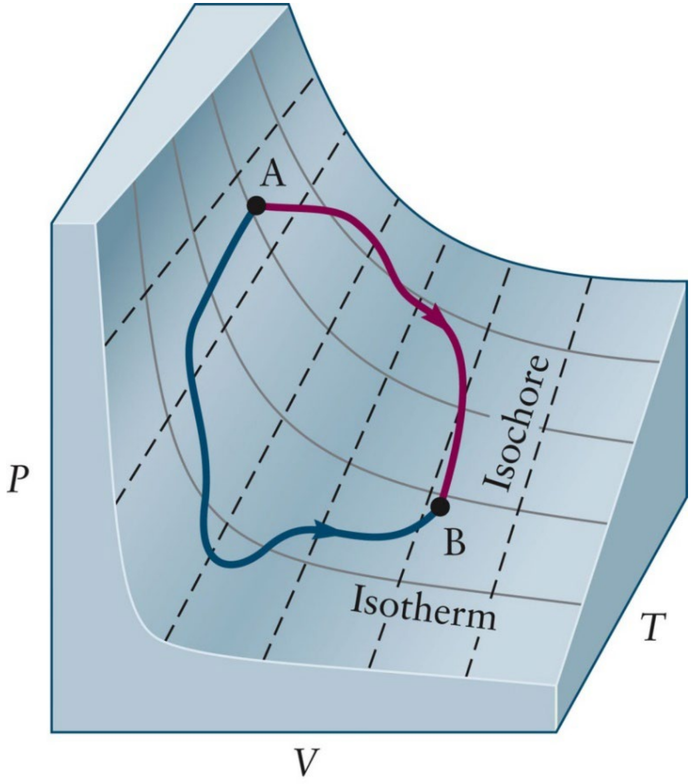
  → A property that does not depend on the size of the sample.

★ **State function** : *E*, *P*, *V*, *T*, *d*, *m*, …

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

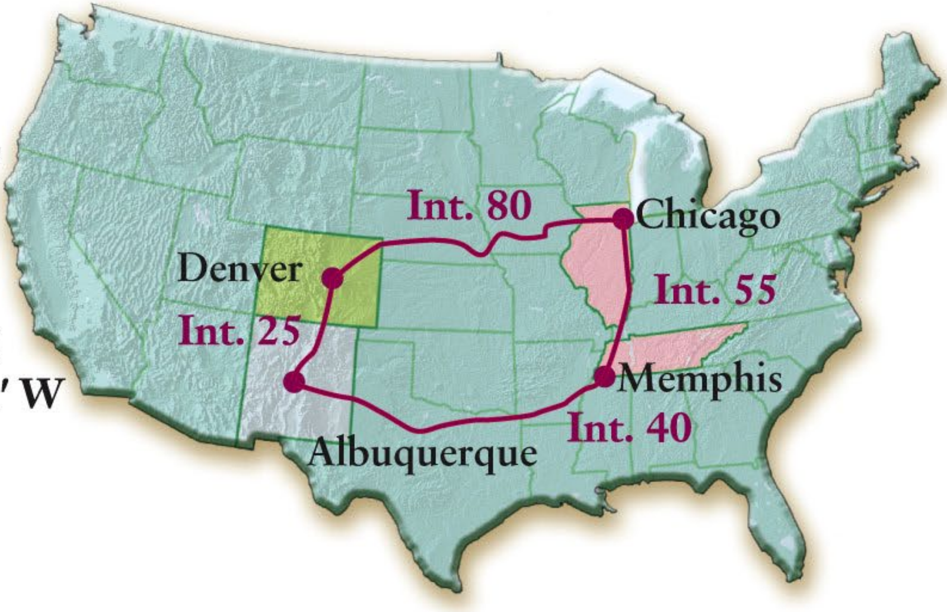
★ **Path function** : *w*, *q*, …

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



"State Properties" of Denver:

Altitude 1 mile
Latitude 39°43′ N
Longitude 105°01′ W



"State Properties" of Chicago:

Altitude 656 ft.
Latitude 41°51′ N
Longitude 87°38′ W

Path values
(distances between Chicago and Denver):
996 miles via Int. 80
1957 miles via Memphis and Albuquerque on Int. 55, Int. 40, and Int. 25

State property differences:
Δ (altitude) = 5280 – 656 = 4624 ft.
Δ (latitude) = 39°43′ – 41°51′ = –2°8′
Δ (longitude) = 105°01′ – 87°38′ = 17°23′

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

→ heat and work are simply different means by which energy is transferred into or out of a system.

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

◆ Work

➢ Mechanical work

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

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

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

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

➢ Pressure-Volume Work (PV-work)

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

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

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

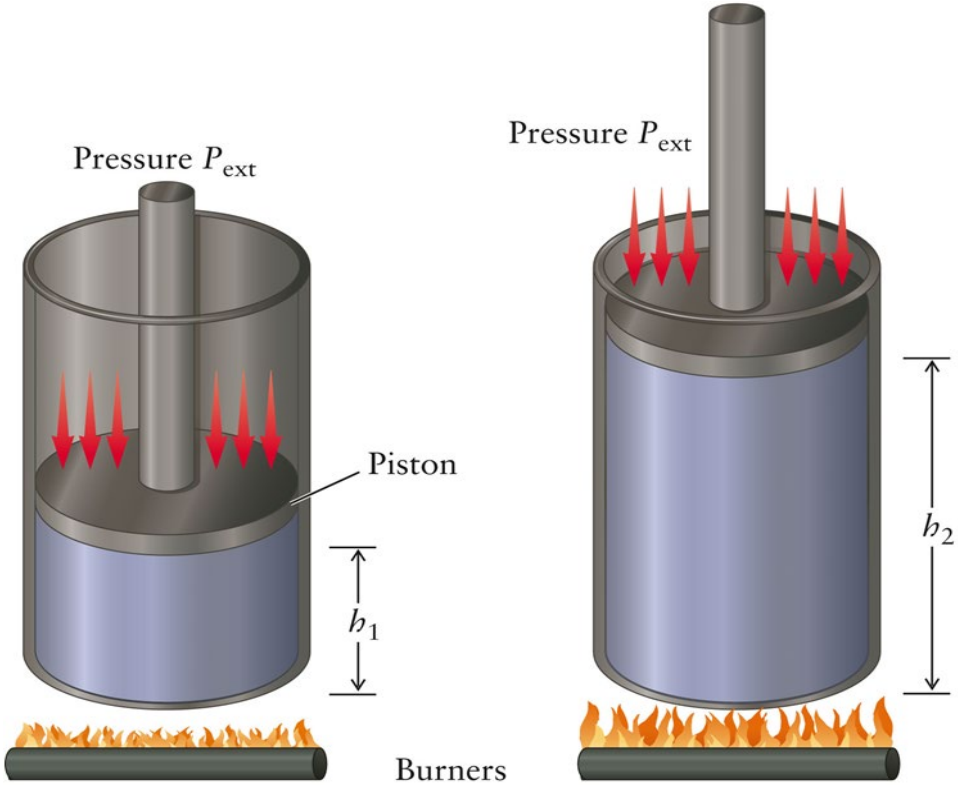
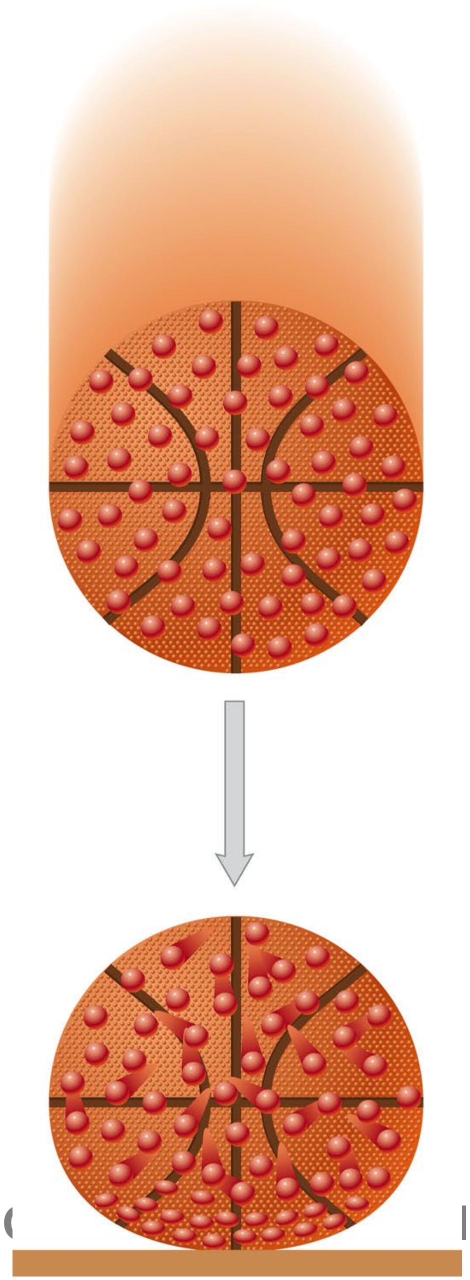


Fig. 12.4. As the gas inside is heated, it expands, pushing the piston against the pressure P_{ext} exerted by the gas outside.

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

→ heat as a means of increasing the internal energy of a system without mechanical interaction.



◆ **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

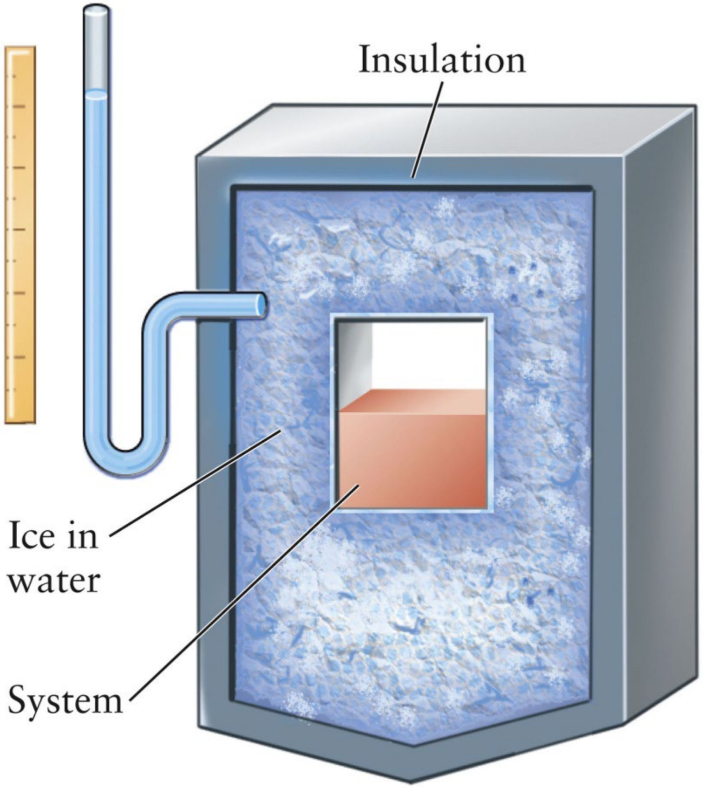


Fig. 12.6. Ice calorimeter

◆ Specific heat capacity, c_s

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

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

◆ Equivalence of heat and work

- Thompson (later Count Rumford)

  ~ Cannon barrel

- Mayer and Joule

  A paddle driven by a falling weight

  1 cal = 4.184 J

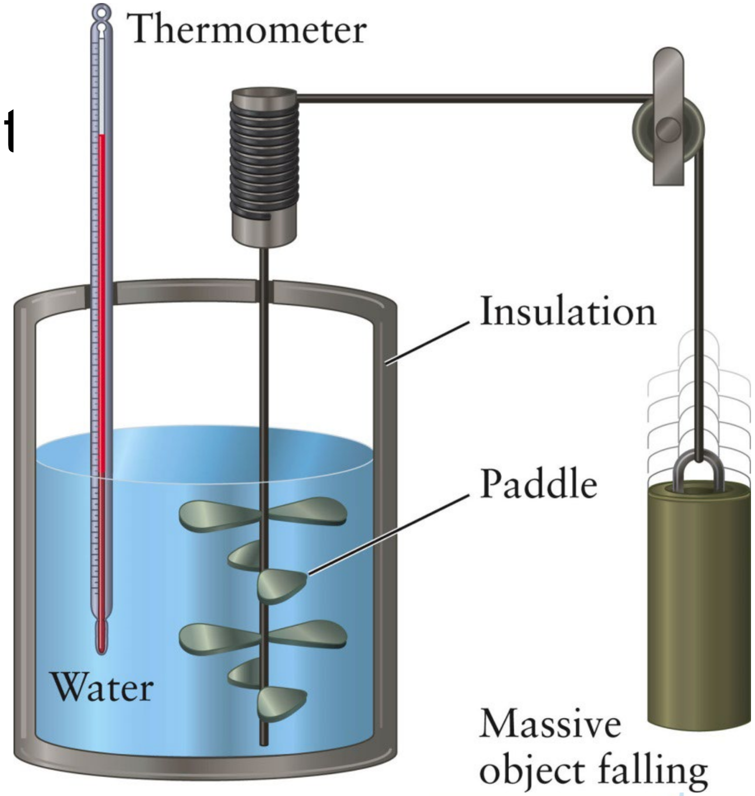


Fig. 12.7. The falling weight turns a paddle, doing work on the system, increasing *T*.

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

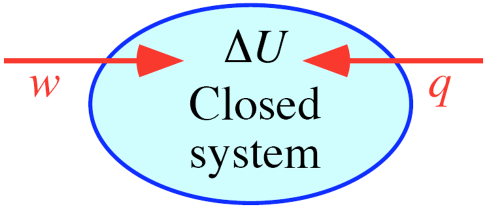
$$\Delta U = q + w$$

q, w : path functions, ΔU : state function

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

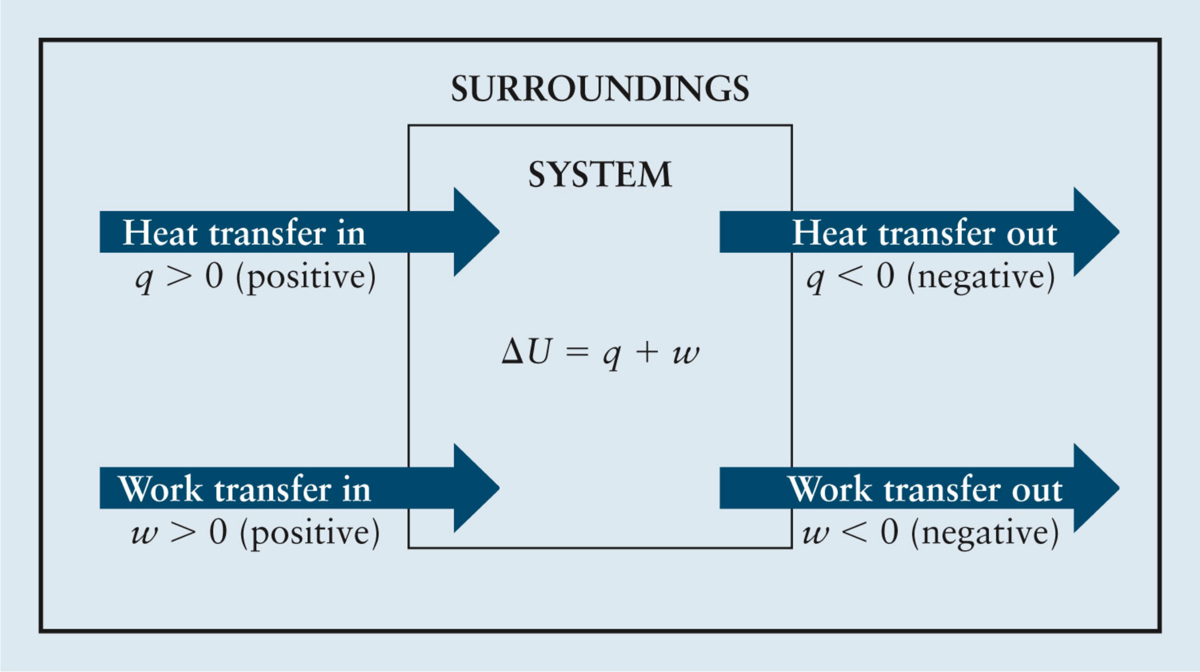
  applicable to any process that begins and ends in equilibrium states

$$\boxed{\Delta U = q + w}$$



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.

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

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**

  $$q_P = n\, c_P\, \Delta T$$

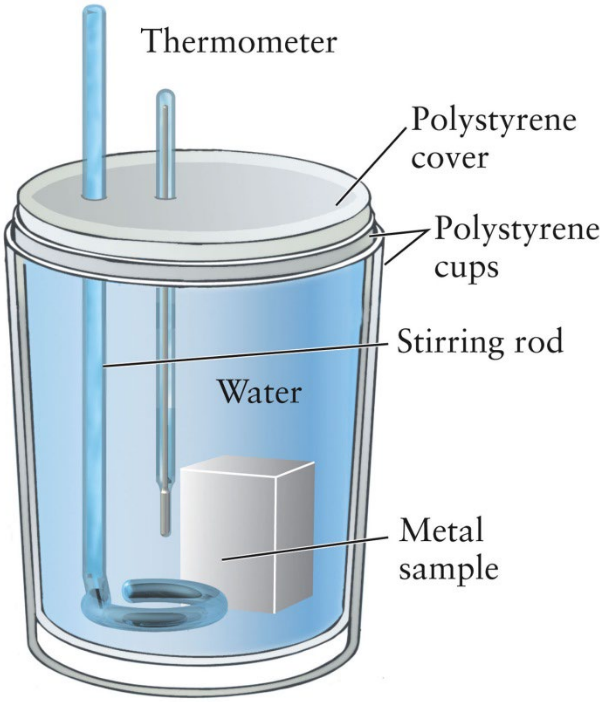


Fig. 12.8. A styrofoam cup calorimeter.

TABLE 12.1

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

Substance	Specific Heat Capacity ($J\ K^{-1}\ g^{-1}$)
$Hg(\ell)$	0.140
$Cu(s)$	0.385
$Fe(s)$	0.449
$SiO_2(s)$	0.739
$CaCO_3(s)$	0.818
$O_2(g)$	0.917
$H_2O(\ell)$	4.18

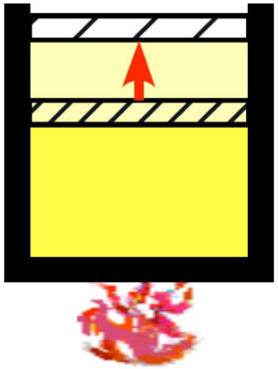
- If C_V and C_P do not change with temperature,

$$q_V = nC_{V,\mathrm{m}}\Delta T \qquad q_P = nC_{P,\mathrm{m}}\Delta T$$

Constant volume

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

$$\boxed{q_V < q_P}$$



Constant pressure

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

Where does the heat go?
How can systems store or release heat as an energy source?

◆Heat Transfer at Constant Volume:

Internal Energy

$q_V = \Delta U$ (constant V)

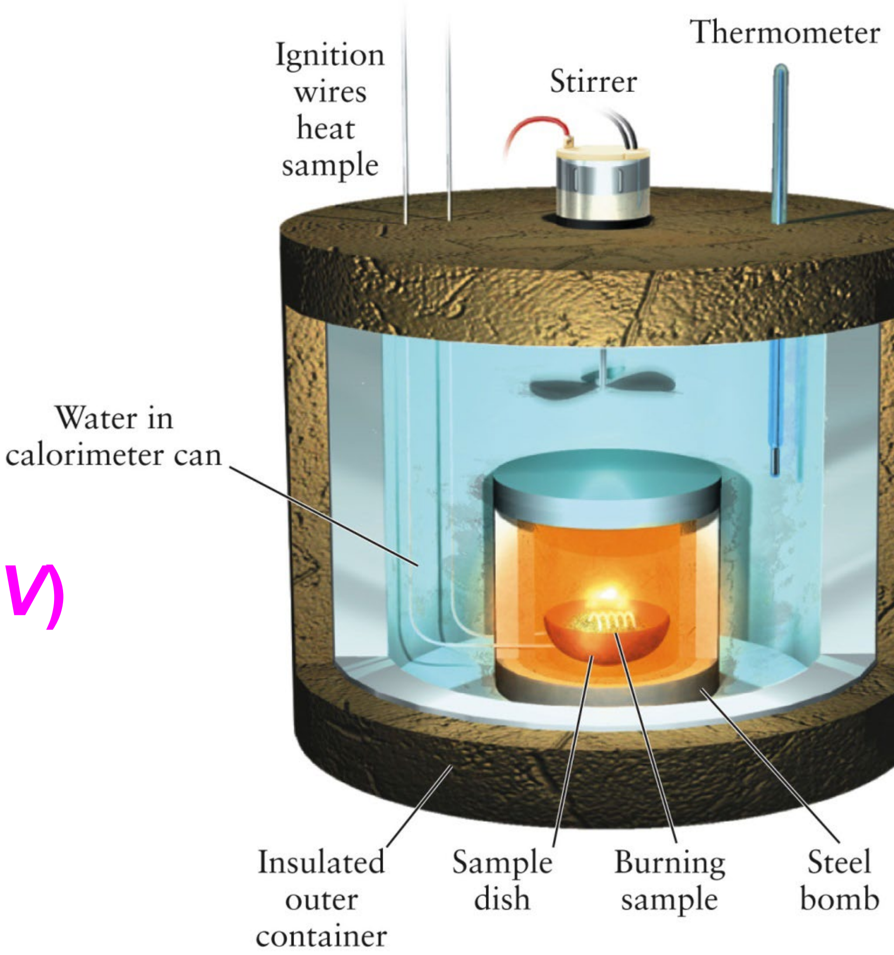


Fig. 12.9. The combustion calorimeter, called a “bomb calorimeter”.

→ H has physical dimensions of energy and is, in effect, a "corrected" internal energy that reflects the consequences of changing V while thermal energy is being absorbed at constant pressure.

◆ Heat Transfer at Constant Pressure: Enthalpy

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

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

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

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

Enthalpy, *H* $\boldsymbol{H = U + PV}$

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

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

9.5 THE KINETIC THEORY OF GASES

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

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

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

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

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

M = molar mass = $N_A m$

12.4 THE FIRST LAW AND IDEAL GAS PROCESSES

◆ Heat Capacities of Ideal Gases

Kinetic energy of an *n* mol of ideal gas

$$E_{kin} = (3/2)\, nRT \;\rightarrow\; \Delta U = (3/2)nR\,\Delta T \qquad (1)$$

→ In a monatomic gas, translational kinetic energy

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

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

Compare (1) and (2).

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

→ For ΔU: the energy change depends only on the temperatures for an ideal gas

At constant pressure,

$$\Delta U = q_P + w$$

$$[\Delta U = nc_V\,\Delta T,\ \ q_P = nc_P\,\Delta T,\ \ w = -\,P\Delta V\,]$$

$\Delta H = q_P = \Delta U + P\,\Delta V$

(at constant P)

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

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

$c_P = c_V + R$	(any ideal gas)
$\Delta U = nc_V\,\Delta T$	(any ideal gas)
$\Delta H = nc_P\,\Delta T$	(ideal gas)

Q: why are the two quantities different?

H: for what is the heat consumed?

→ Now we have all the data needed to calculate heat and work for a variety of processes involving an ideal gas

◆ Heat and Work for Ideal Gases

Along the path A → C → B,

$$w_{AC} = -P_{ext}\Delta V = -P_A(V_B - V_A)$$
$$w_{CB} = 0$$

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

$$q_{AC} = q_p = -nc_p\Delta T = (5/2)nR(T_C - T_A)$$
$$= (5/2)(P_CV_C - P_AV_A)$$

$$q_{CB} = q_v = -nc_v\Delta T = (3/2)nR(T_B - T_C)$$
$$= (3/2)(P_BV_B - P_CV_C)$$

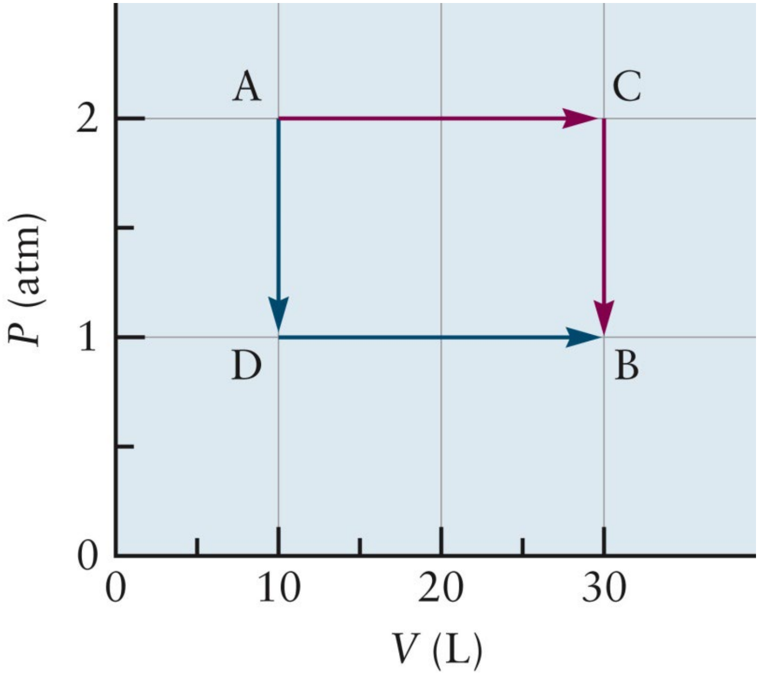


Fig. 12.10. Two different processes between the states A and B.

$$q_{ACB} = q_{AC} + q_{CB}$$
$$= (5/2)(P_CV_C - P_AV_A) + (3/2)(P_BV_B - P_CV_C)$$
$$= 5570 \text{ J}$$

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

State function ΔU is independent of paths

Similarly, along the path A → D → B,

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

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

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

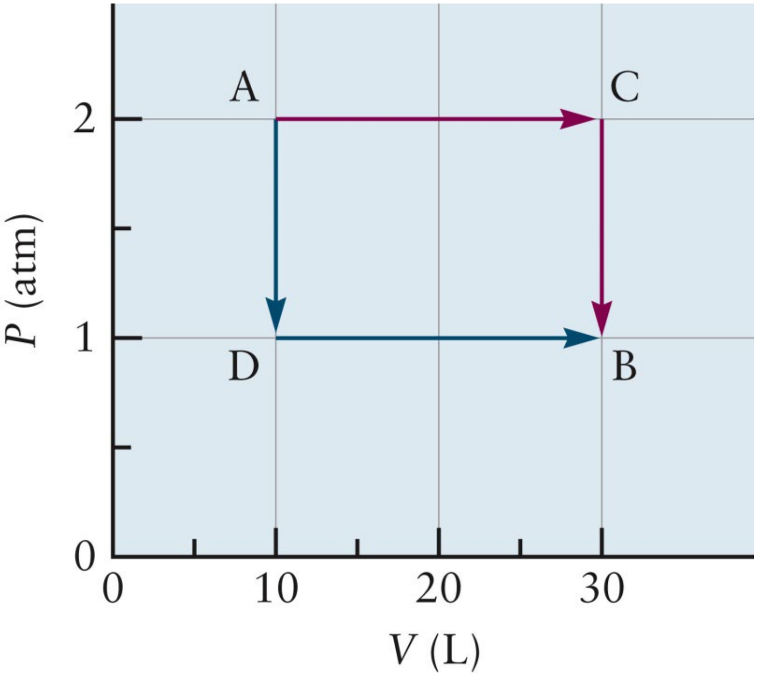


Fig. 12.10. Two different processes between the states A and B.

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, $q_P = \Delta H$

$$q_{\mathrm{P}} = \Delta H = H_{\mathrm{f}} - H_{\mathrm{i}} = H_{\text{products}} - H_{\text{reactants}} = \Delta H_{\text{reaction}}$$

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

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

◆Exothermic Reaction

$2\ Al(s) + Fe_2O_3(s) \rightarrow 2\ Fe(s) + Al_2O_3(s)$

(b)

◆Endothermic Reaction

$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s)$
$\rightarrow Ba(NO_3)_2(aq) + 2\ NH_3(aq) + 10\ H_2O(l)$

(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.

$C(s,gr) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5\ kJ$

$CO(g) + (1/2)\ O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283.0\ kJ$

$C(s,gr) + (1/2)\ O_2(g) \rightarrow CO(g)$ $\Delta H = ?$

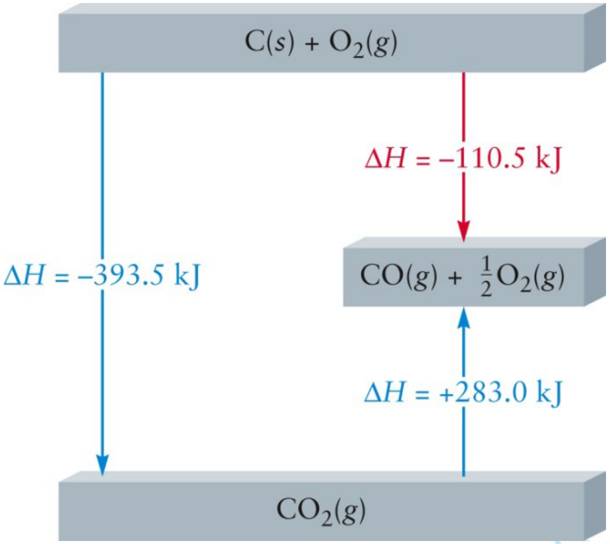


Fig. 12.17 Hess's law.

$C(s,\text{gr}) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

$CO(g) + (1/2)\ O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283.0$ kJ

$C(s,\text{gr}) + (1/2)\ O_2(g) \rightarrow CO(g)$ $\Delta H = ?$

$C(s,\text{gr}) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_1 = -393.5$ kJ

$CO_2(g) \rightarrow CO(g) + (1/2)\ O_2(g)$ $\Delta H_2 = +283.0$ kJ

$C(s,\text{gr}) + (1/2)\ O_2(g) \rightarrow CO(g)$ $\Delta H = \Delta H_1 + \Delta H_2$

$= -110.5$ kJ

◆ Enthalpy of phase change at constant *T* & *P*

$H_2O(s) \rightarrow H_2O(l)$ $\Delta H_{fus} = +6.007\ \text{kJ mol}^{-1}$

$H_2O(l) \rightarrow H_2O(s)$ $\Delta H_{freez} = -6.007\ \text{kJ mol}^{-1}$

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H_{vap} = +40.66\ \text{kJ mol}^{-1}$

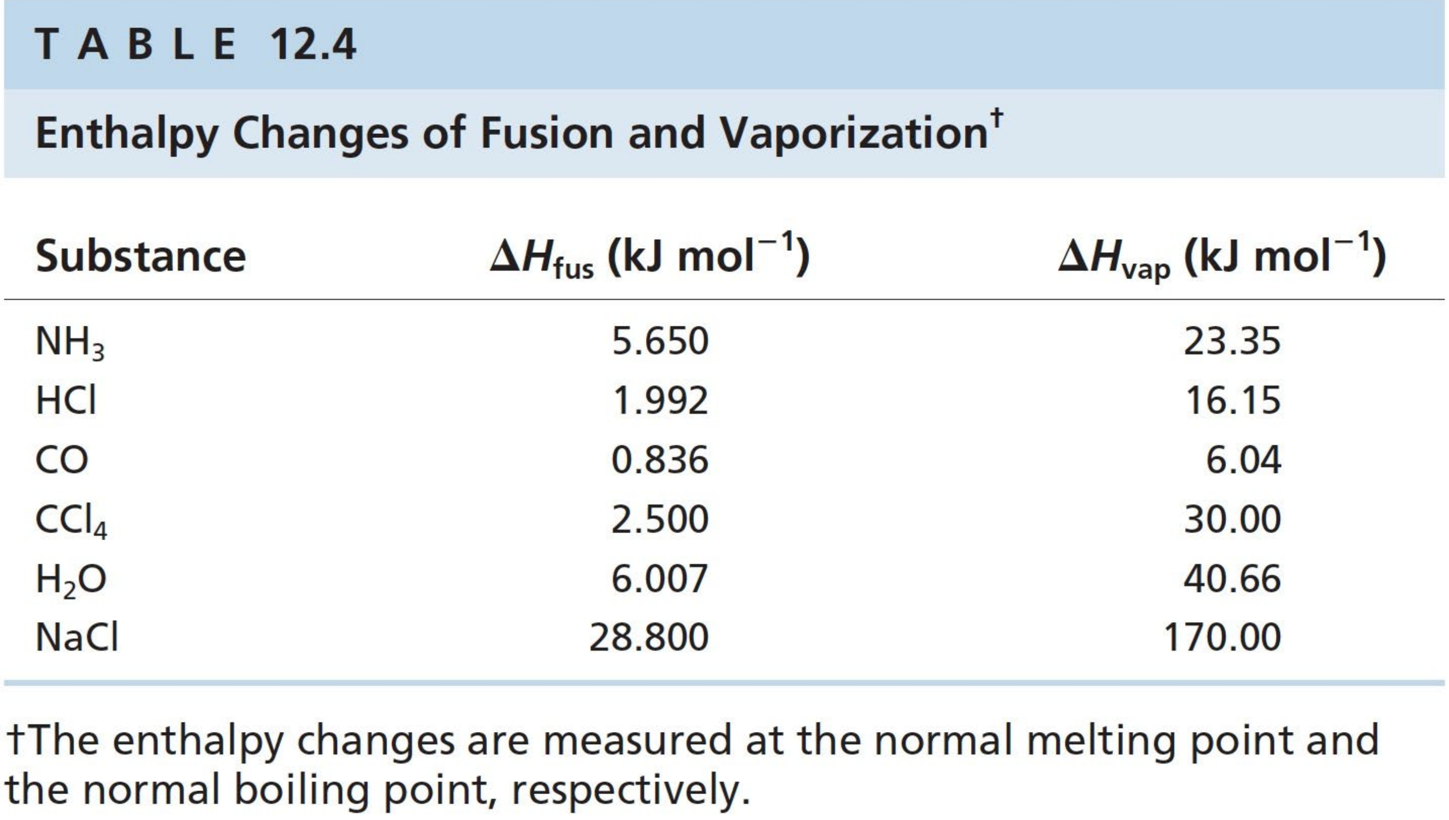


TABLE 12.4

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_2O	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.

→ Absolute values of the enthalpy of a substance, like absolute values of the internal energy, cannot be measured or calculated. Only changes in enthalpy can be measured.

◆ 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 $\Delta H_f°$** 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**

$H_2(g) + (1/2)\,O_2(g) \rightarrow H_2O(l)$, $\Delta H_f°(H_2O(l)) = -285.83\ \text{kJ mol}^{-1}$

$C(s, \text{gr}) \rightarrow C(s, \text{dia})$, $\Delta H_f°\ (C(s, \text{dia})) = +1.895\ \text{kJ mol}^{-1}$

→ assign zero enthalpy to the form that is most stable at 1 atm and 298.15 K.

$$2\,C(gr) + 3\,H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l) \qquad \Delta H^\circ = -277.69\ \underline{kJ}$$

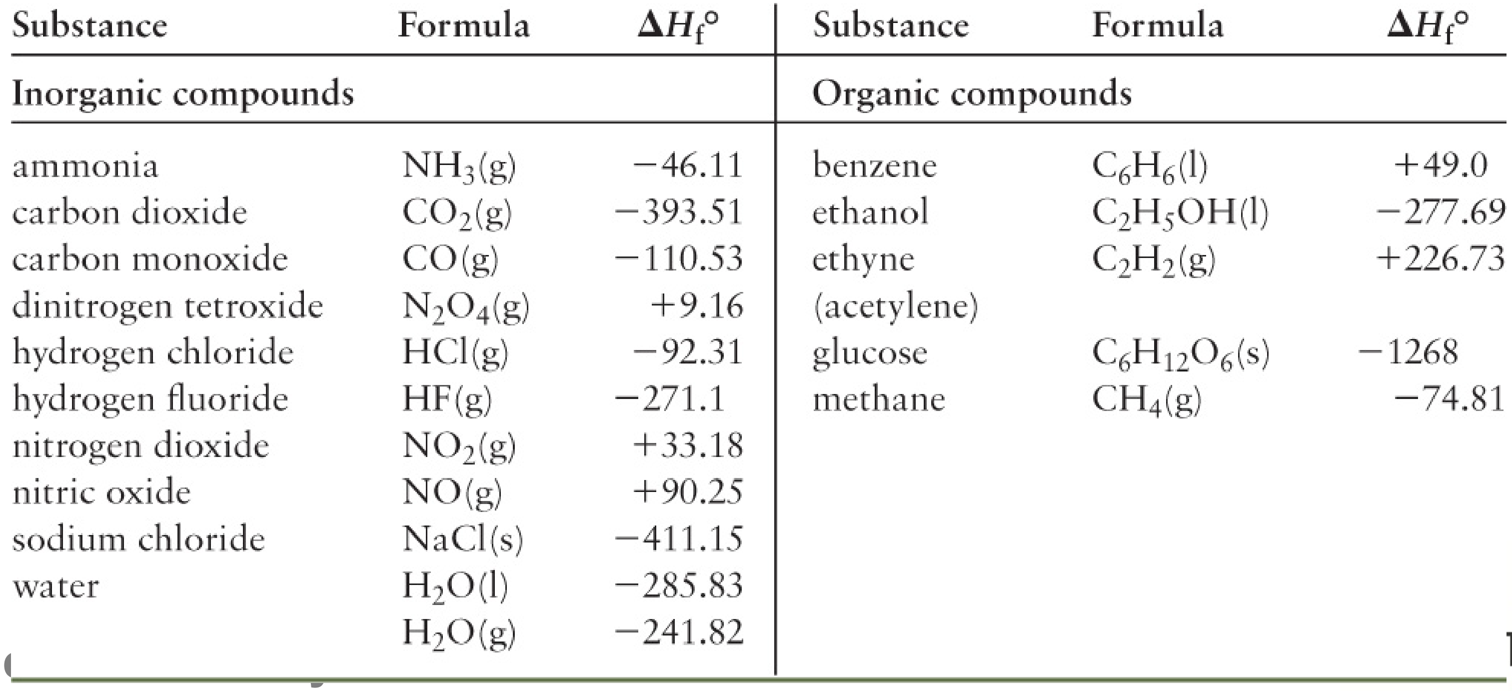
$$\Delta H_f^\circ(C_2H_5OH(l)) = -277.69\ \underline{kJ/mol}$$

$$C(gr) \rightarrow C(dia) \qquad \Delta H^\circ = +1.9\ kJ$$

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

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

- Standard Enthalpies of Formation at 25 ^oC ($kJ \cdot mol^{-1}$) (Appendix D)



Substance	Formula	ΔH_f°	Substance	Formula	ΔH_f°
Inorganic compounds			**Organic compounds**		
ammonia	$NH_3(g)$	−46.11	benzene	$C_6H_6(l)$	+49.0
carbon dioxide	$CO_2(g)$	−393.51	ethanol	$C_2H_5OH(l)$	−277.69
carbon monoxide	$CO(g)$	−110.53	ethyne (acetylene)	$C_2H_2(g)$	+226.73
dinitrogen tetroxide	$N_2O_4(g)$	+9.16			
hydrogen chloride	$HCl(g)$	−92.31	glucose	$C_6H_{12}O_6(s)$	−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	$H_2O(l)$	−285.83			
	$H_2O(g)$	−241.82			

◆ Standard enthalpy change of reaction

$$aA + bB \longrightarrow cC + dD, \qquad \Delta H^\circ$$

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

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

◆ Bond enthalpy

~ Enthalpy when a bond is broken in the gas phase

Bond enthalpy of a C—H bond in $CH_4(g)$ ~ measured

$$CH_4(g) \rightarrow CH_3(g) + H(g), \qquad \Delta H^\circ = +438\ \text{kJ}$$

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:

$$CH_3CH_2I(g) + H_2O(g) \longrightarrow CH_3CH_2OH(g) + HI(g)$$

- Breaking the bonds

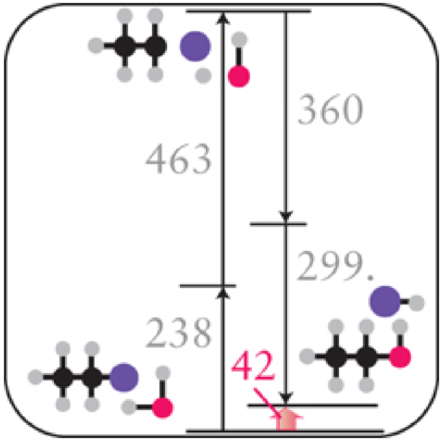
$\Delta H_B^o(\text{C-I}) + \Delta H_B^o(\text{O-H}) = \Delta H° = 238 + 463 \text{ kJ} = +701 \text{ kJ}$

- Forming the bonds

$\Delta H_B^o(\text{C-O}) + \Delta H_B^o(\text{H-I}) = \Delta H° = 360 + 299 \text{ kJ} = +659 \text{ kJ}$

- The overall enthalpy change:

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



EXAMPLE 12.9 $\Delta H_f^o(CCl_2F_2(g)) = ?$ Freon-12

what if the standard enthalpy of formation is not available?

$$C(s,gr) + Cl_2(g) + F_2(g) \rightarrow CCl_2F_2(g) \qquad \Delta H = ?$$

$$\uparrow \Delta H_2$$

$$C(s,gr) + Cl_2(g) + F_2(g) \xrightarrow[\Delta H_1]{} C(g) + 2\ Cl(g) + 2\ F(g)$$

$$\Delta H_1 = \Delta H_f^o(C(g)) + 2\ \Delta H_f^o(Cl(g)) + 2\ \Delta H_f^o(F(g))$$
$$= 716.7 + 2(121.7) + 2(79.0) = 1118\ kJ$$

$$\Delta H_2 = -\ (2\ \Delta H_B^o(C\text{-}Cl) + 2\ \Delta H_B^o(C\text{-}F))$$
$$= -\ (2(328) + 2(441)) = -1538\ kJ$$

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

→ Although…most thermodynamic processes conducted in laboratory work are irreversible

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

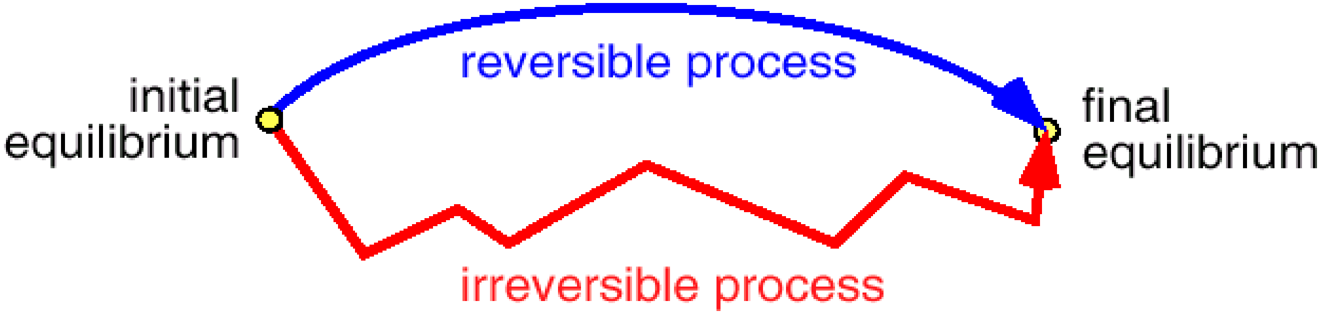
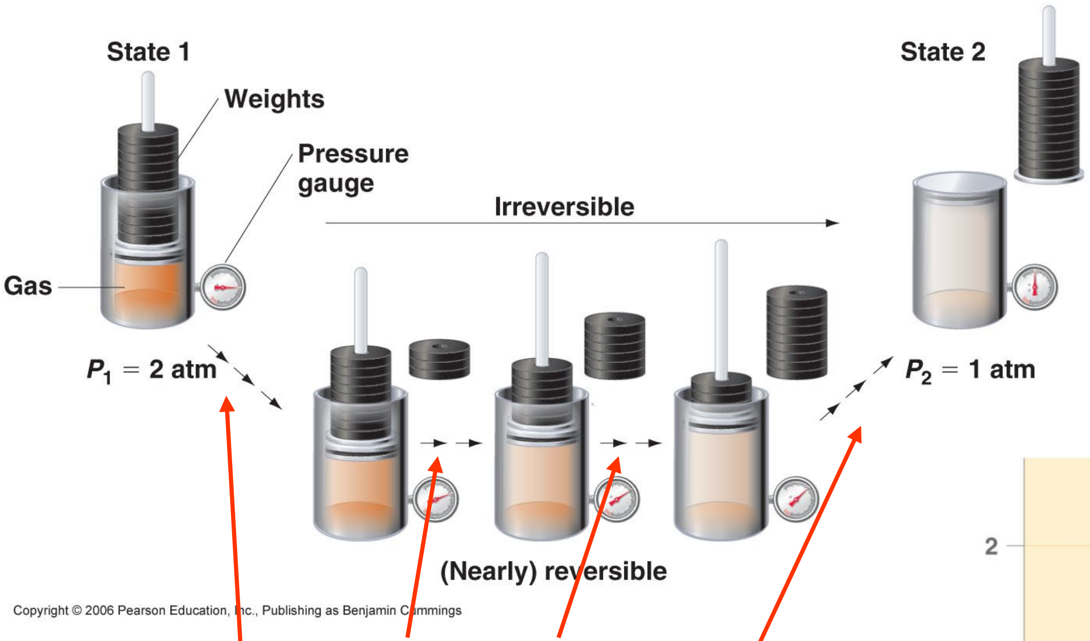


Fig. 11.3 Irreversible and ***nearly reversible*** *isothermal expansion*



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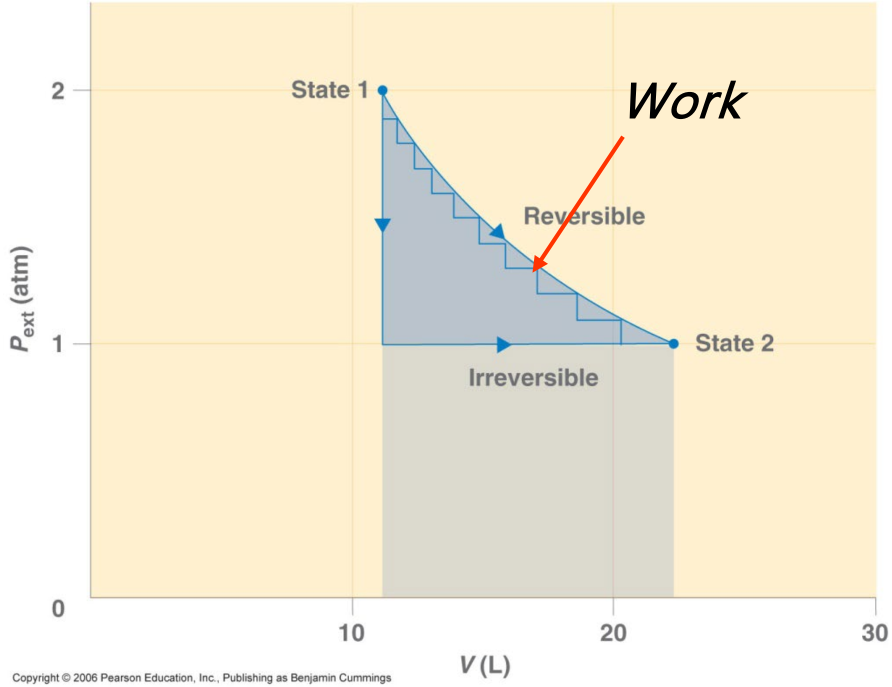
Work done, $w = -P_{ext}\Delta V$

→ *area under* P_{ext} *vs.* V

If each step size, $\Delta P \approx dP$*, is infinitesimally small, two states are nearly reversible and can be consider as in equilibrium.*

Likewise, whole processes can be treated continuously up to State 2 and as nearly reversible processes.

How is reversible process? $P = P_{ex}$



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◆ Isothermal Processes

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

$\Delta U = 0$, $w = -q$ **isothermal** process

For a reversible process,

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

P_{ext} changes continuously as V increases.

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

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

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

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

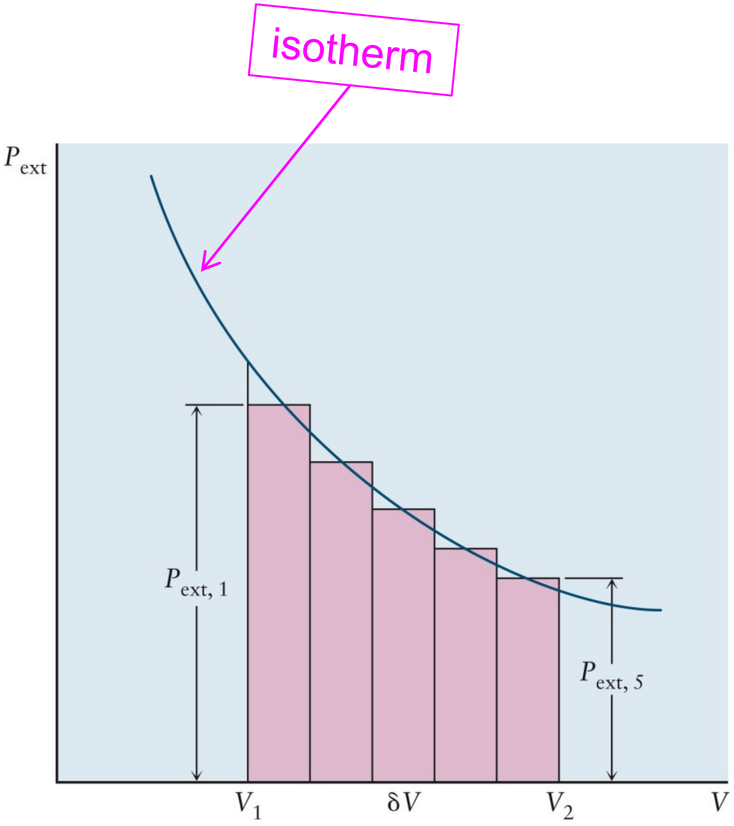


Fig. 12.19 Sum of the rectangles is approximated as the work

EXAMPLE 12.10 Calculate q and w along a process in which 5.00 mol of gas expands reversibly at constant T = 298 K From P = 10.00 to 1.00 atm.

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

$$\mathrm{w} = -\mathrm{nRTln}\frac{\mathrm{V_2}}{\mathrm{V_1}} = -\mathrm{nRTln}(10.0) = -28.5\ \mathrm{kJ}$$

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

◆ Adiabatic Processes

q = 0 → ΔU = w

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

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

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

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

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

$$\Delta U = w = nc_V \Delta T$$

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

$$= nc_V \Delta T + nR\Delta T = nc_P \Delta T$$

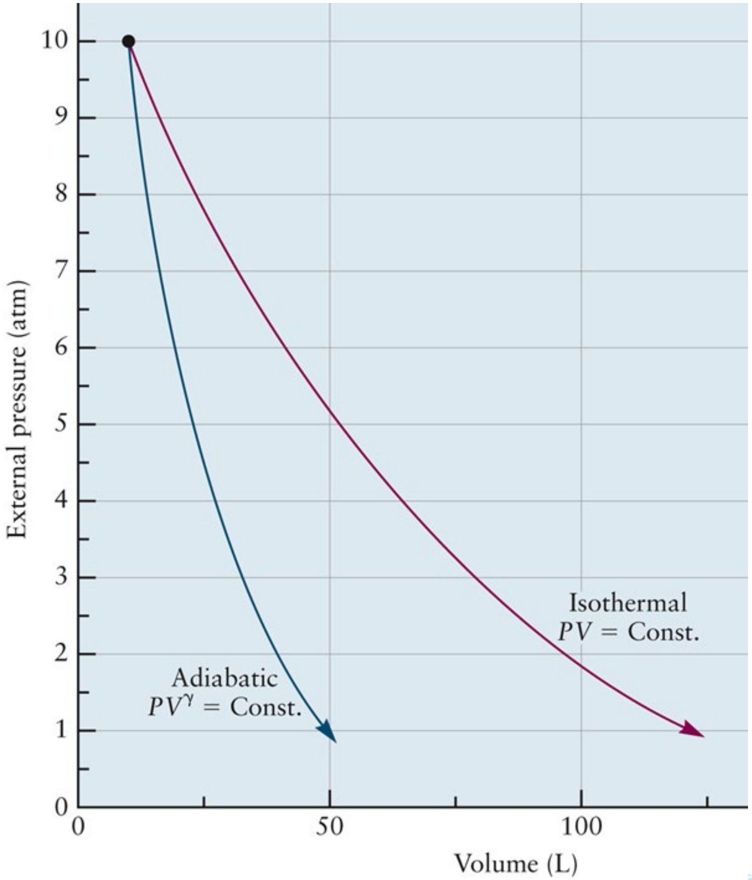


Fig. 12.20. Comparison of reversible isothermal and adiabatic expansions.

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

$$\Delta U = w = nc_V\Delta T$$

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

$$= nc_V\Delta T + nR\Delta T = nc_P\Delta T$$

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

where $\gamma = C_P/C_V$

$$\boxed{\begin{aligned} T_1V_1^{\gamma-1} &= T_2V_2^{\gamma-1} \\ P_1V_1^{\gamma} &= P_2V_2^{\gamma} \end{aligned}}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

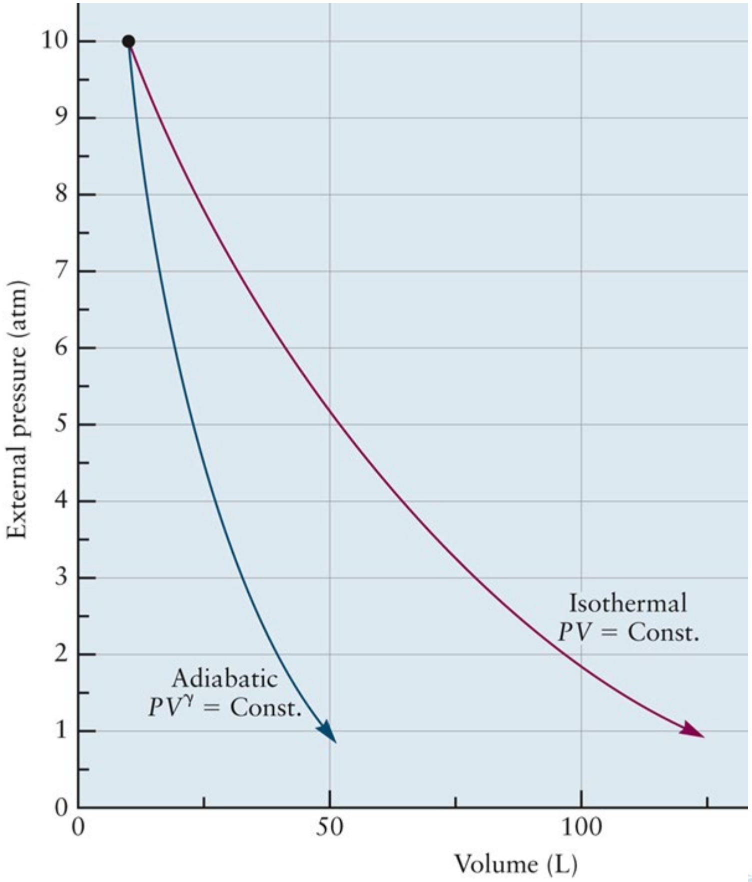


Fig. 12.20. Comparison of reversible isothermal and adiabatic expansions.

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.

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

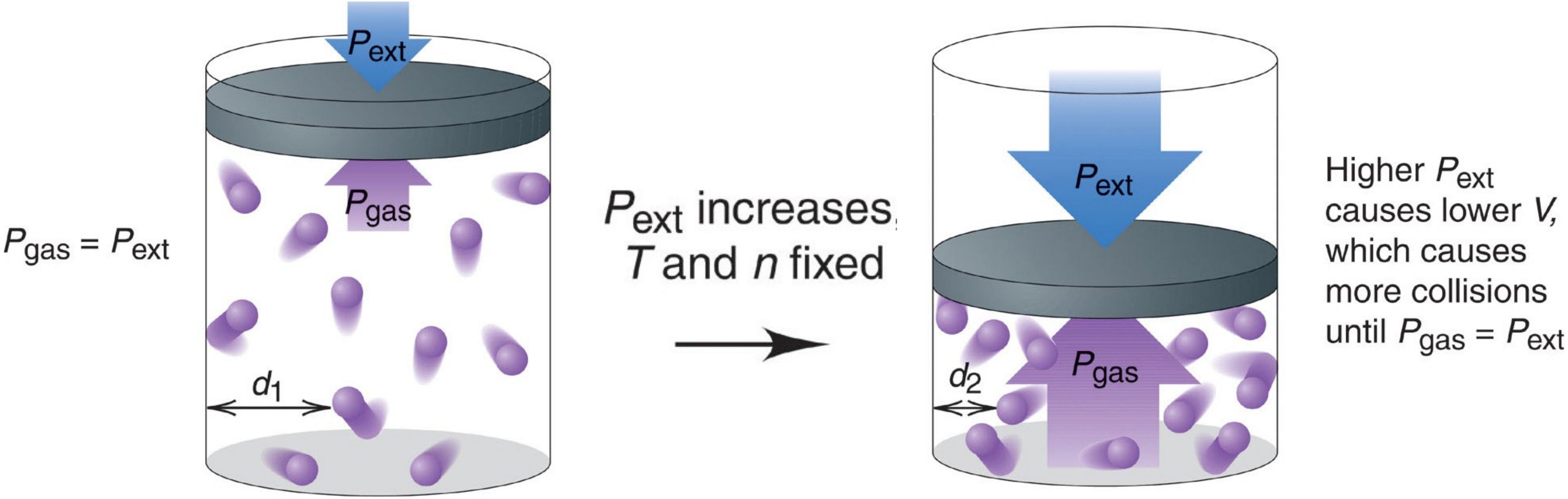
$$\frac{P_1}{P_2} V_1^{\gamma} = V_2^{\gamma} = V_2^{5/3} \qquad V_2 = 48.7\ L \qquad T_2 = \frac{P_2 V_2}{nR} = 119\ K$$

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

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

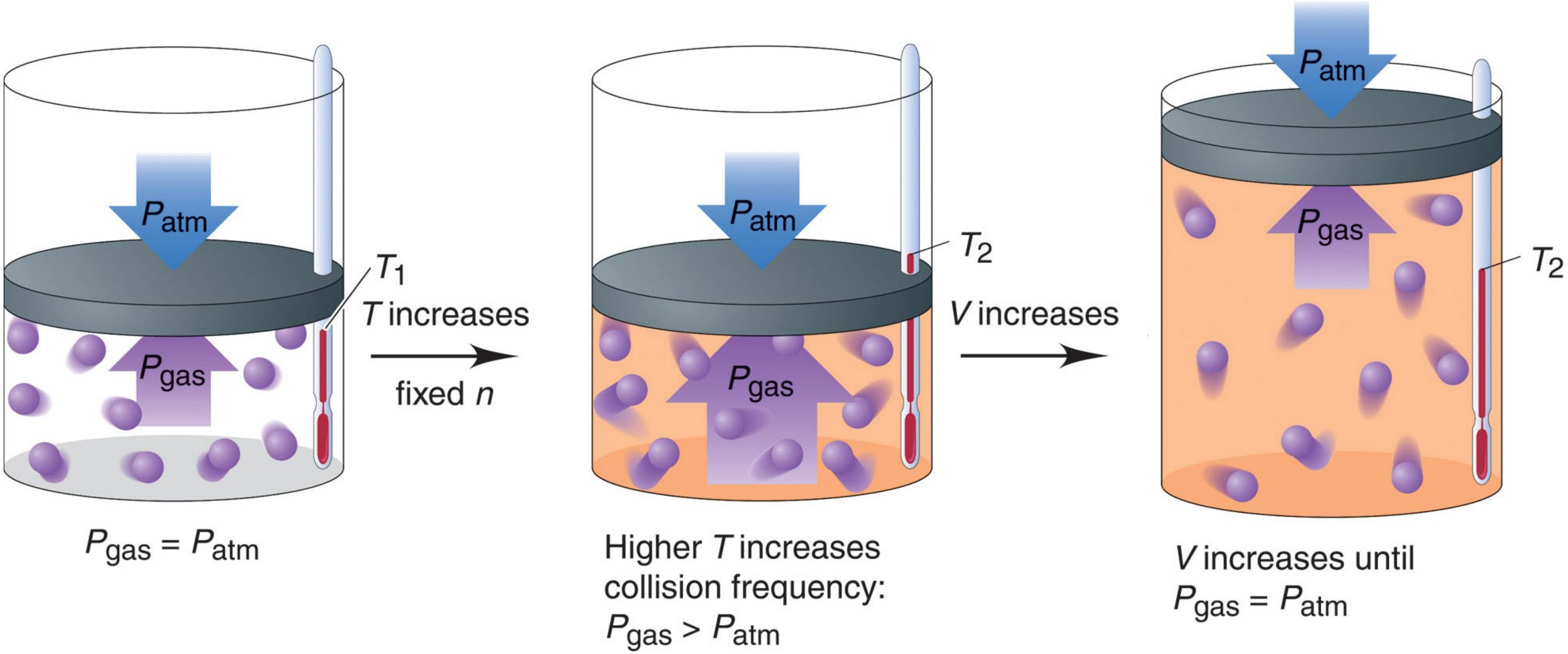
Supplementary: connection between micro- and macro-scopic description

A molecular description of Boyle's Law



PV=nRT

A molecular description of Charles's Law



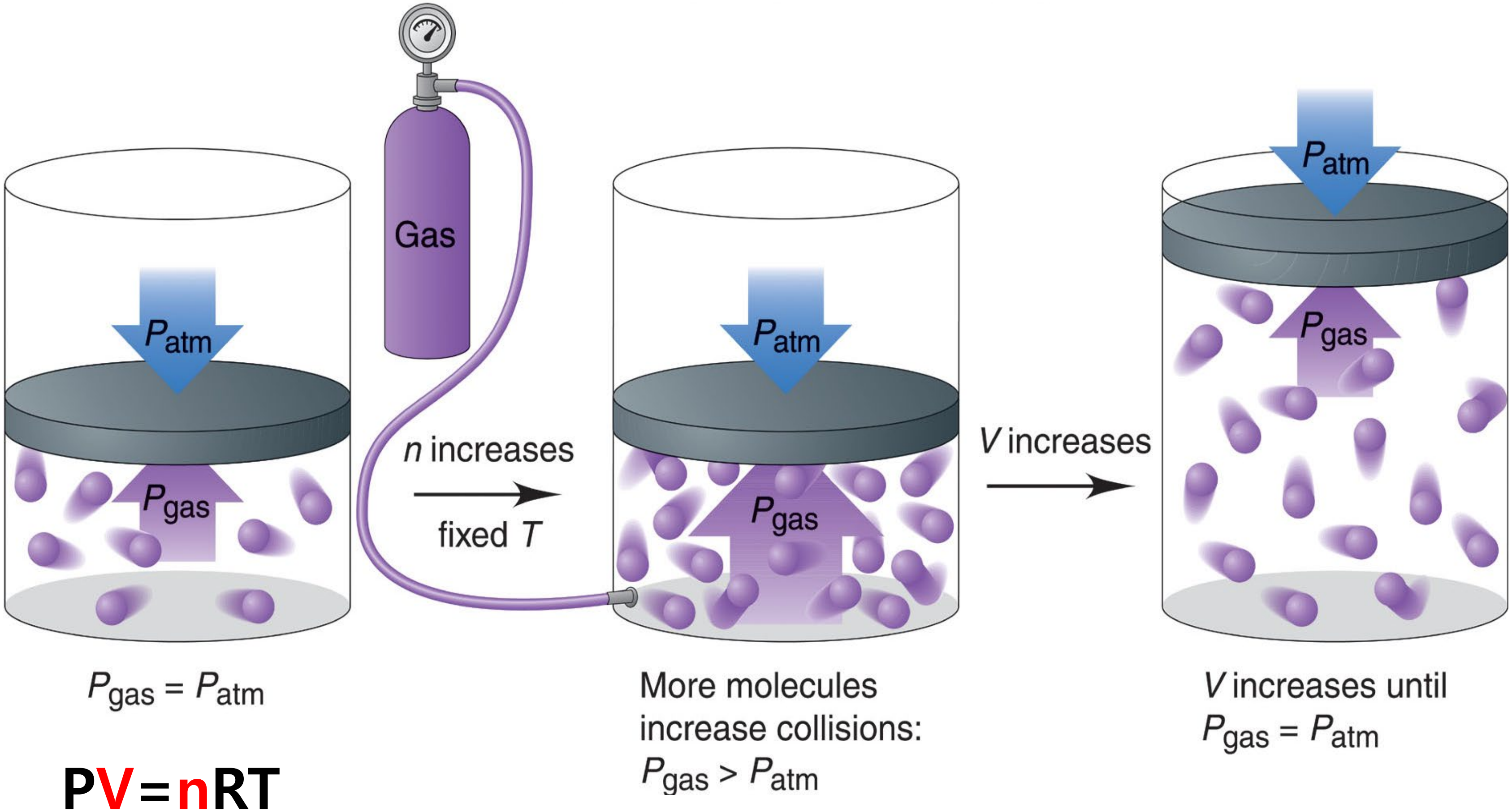
$P_{gas} = P_{atm}$

Higher T increases collision frequency: $P_{gas} > P_{atm}$

V increases until $P_{gas} = P_{atm}$

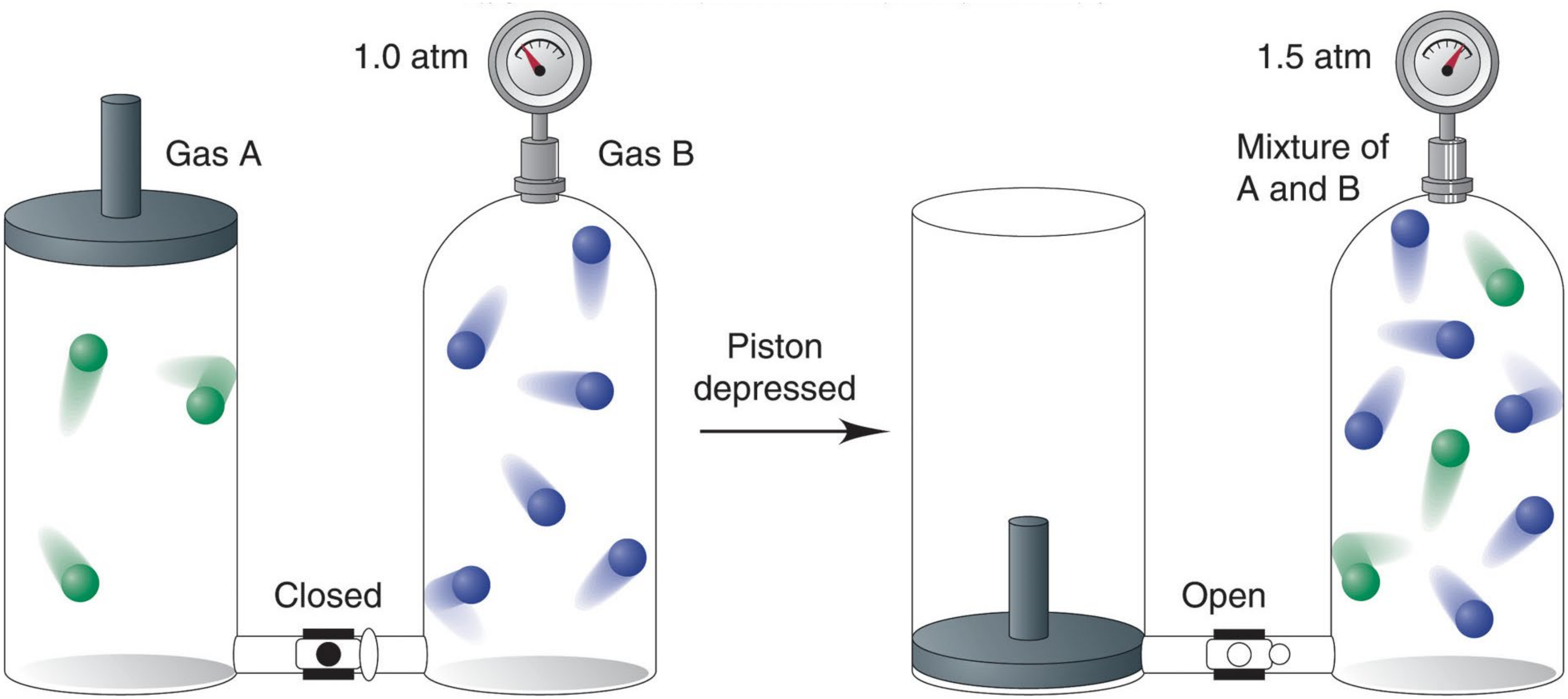
PV=nRT

A molecular description of Avogadro's Law



$PV=nRT$

A molecular description of Dalton’s law of partial pressures.



$P_A = P_{total}$
$= 0.50 \text{ atm}$
$n_A = 0.30 \text{ mol}$

$P_B = P_{total}$
$= 1.0 \text{ atm}$
$n_B = 0.60 \text{ mol}$

$P_{total} = P_A + P_B$
$= 1.5 \text{ atm}$
$n_{total} = 0.90 \text{ mol}$
$X_A = 0.33 \text{ mol}$
$X_B = 0.67 \text{ mol}$