Physical Chemistry

المحـــاضـرة 8

المرحلــة الثانـية

أ.د. حـــســن صبـيـح جبـر

The first law of thermodynamics

- 1st law of thermodynamics is an extension of the law of conservation of energy
- The change in internal energy of a system is equal to the heat added to the system minus the work done by the system

Energy Statement

"Energy can neither be created nor destroyed during a process; but can be only converted from one form to another"

Energy Transfer in form of Heat by 3 ways:

1- Conduction:

Transfer of Energy from a more energetic particle of a substance to the adjacent less energetic one, as a result of interaction between them.

2- Convection:

Transfer of Energy between a solid surface and the adjacent fluid that is in motion. It involved both, the combined effect of conduction and fluid motion.

3- Radiation:

Transfer of Energy due to the emission of electromagnetic waves.

1st law formulation

$$\Delta U = q - W$$

Where ΔU is the internal energy

q is the heat added to the system or heat remove form it.

w is the work done by the system or work done on it.

q positive (+q)	heat added to the system
q negative (-q)	heat remove form the system
w positive (+w)	Work done on the system
w negative (-w)	Work done by the system

University of Al Muthana, college of science, chemistry department

The internal energy

In thermodynamics, the total energy of a system is called its **internal energy**, U. The Internal energy is the **total kinetic** and **potential energy** of the molecules in the system. We denote by ΔU the change in internal energy when a system changes from an initial state i with internal energy U_i to a final state f of internal energy U_f :
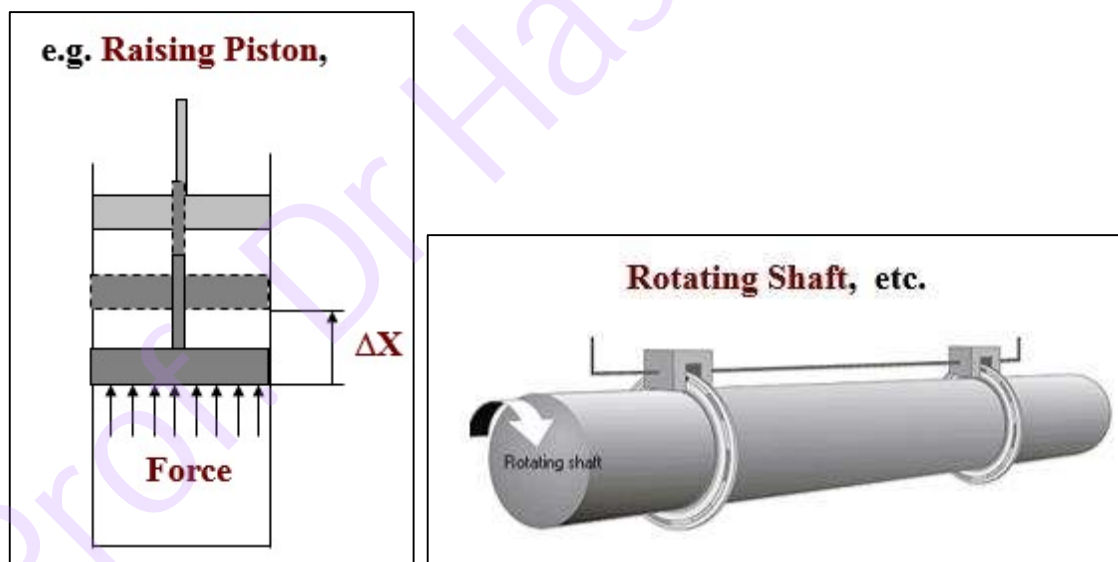
$$\Delta U = U_f - U_i$$

The internal energy is an extensive property of a system (Section F.3) and is measured in joules (1 J = 1 kg m^{2}s^{-2}).

Note/ at the isothermal process (constant temperature) ΔU *equal* **Zero** *($\Delta U = 0$).*

Work

Work is the Energy transfer associated with a Force acting through a distance. Denoted by J or kJ.

Both q and w are Path Functions which have Inexact Differentials, designated by symbol δ.

Thus, a differential amount of Heat or Work is represented as δq or δw; instead of dq or dw.

Integral of δW is $\neq$ (W$_2$ − W$_1$).

University of Al Muthana, college of science, chemistry department

1- Expansion work

The work arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere.

a- The general expression for work

Work is movement an object a distance Δz against an opposing force of magnitude F is

$dw = -Fdz$ ----- 1

where $F = p.A$ ---- 2

$dw = -p_{ex}. Adz$ ----- 3

The quantity Adz is the change in volume, dV

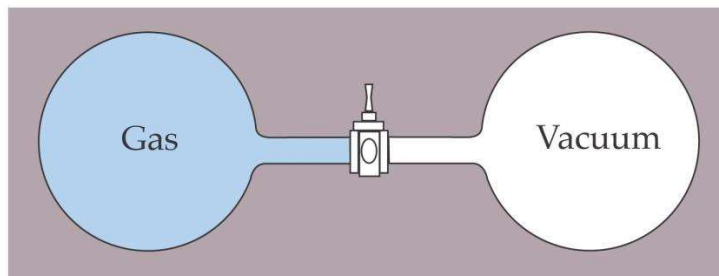$dw = -p_{ex} dv$ ----- 4

$$w = -\int_{V_i}^{V_f} p_{ex} dV \qquad ----- 5$$

b- Free expansion

Free expansion is expansion against zero opposing force. It occurs when $p_{ex} = o$. According to eqn 5, dw = 0 for each stage of the expansion. Hence, overall:

w = 0

For a gas at low density – an ideal gas-, a free expansion does not change the temperature of the gas

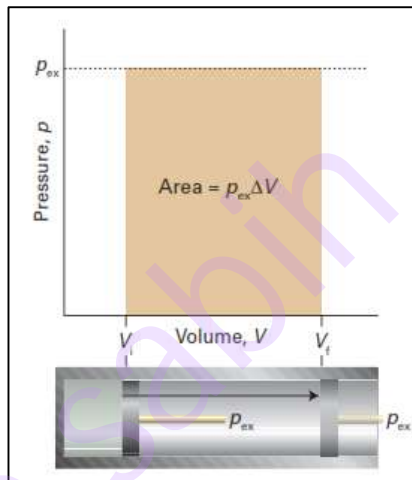University of Al Muthana, college of science, chemistry department

(c) Expansion against constant pressure

A chemical example of this condition is the expansion of a gas formed in a chemical reaction in a container that can expand. We can evaluate eqn 5 by taking the constant P_{ex} outside the integral:

$$w = -p_{ex}\int_{V_i}^{V_f} dV = -p_{ex}(V_f - V_i)$$

$$w = -P_{ex}\Delta V \qquad \text{------ 6}$$

(d) Reversible expansion

A **reversible change** in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. The key word 'infinitesimal' sharpens the everyday meaning of the word 'reversible' as something that can change direction. Such a system is not in mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible.

To achieve reversible expansion we set P_{ex} equal to P at each stage of the expansion.

$$dw = -p_{ex}dV = -pdV \qquad \text{-------- 7}$$

Then we can express p in terms of V and evaluate the integral.

$$w = -\int_{V_i}^{V_f} pdV$$

$$\text{------- 8}$$

(e) Isothermal reversible expansion

Because the equation of state is $pV = nRT$, we know that at each stage $p = nRT/V$, with V the volume at that stage of the expansion. The temperature T is constant in

University of Al Muthana, college of science, chemistry department

an isothermal expansion, so (together with *n* and *R*) it may be taken outside the integral.

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$ ------ 9

According to Boyle's Law $\frac{V_f}{V_i} = \frac{P_i}{P_f}$

$$w = -nRT \ln \frac{P_i}{P_f}$$ ------- 10

(f) The work of gas production

The gas drives back the atmosphere. We can neglect the initial volume because the final volume (after the production of gas) is so much larger and

$\Delta V = V_f - V_i \approx V_f = nRT/P_{ex}$.

Therefore

$$w = -p_{ex}\Delta V \approx -p_{ex} \times \frac{nRT}{P_{ex}} = -nRT$$

2- Isochoric work

Isochoric implies constant volume, V and dV = 0. According to eqn 5, dw = 0

w = 0

EX/ Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce $FeCl_2$ (aq) and hydrogen in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C. if you known A.Wt of Fe = 55.85 g mol^{-1}.

(a)

      w = 0 because the volume cannot change, so no expansion work is done

(b)

      w = -nRT

$$n = \frac{wt}{A.wt} = \frac{50g}{55.85g.mol^{-1}} = 0.895mol$$

R = 8.314 J K^{-1} mol^{-1}

T = 25°C + 273 = 298 K

      w = - (0.895 mol) (8.314 J K^{-1} mol^{-1}) (298 K)

$$w = -2217.4\,J \times \frac{1kJ}{1000J}$$

      w = -2.2 kJ

EX/ A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate *work (w).*

EX// A chemical reaction takes place in a container of cross-sectional area 50.0 cm^2 . As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system.

EX/ A sample of argon (molar mass 39.9 g mol^{-1}) of mass 6.56 g occupies 18.5 dm^3 at 305 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 7.7 kPa until its volume has increased by 2.5 dm^3. (b) Calculate the work that would be done if the same expansion occurred reversibly.