◆ Colligative properties

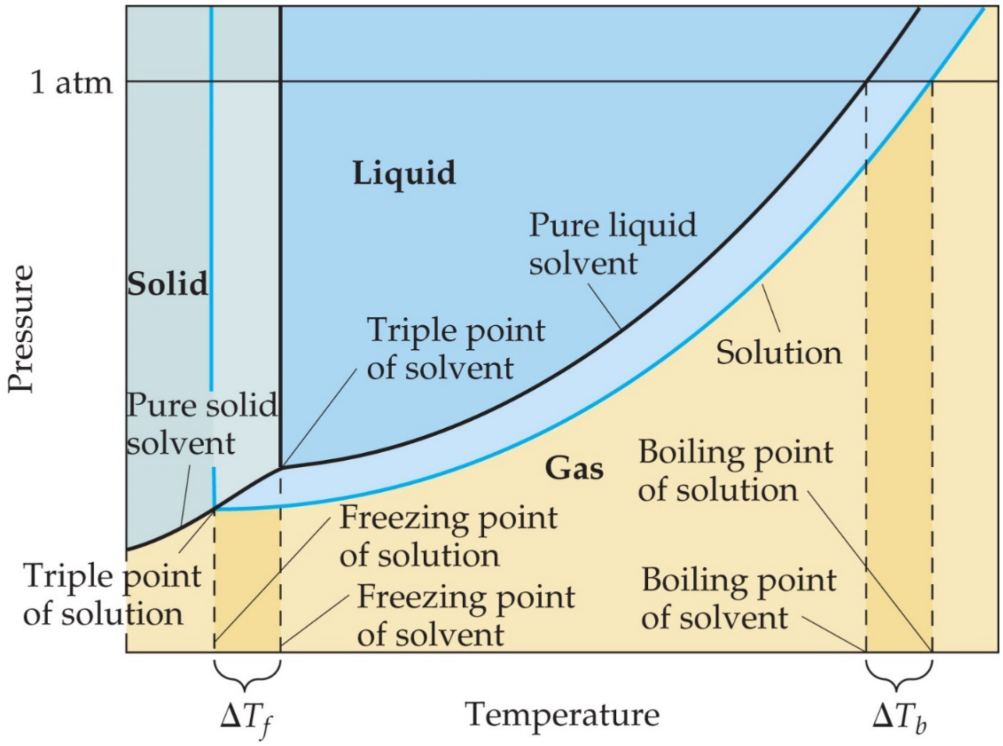
Collective properties depending on the *number* of dissolved particles rather than the *nature* of the particular particles involved

→ Determination of ***Molar mass (mass per mole), molality(m)***

Let us consider

Nonvolatile solute, Nonelectrolyte, Binary solution

- ❖ **Vapor pressure lowering**
- ❖ **Boiling-point elevation**
- ❖ **Freezing-point depression**
- ❖ **Osmosis**



Osmosis is the movement of **solvent** particles from a region of lower to a region of higher concentration through a semi-permeable membrane. (Larger solute molecules can not pass through the membrane.)

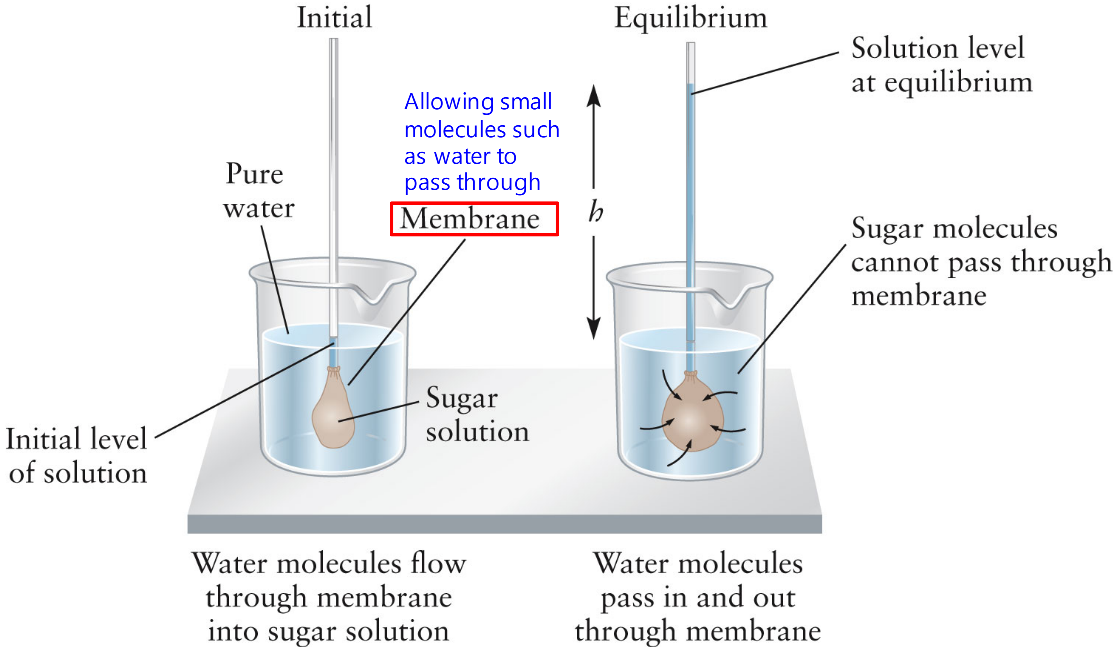


Fig. 11.14 Measurement of the osmotic pressure.

➢ Raoult's law

The solvent vapor pressure changes with the composition of the solution at a fixed temperature.

$P_1°$: vapor press of pure solvent

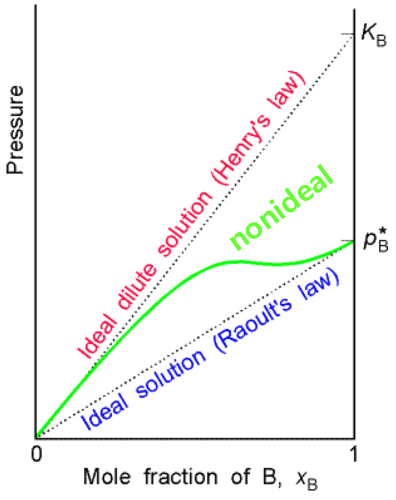
$$P_1 = X_1P_1°$$

➢ Henry's Law

For X_2 <<1, $\boxed{P_2 = k_2X_2}$

k_2 : Henry's law constant

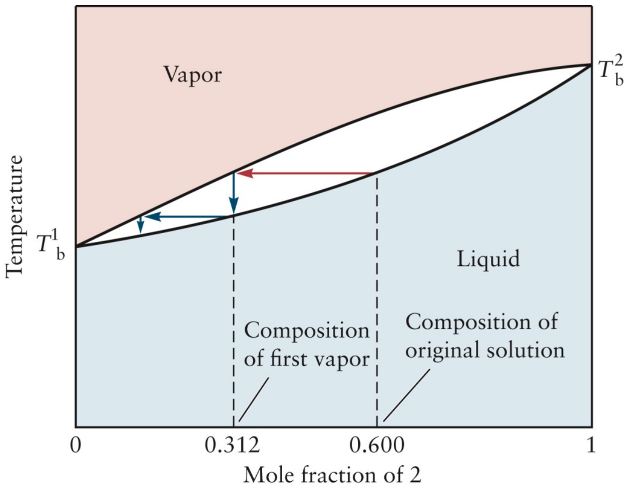
~ Henry's law applies to a volatile *solute* in a dilute solution.

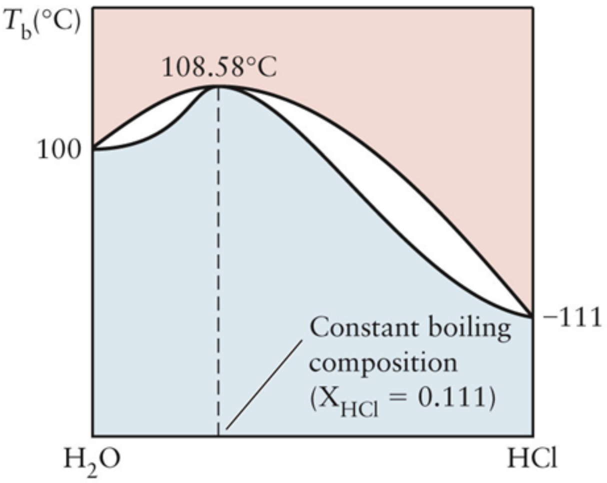


➢ Fractional Distillation

~ Separation of two or more components of a liquid solution by successive evaporation and condensation on the basis of their different boiling points

An azeotrope behaves like a single-component fluid.





(a) Constant boiling maximum

UNIT IV

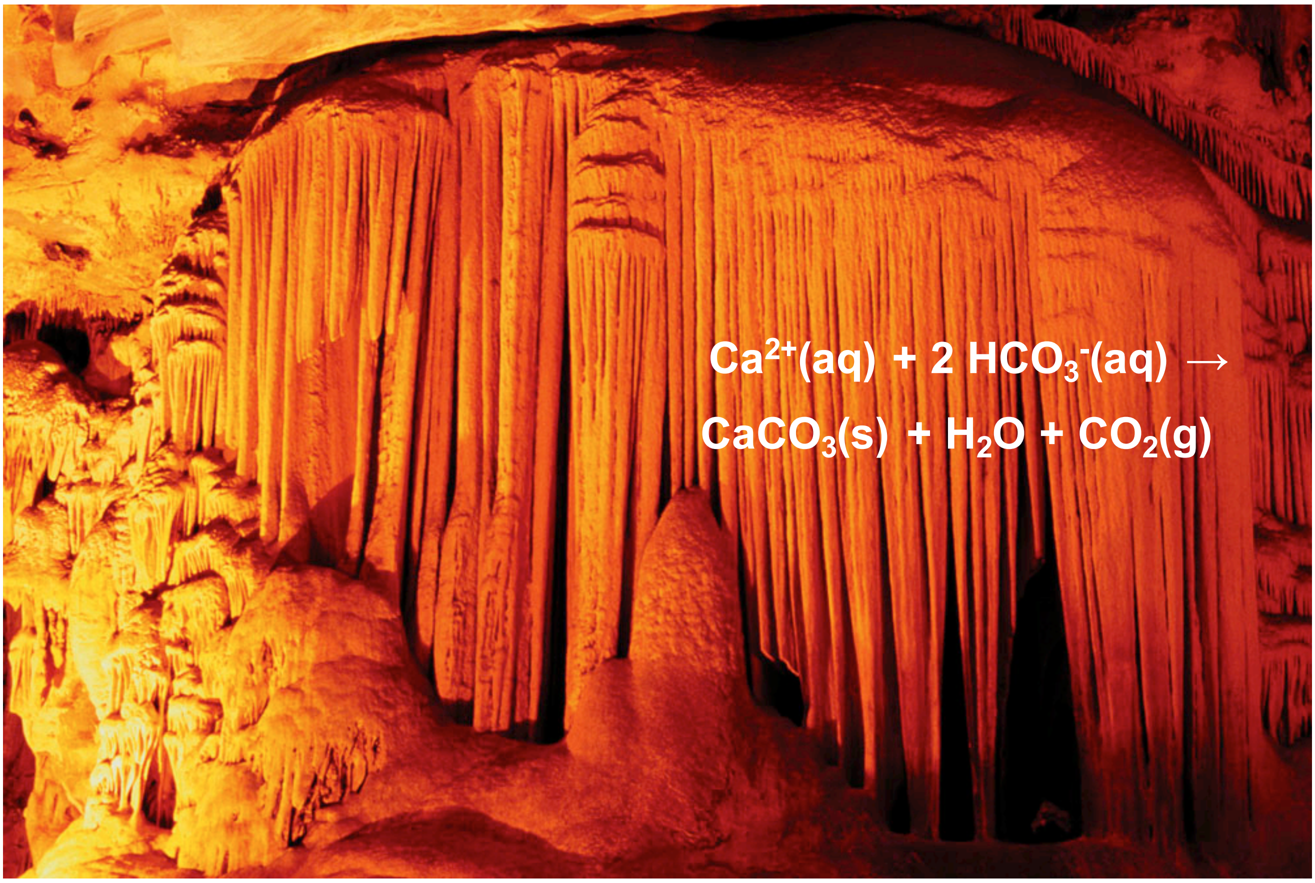
EQUILIBRIUM IN CHEMICAL REACTIONS

CHAPTER 12
Thermodynamic Processes and Thermochemistry

CHAPTER 13
Spontaneous Processes and Thermodynamic Equilibrium

CHAPTER 14
Chemical Equilibrium

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

12.1 Systems, States, and Processes

12.2 The First Law of Thermodynamics: Internal Energy, Work, and Heat

12.3 Heat Capacity, Calorimetry, and Enthalpy

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 → mechanical

Diesel locomotive

chemical →
electrical → mechanical

How to measure the heat transfer in a chemical reaction?

@ constant pressure
➔ Chemical equilibrium

Thermodynamics

What types of chemical and physical processes are possible and under what conditions and to calculate quantitatively the properties of the equilibrium state that ensues when a process is conducted.

➔ Determine whether a process is is possible
But not say how rapidly the process will occur

Thermodynamics

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

√ Study of **transformation of energy** from one form to another (direction!)

√ 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:

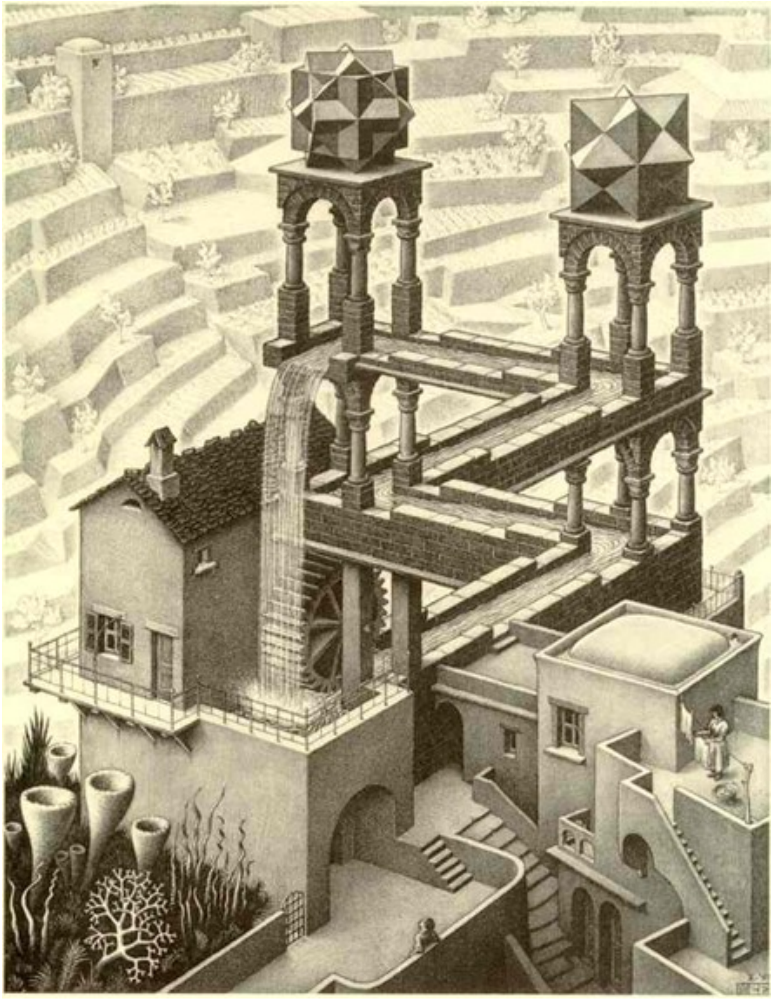
Unavailability of 0 K

~ 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

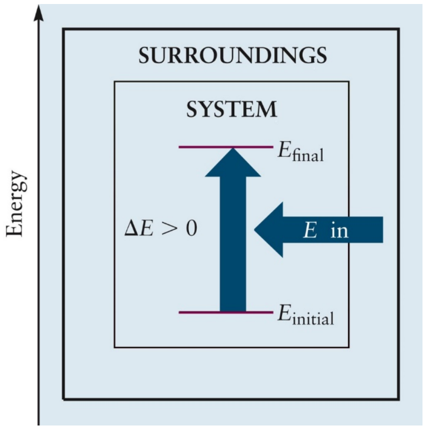
“Waterfall”(1961)

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

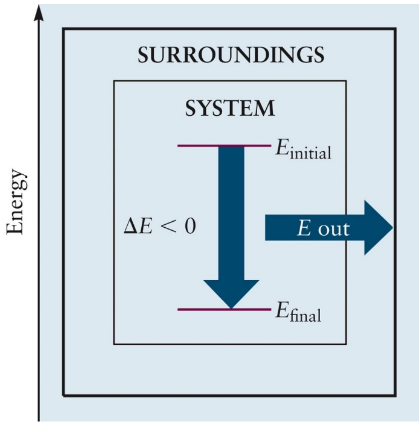
12.1 SYSTEMS, STATES, AND PROCESSES

- **System** : Anything of our interest (A)
- **Surroundings:** Everything else (1-A)
- **Universe** = system + boundary + surroundings (1)

Matter & Energy: conserved but exchanges

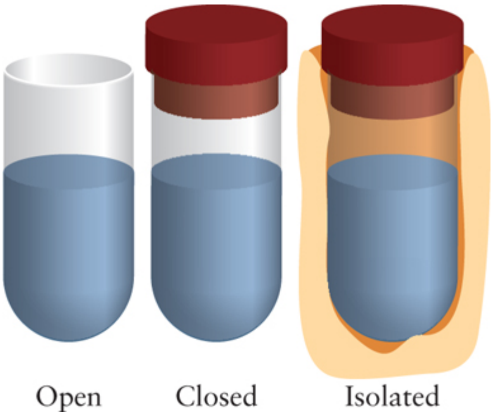


The system gains energy from the surroundings.



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 ➔ isolated

(b) Coolant in a refrigerator coil ➔ closed

(c) A bomb calorimeter in which benzene is burned ➔ isolated

(d) Gasoline burning in an automobile engine ➔ open

(e) Mercury in a thermometer ➔ closed

(f) A living plant ➔ open

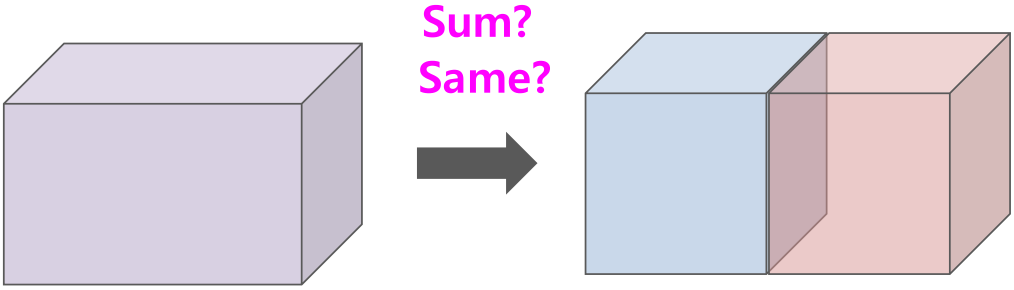
P, V, T and U (E)

- **Extensive property** : $\boxed{m, V}$ **Sum**

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

- **Intensive property** : $\boxed{P, T}$ **Same**

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



Sum?
Same?

◆ **Thermodynamic state** ~ A macroscopic condition of a system

Properties uniquely determined at fixed values independent of time (none of properties changes with 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

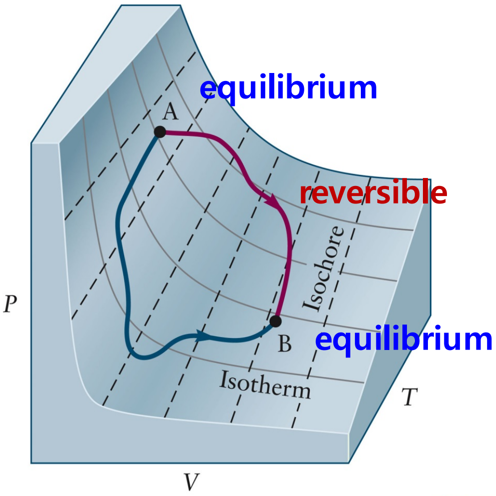


Fig. 12.1 P-V-T surface of 1 mol of ideal gas

◆ 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

NOT thermodynamic equilibrium states

~ abrupt, finite, real changes in external conditions

~ many irreversible paths between thermodynamic states

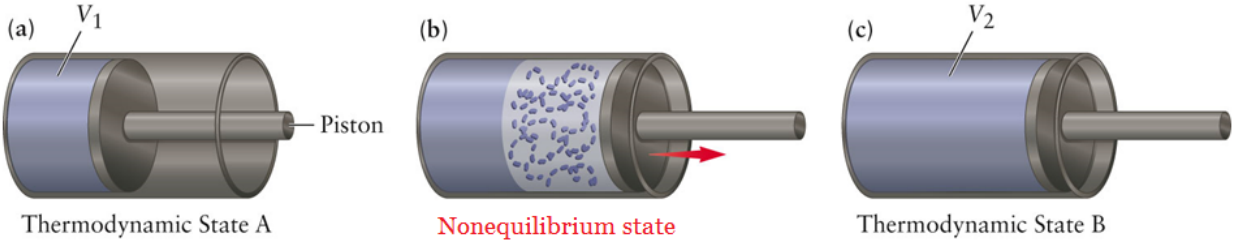


Fig. 12.2. Stages in an irreversible expansion of a gas from an initial state (a) of volume V_1 to a final state (c) with volume V_2. In the intermediate stage (b) the system is not in equilibrium.

★ State function : $\boxed{E,\ U,\ P,\ V,\ T,\ d,\ m,}$ …

→ A property that depends only on the current state of the system and is independent of how that state was prepared (only consideration for initial and final states).

★ Path function : $\boxed{w,\ q,\ \ldots}$

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

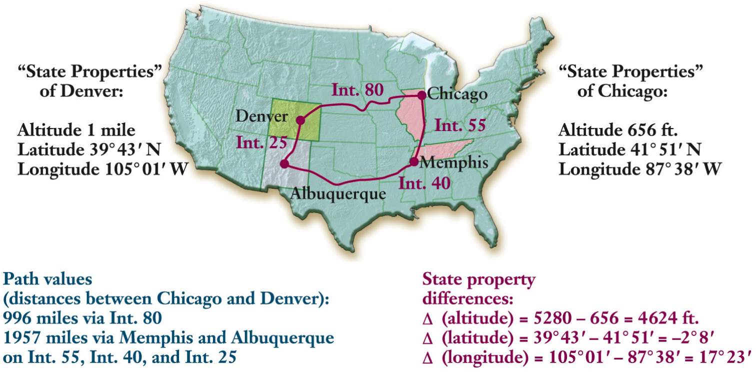


Fig. 12.3. Differences in state properties are independent of the path followed.

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

$$\boxed{P,\ V,\ T \text{ and } U\ (E)}$$

Work: w

+ Heat: *q* (@constant P or V)

Internal energy U

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◆ **Work**

➢ **Mechanical work**

(1) $w = F(r_f - r_i)$ (force along direction of path)

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

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

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

➢ **Pressure-Volume Work (PV-work)**

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

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

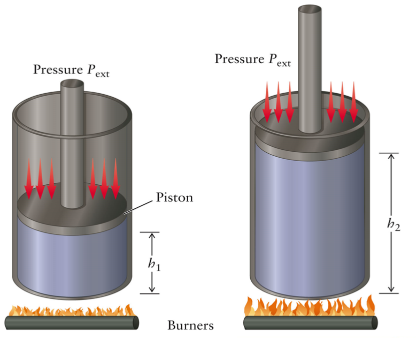


Fig. 12.4. As the gas inside is heated, it expands, pushing the piston against the pressure P_{ext} exerted by the gas outside.

➢ Pressure-Volume Work (PV-work)

$$w = -F_{\text{ext}}(h_{\text{f}} - h_{\text{i}}) = -P_{\text{ext}}A\Delta h$$

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

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

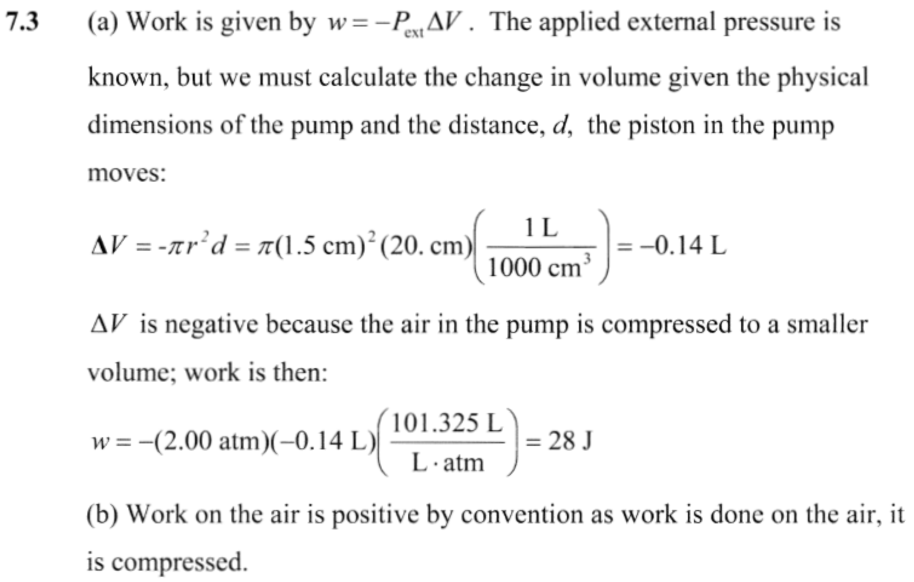
1 L atm = $(10^{-3}\ \text{m}^3)(1.01325 \times 10^5\ \text{kg m}^{-1}\ \text{s}^{-2})$ = **101.325 J**

A238

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.

◆ Heat (or thermal energy), *q*

- ~ Amount of energy transferred between two substances at different temperature
- ~ Changes the internal energy of a system

◆ 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

~ Amount of heat transfer vs. work

Example 12.2

Suppose a 10.00 kg mass drops through a height difference of 3.00 m, and the resulting work is used to turn a paddle in 200.0 g water, initially at 15.00 °C. The final water temperature is found to be 15.35 °C. Assuming that the work done is used entirely to increase the water temperature, calculate the conversion factor between joules and calories.

$$\left.\begin{aligned} w &= -Mg\Delta h = -(10\,kg)(9{,}087\,ms^{-2})(-3\,m) = 294\,J \\ q &= Mc_s\Delta T = (200\,g)(1\,cal\,K^{-1}g^{-1})(0.35\,K) = 70\,cal \end{aligned}\right\}\text{1 cal = 4.184 J}$$

◆ Thompson (later Count Rumford)

~ Cannon barrel

➢ Mayer and Joule

A paddle driven by a falling weight

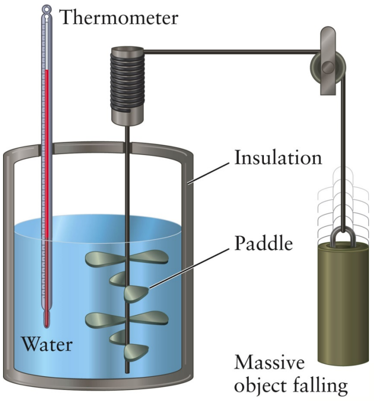


Fig. 12.7. The falling weight turns a paddle, doing work on the system, increasing *T*.

◆ 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

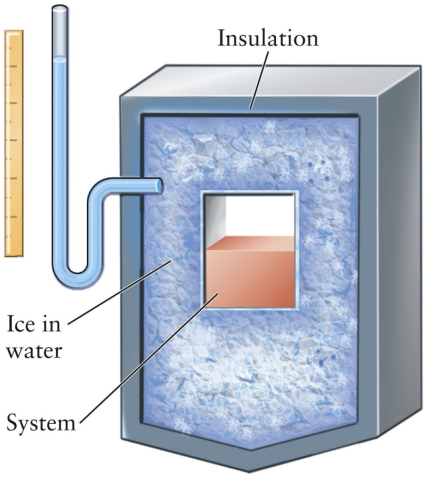
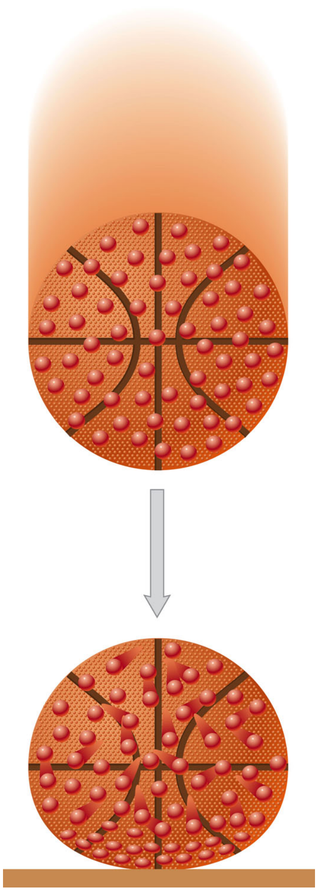


Fig. 12.6. Ice calorimeter



◆ Internal energy, *U*

= Σ total energies

= Σ(KE + PE + bond energies of molecules)

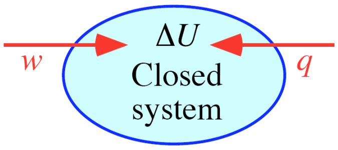
in a system

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.

➢ The first law of thermodynamics (closed system)

applicable to any process that begins and ends in equilibrium states

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



If the energy change is caused by mechanical contact of the system with its surroundings, work is done.
If it is caused by thermal contact, heat is transferred.

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

The total energy of an isolated system is constant.

Work (or Heat) is a transient form of energy
Work induces a concerted motion
Heat induces a random motion

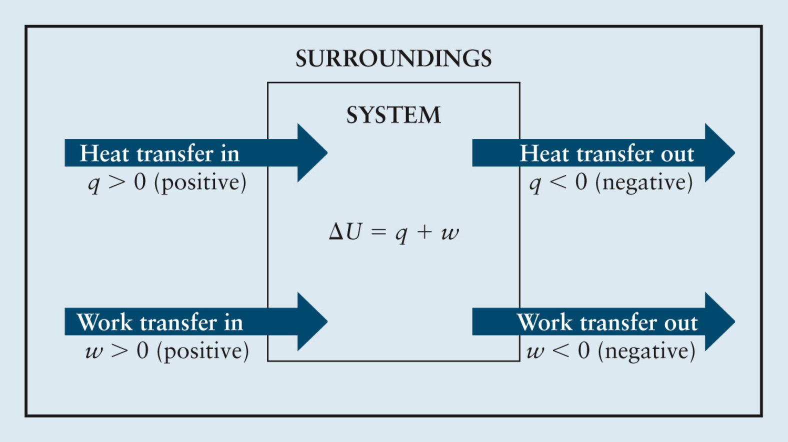
◆ The First Law of Thermodynamics

➢ Principle of conservation of energy

$$\Delta U = q + w$$

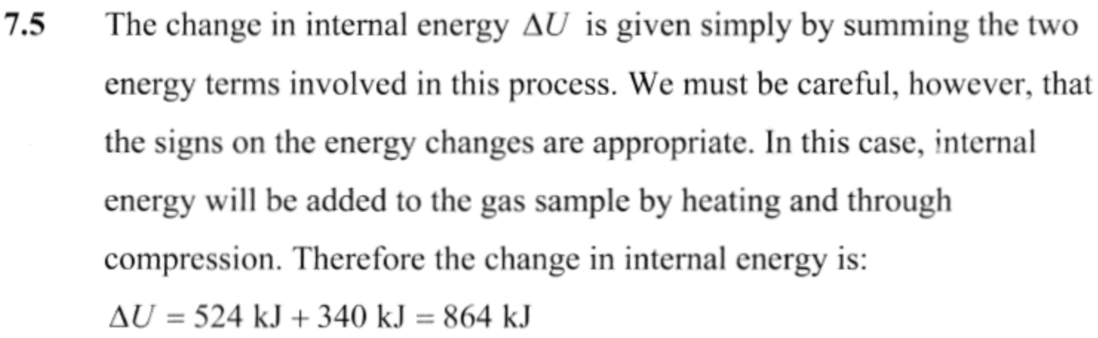
q, w : path functions, ΔU : state function

Change in internal energy in a process is the sum of the heat and the work transfer.
The total energy is conserved while it is exchanged b/w the system and the surroundings.



$$\Delta U_{\text{univ}} = \Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$$
$$= (q_{\text{sys}} + w_{\text{sys}}) + (q_{\text{surr}} + w_{\text{surr}})$$
$$= \underbrace{(q_{\text{sys}} + w_{\text{sys}})}_{\text{Energy gained}} + \underbrace{(-q_{\text{sys}} - w_{\text{sys}})}_{\text{Energy lost}} = 0$$

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:

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

P, V and ΔU (E) → q (ΔT)

- **The First Law of Thermodynamics**
  - Principle of conservation of energy

$$\Delta U = q + w$$

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

q, w : path functions, ΔU : state function

12.3 HEAT CAPACITY, CALORIMETRY, AND ENTHALPY

- **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

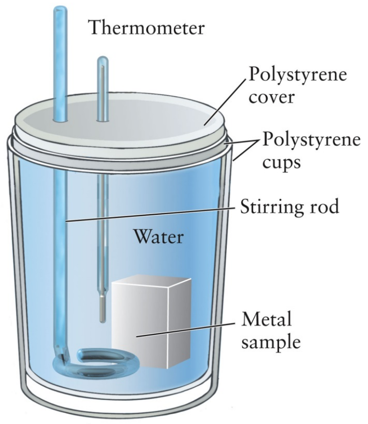


Fig. 12.8. A styrofoam cup calorimeter.

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

◆ 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**

$$q_V = n\, c_V\, \Delta T$$

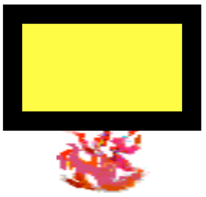
➢ **Molar heat capacity at constant pressure, c_P**

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

- If C_V and C_P do not change with temperature,

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

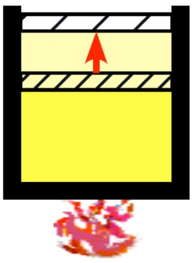
Constant volume



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

Speed of molecules increases

$$\boxed{q_V < q_P}$$



Constant pressure

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

To achieve the identical temperature change, C_p is greater than C_v.

◆ Heat Transfer at <u>Constant Volume</u>: Internal Energy

$q_V = \Delta U$ (constant V)

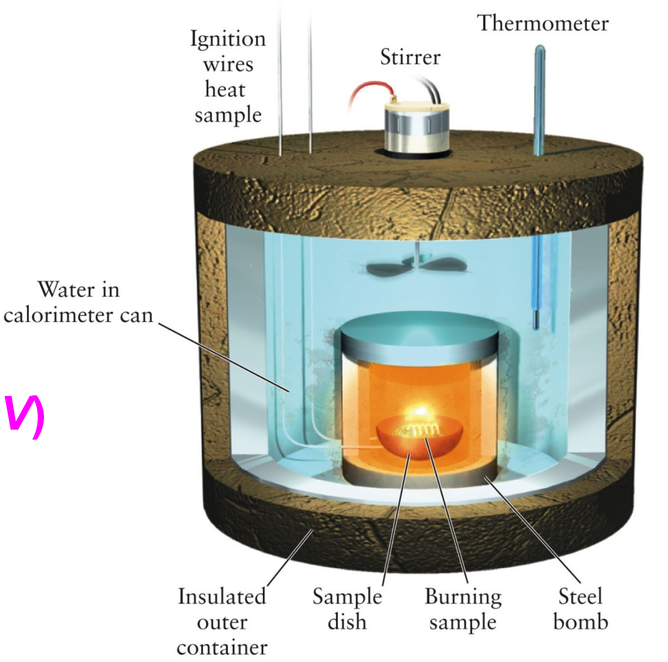


Fig. 12.9. The combustion calorimeter, called a "bomb calorimeter".

◆ Heat Transfer at <u>Constant Pressure, q_p</u>: Enthalpy

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

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

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

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

Enthalpy (H) $\quad H = U + PV$

$\Delta H = q_P = \Delta U + P\,\Delta V$ (at constant P)

$\Delta H = \Delta U + \underbrace{\Delta\,(PV)}$ (in general)

Correction term,
P-V work, expansion work

12.4 THE FIRST LAW AND IDEAL GAS PROCESSES

◆ Heat Capacities of Ideal Gases

Kinetic energy of an *n* mol of ideal gas

$\bar{\varepsilon} = \frac{3}{2}k_B T$ ($k_B = R/N_A$)

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

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

$\Delta U = q_V = nc_V\, \Delta T$ (ideal gas) (2)

Compare (1) and (2).

$c_V = (3/2)R$ (monatomic ideal gas)

(b) At constant pressure,

$\Delta U = q_P + w$

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

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

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

$c_P = c_V + R = (5/2)R$ (any ideal gas)

$\Delta U = nc_V\, \Delta T$ (any ideal gas)

$\Delta H = nc_P\, \Delta T$ (ideal gas)

Summary

◆ **The First Law of Thermodynamics**

- Principle of conservation of energy

$$\Delta U = q + w$$

$$\Rightarrow q = \Delta U - w$$

◆ **Heat Transfer at Constant Pressure, q_p: Enthalpy**

$\Delta H = q_P$	(at constant P)
$\Delta H = \Delta U + \Delta(PV)$	(in general)
$\Delta H = nc_P \Delta T$	(ideal gas)