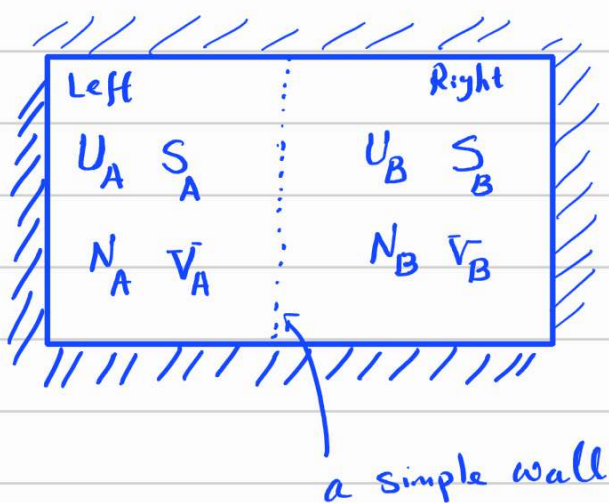


Thermodynamical Equilibrium التوازن الديناميكي الحراري

Thermodynamical Laws القوانين الديناميكي الحراري

① What is the concept of thermodynamical Equilibrium?



$U \equiv$ Internal Energy

$S \equiv$ Entropy

$N =$ Number of Particles

$V =$ Volume

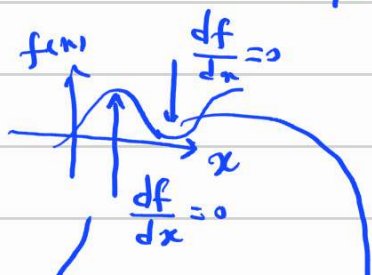
①-1 ☆ Thermal Equilibrium

$\Rightarrow$ التوازن حراري $T_A = T_B$

$$S_{\text{total}} = S_A + S_B$$

$$U_{\text{total}} = U_A + U_B = \text{Constant: cts. ثابت}$$

For Equilibrium: $S_{\text{total}} \equiv \text{Extremum ?}$



$$\star \left. \frac{\partial S_{\text{total}}}{\partial U_A} \right|_{N_A=\text{cts}, V_A=\text{cts}} = 0$$

$$\hookrightarrow \frac{d^2 f}{dx^2} < 0 \quad \hookrightarrow \frac{d^2 f}{dx^2} > 0$$

Principle of Statistical Mechanics

$$\left. \frac{\partial S_{\text{total}}}{\partial U_A} \right|_{\substack{N_A = \text{cts} \\ V_A = \text{cts}}} = 0 \quad \text{or} \quad \left. \frac{\partial S_{\text{total}}}{\partial U_B} \right|_{\substack{N_B = \text{cts} \\ V_B = \text{cts}}} = 0$$

$$0 = \frac{\partial S_{\text{total}}}{\partial U_A} = \frac{\partial [S_A + S_B]}{\partial U_A} = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 \quad \text{I}$$

$$0 = dU_{\text{total}} = d(U_A + U_B) = dU_A + dU_B = 0$$

Isolated System

$$dU_A = -dU_B \quad \text{II}$$

$$\begin{array}{l} \text{I} \\ \text{II} \end{array} \rightarrow \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{-dU_B} = 0 \Rightarrow \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad \star \star$$

$N = \text{cts}$
 $V = \text{cts}$

Energy Conservation (First law of thermodynamics)

$$dU = Tds - \underbrace{p}_{=0} dV + \underbrace{\mu}_{=0} dN \Rightarrow dU - \underbrace{\mu dN + p dV}_{\substack{N = \text{cts} \\ V = \text{cts}}} = Tds$$

$$\Rightarrow dU = Tds \rightarrow \boxed{\frac{ds}{dU} = \frac{1}{T}}$$

For Thermal Equilibrium with $N = \text{cts}$
 $V = \text{cts}$

$$\frac{1}{T_A} = \frac{1}{T_B} \Rightarrow \boxed{T_A = T_B}$$

(1-2) ★ Mechanical Equilibrium. /
توازن ميكانيكي

$$\boxed{P_A = P_B}$$

$$\left. \frac{\partial S_{\text{total}}}{\partial V_A} \right|_{\substack{N = \text{cts} \\ U = \text{cts}}} = 0 \Rightarrow \left. \frac{\partial S_A}{\partial V_A} \right|_{\substack{N_A = \text{cts} \\ U_A = \text{cts}}} = \left. \frac{\partial S_B}{\partial V_B} \right|_{\substack{N_B = \text{cts} \\ U_B = \text{cts}}}$$

$$dU = Tds - PdV \rightarrow \begin{cases} U_A = \text{cts} \\ U_B = \text{cts} \\ dU_A = 0 \\ dU_B = 0 \end{cases}$$

$$Tds = PdV \Rightarrow \left. \frac{dS}{dV} \right| = \frac{P}{T}$$

Mechanical
↑ Equilibrium

$$\begin{matrix} U = \text{cts} \\ N = \text{cts} \end{matrix}$$

مميز

$$\frac{P_A}{T_A} = \frac{P_B}{T_B}$$



$$P_A = P_B$$

If $T_A = T_B$

(1-3) ☆ Chemical Equilibrium توازن الكيمياء

$$0 = \frac{\partial S_{\text{total}}}{\partial N_A} \Rightarrow$$

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

$$dU=0 \leftarrow \begin{cases} U_A = \text{cts} \\ U_B = \text{cts} \end{cases}$$

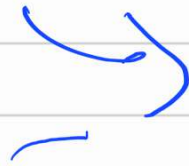
$$dV=0 \leftarrow \begin{cases} V_A = \text{cts} \\ V_B = \text{cts} \end{cases}$$

$$dU + PdV - \mu dN = Tds$$

$$\frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

$$\begin{matrix} U = \text{cts} \\ V = \text{cts} \end{matrix}$$

$$\frac{\mu_A}{T_A} = \frac{\mu_B}{T_B}$$



$$\mu_A = \mu_B$$

If $T_A = T_B$

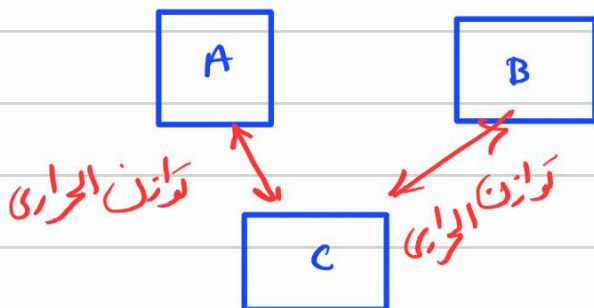
The lower value of μ , the higher
desire to absorb particles

② A glance & brief about thermodynamical laws.

موجز عن القوانين الديناميكية الحرارية

②-1 Zeroth Law قانون صفر

Two systems which are in thermal Equilibrium with
third system separately, are thermally Equilibrium
together



$$T_A = T_C$$

$$T_B = T_C$$

$$\Rightarrow T_A = T_B$$

2-2 First Law

المبدأ الأول

Conservation of Energy.

$$dU = \delta Q + \delta W$$

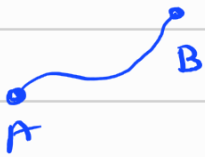
Change in Internal Energy is due to

either change in heat or/and work.

$$dU = Tds - PdV + \mu dN$$

General Form.

U : is state Parameter : this means that



$$\Delta U = U_B - U_A \text{ and it is independent}$$

from selected path.

2-3 Second Law

$$ds \geq \frac{\delta Q}{T}$$

Q_1

W

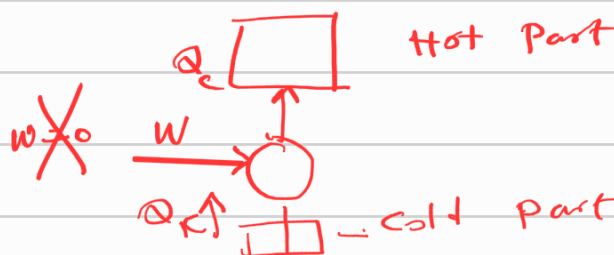
Q_2

~~$Q_2 \neq 0$~~

There is No Ideal car

→ The efficiency of Machine is less than 100%
For Reversible Process $ds = \frac{\delta Q}{T}$

For Irreversible proc $ds > \frac{\delta Q}{T}$



There is No Ideal Refrigerator

(2-4) Third Law: {
Nernst Statement
Planck Statement
Simon Statement
القانون الثالث

$$\text{If } T \rightarrow 0 \quad \Delta S \rightarrow 0$$

$$\lim_{T \rightarrow 0} C_p - C_v \rightarrow 0$$

or at Zero Temperature (-273°)

No Ideal Gas

The Zero Kelvin is Not accessible.

لا يمكن الوصول الى صفر مطلق

الانقسام والاندماج