سنتر فيوتشر

Subject: كيمياء إعدادى

Chapter: الثرمو (٣)

* Adiabatic Expansion or Contraction of ideal gas :-

→ Adiabatic = isolated

معزول = اديباتيكى

* Adiabatic change :- التغير الأديباتيكى

the process in which system doesn't gain or loss heat

النظام معزول يعنى ان النظام لا يفقد او يكتسب أى حرارة

$$q_{in} = q_{out} = zero$$

* Reservoir المستودع الحرارى

is any body Can supply or absorb heat without any change
in temperature

هو أى جسم يستطيع أن يمد أو يمتص حرارة دون أى تغير
فى درجة الحرارة

* Heat engine المحرك الحرارى

is device that Convert heat into work
the heat engine Can be charaterize by the following :-

1- receive heat from high temperature source
2- Convert this heat into work
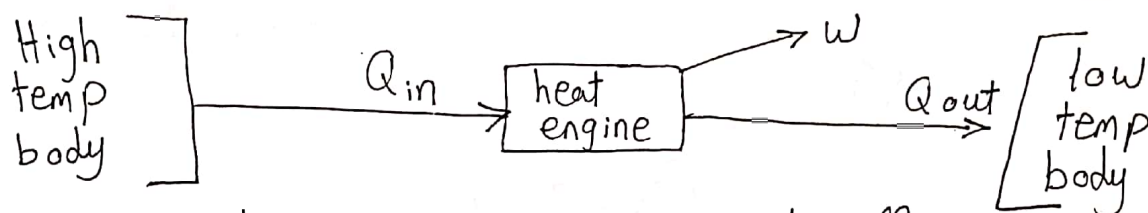3- reject remaining waste heat to low temperature sink
4- operate in cycle

> Second Law of thermodynamic

kelvin-Planck statement
related to -Heat engine
           - Pump

Clausius statement
related to refrigerator
المبرد

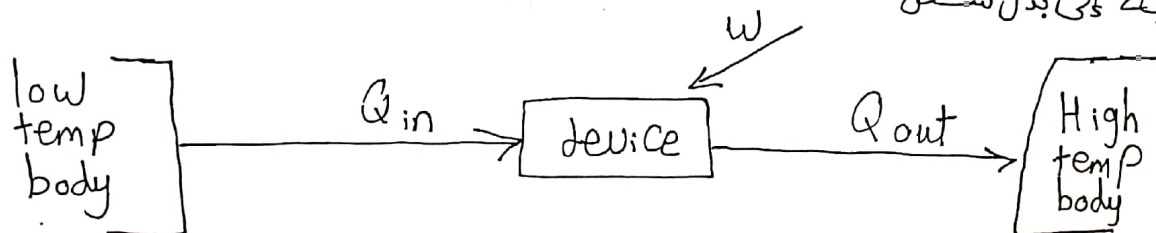↪ **Kelvin-Planck statement of second law of thermodynamic**

It's impossible for any device operate on cycle to recieve heat from reservoir and produce net amount of work

مستحيل وجود آلة تحول Q إلى W بنسبة 100% أي لايتوجد آلة كفائتها 100%


```
High          Qin    ┌────────┐   → W          ┌  low
temp   ]─────────────│ heat   │─────────────→  │  temp
body                 │ engine │   Q out        │  body
                     └────────┘
```

⟹ No heat engine have thermal efficiency 100%

↪ **Clausius statement of second law of thermodynamic**

It's impossible to construct device operate on cycle transefer heat from low temp body to high temp body <u>without doing work</u>

من المستحيل بناء آلة تنقل درجة الحرارة من الجسم البارد إلى الجسم الساخن دون الحاجة إلى بذل شغل

```
low           Qin    ┌────────┐  W              ┌  High
temp   ]─────────────│ device │ ↙               │  temp
body                 └────────┘   Q out    →    │  body
```

⊛ **Thermal efficiency** (μ_{th}) :- الكفاءة الحرارية

thermal efficiency $= \dfrac{\text{Net work output}}{\text{Net heat input}}$ محصلة الشغل الخارج / محصلة الحرارة الداخلة

$$\mu_{th} = \frac{W_{net,out}}{Q_{in}}$$

but $W_{net,out} = Q_{in} - Q_{out}$

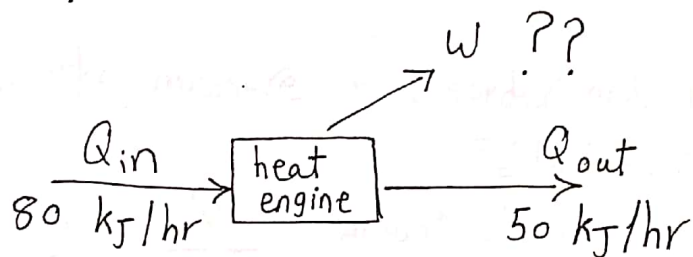$$\mu_{th} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

$$\mu_{th} = \frac{T_2 - T_1}{T_2}$$

as T_2 is temp of high temp reservoir
T_1 is temp of low temp reservoir

Example 1

Heat is transferred to heat engine from furance at rate 80 kJ/hr, if the rate waste heat rejection is 50 kJ/hr Determine the work output and the thermal efficiency for heat engine ?

$$W \ ??$$

$$\xrightarrow[80 \ kJ/hr]{Q_{in}} \boxed{\begin{array}{c} heat \\ engine \end{array}} \xrightarrow[50 \ kJ/hr]{Q_{out}}$$

$$Q_{in} = W + Q_{out}$$

$$W = Q_{in} - Q_{out} = 80 - 50 = 30 \ kJ/hr$$

thermal efficiency of heat engine

$$\eta_{th} = \frac{W_{net, \ out}}{Q_{in}} = \frac{30}{80} = 37.5 \ \%$$

Third Law of thermodynamic

As the system approaches absolute Zero ($0°k$ or $-273°C$)
all the processes cease توقف and the entropy of the system
approaches تصل a minimum value

Entropy It is the measure of disorder and randomness
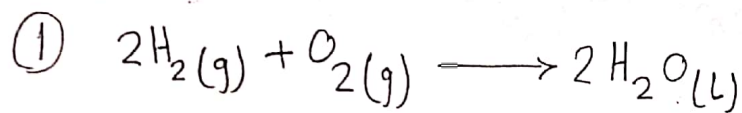هي مقياس الفوضى والعشوائية

$$Entropy\ (S) = \frac{Q}{T} \quad \frac{amount\ of\ heat}{temp\ in\ °k}$$

$$\Delta S = S_2 - S_1$$

net change = entropy in   -   entropy in
in entropy   final state   initial state

$$\Rightarrow \quad S_{gas} > S_{liquid} > S_{solid}$$

Example Predict the value of entropy :

① $2H_2(g) + O_2(g) \longrightarrow 2H_2O_{(L)}$

$$\Delta S_{total} = 2S°_{H_2O(L)} - (2S°_{H_2(g)} + S°_{O_2(g)}) = -ve$$

② $NH_4Cl_{(s)} \longrightarrow NH_3(g) + HCl_{(g)}$
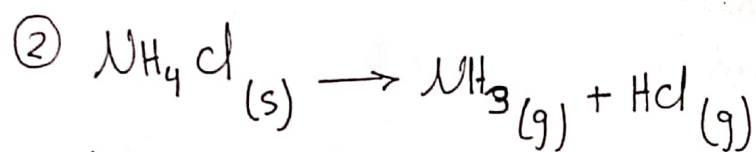
$$\Delta S_{total} = [S°_{NH_3(g)} + S°_{HCl(g)}] - S°_{NH_4Cl(s)} = +ve$$

③ $H_2(g) + Br_2(g) \longrightarrow 2HBr_{(g)}$
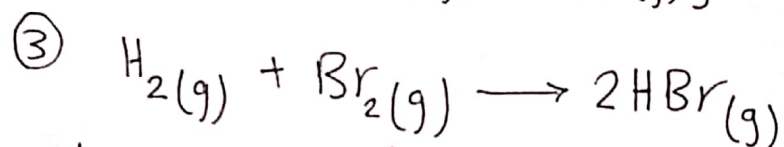
the same no. of molecules in reactant & product and molecules are
diatomic, and we Can't predict the value of ΔS

$$aA + bB \longrightarrow cC + dD$$

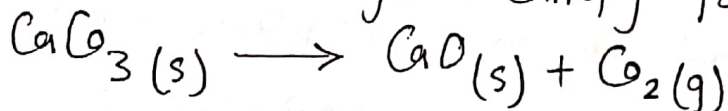متفاعلات reactant   نواتج product

$$\Delta S_{rxn} = \Sigma n (\Delta s)_{product} - \Sigma n (\Delta s)_{reactant}$$

$$\Delta S_{rxn} = [c S_C^o + d S_D^o] - [a S_A^o + b S_B^o]$$

as S^o is standard entropy of different substance from table

__Example__ Calculate the change in entropy for the reaction

$$CaCO_{3\ (s)} \longrightarrow CaO_{(s)} + CO_{2\ (g)}$$

as $S^o_{CaCO_3} = 92.9 \ J/mol \ ^ok$

$S^o_{CaO} = 39.81 \ J/mol \ ^ok$

$S^o_{CO_2} = 213.6 \ J/mol \ ^ok$

$$\Delta S^o = \Sigma n S^o_{product} - \Sigma n S^o_{react}$$

$$= [S^o_{CaO} + S^o_{CO_2}] - [S^o_{CaCO_3}] = [39.81 + 213.6] - [92.9]$$

$$= 160.5 \ J/mol \ ^ok$$

(*) $\boxed{S_{Solution} > S_{solvent + solute}}$

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(*)

system ①	system ②

$T_1 = 10 \ ^oC$ $T_2 = 100 \ ^oC$ $\begin{cases} T_2 > T_1 \\ S_2 > S_1 \end{cases}$
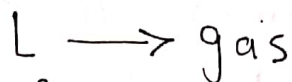
وذلك لأن بزيادة درجة الحرارة تزداد طاقة التنشيط وطاقة الحركة

للجزيئات المكونة للـ system

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$$
$$Total$$

$$\Delta S_{total} \begin{cases} > 0 \ (+ve) & \text{spontaneous process} \\ Zero & \text{at equilibrium} \\ < 0 \ (-ve) & \text{non-spontaneous process} \end{cases}$$

Example) predict the value of entropy
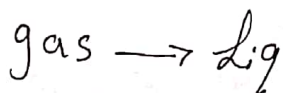
1- when liquid vaporized or at vaporization التبخير

$$L \longrightarrow gas$$
$$\Delta S = S^{\circ}_{gas} - S^{\circ}_{liq} = +ve$$

2- when solid is melted

$$Solid \longrightarrow liquid$$
$$\Delta S = S^{\circ}_{liq} - S^{\circ}_{solid} = +ve$$

3- when gas liquified

$$gas \longrightarrow Liq$$
$$\Delta S = S^{\circ}_{liq} - S^{\circ}_{gas} = -ve$$

⊛ Relation between Entropy and Volume & pressure

↳ Entropy increase as pressure decrease

$$S \propto \frac{1}{P} \qquad but \qquad P \propto \frac{1}{V}$$

$$\therefore S \propto V$$

(Gibbs free energy) is another function used to express the spontaneity of reaction

$$G = H - TS$$
$$\Delta G = \Delta H - \Delta(TS)$$
$$\Delta G = \Delta H - (T\Delta S + S\Delta T)$$

at Const temp
$$\Delta T = Zero$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

where ΔG is net change in free energy

ΔH is net change in enthalpy or heat Content
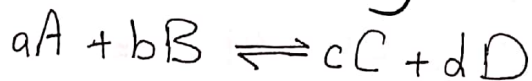
T is absolute temperature

ΔS is net change in entropy

if $\Delta G < Zero$ $\quad A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$

$\Longrightarrow$ Spontenous reaction in forward reaction

if $\Delta G = Zero \Longrightarrow$ at equilibrium

if $\Delta G > Zero \Longrightarrow$ & non-spontaneous reaction in forward direction
spontaneous reaction in opposite direction

※ Standard Free energy ΔG^0 (at 1 atm & 25°c)

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G^0_{rxn} = \Sigma n \Delta G^0_{product} - \Sigma n \Delta G^0_{reactant}$$
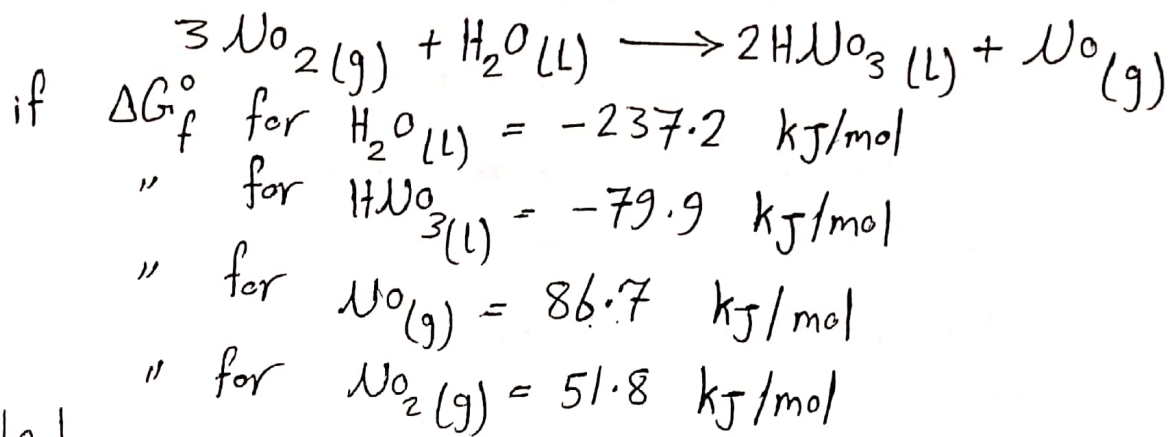
$$[c \Delta G^0_C + d \Delta G^0_D] - [a \Delta G^0_A + b \Delta G^0_B]$$

ملاحظه standard free energy of formation for any element in it's stable state at 1 atm & 25°c = Zero

Ex:- $G^0_{O_2}$ = Zero & $G^0_{H_2}$ = Zero & G^0_{Carbon} = Zero

Example: Calculate ΔG° for the reaction

$$3 NO_2(g) + H_2O(L) \longrightarrow 2 HNO_3(L) + NO(g)$$

if ΔG_f° for $H_2O(L) = -237.2$ kJ/mol

" for $HNO_{3(l)} = -79.9$ kJ/mol

" for $NO(g) = 86.7$ kJ/mol

" for $NO_2(g) = 51.8$ kJ/mol

soln)

$$\Delta G^\circ_{rxn} = \sum n \Delta G^\circ_{product} - \sum n \Delta G^\circ_{reactant}$$

$$[2 G^\circ_{HNO_3} + G^\circ_{NO}] - [3 G^\circ_{NO_2} + G^\circ_{H_2O}]$$

$$[2 \times -79.9 + 86.7] - [3(51.8) + (-237.2)]$$

$$= 8.7 \text{ kJ/mol}$$

Example:- Calculate ΔG° for the reaction

$$O_3(g) + NO(g) \longrightarrow NO_2(g) + O_2(g) \quad \text{at } 25^\circ c$$
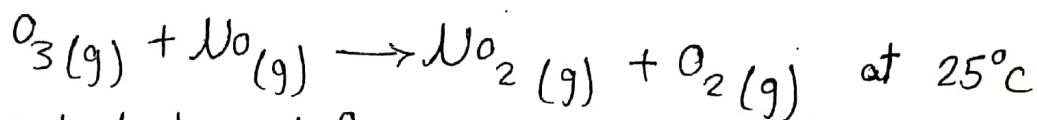
if $\Delta H^\circ = -199$ kJ/mol , $\Delta S^\circ = -41.1$ J/mol °k

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -199 \text{ kJ/mol} - (298 \times -4.1 \times 10^{-3} \text{ kJ/mol °k})$$

$$= -197.77 \text{ kJ/mol}$$

(*) Relation between Free Energy & chemical Equilibrium

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

as ΔG is net change in Free energy

ΔG° is change in standard Free energy

R التثابت العام للغازات = 8.314 J/mol °k

Q is reaction quotient = حاصل ضرب تركيز النواتج / حاصل ضرب تركيز المتفاعلات

at equilibrium $\Delta G = $ Zero

$$\Delta G^{\circ} = -RT \ln k \qquad \text{as } Q = k \quad \text{equilibrium Constant}$$

Example :-

The equilibrium Constant for reaction $AgBr_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)}$
is solubility product Constant $k_{sp} = 7.7 \times 10^{-13}$ at $25°C$
Calculate ΔG for the reaction when $[Ag^{+}] = 1 \times 10^{-2} M$
and $[Br^{-}] = 1 \times 10^{-3} M$

Soln :-

$$\Delta G^{\circ} = -RT \ln k_{sp}$$

$$\Delta G^{\circ} = -8.314 \text{ J/mol °k} (298°k) \ln (7.7 \times 10^{-13})$$

$$\Delta G^{\circ} = 69.1 \text{ kJ/mol}$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$= 69.1 \times 10^3 \text{ J/mol} + 8.314 \text{ J/mol °k} (298°k) \ln \frac{[Ag^{+}][Br^{-}]}{AgBr}$$

$$= 69.1 \times 10^3 \text{ J/mol} + 8.314 \text{ J/mol °k} (298°k) \ln \frac{1 \times 10^{-2} \times 1 \times 10^{-3}}{1}$$

$$\Delta G = 40.6 \text{ kJ/mol}$$

$$\Delta G = +ve$$

∴ non-spontaneous reaction

* At phase transition $\Longrightarrow$ ΔG = Zero
the system was at equilibrium

i.e :- at boiling point $\underline{or}$ at the melting point

$$0 \overset{\Delta G}{\cancel{}} = \Delta H - T\Delta S$$

$$\Delta H = T\Delta S$$

$$\therefore \Delta S = \frac{\Delta H}{T} \qquad \& \cdot T = \frac{\Delta H}{\Delta S}$$

<u>Example 1-</u> Calculate the molar entropy of vaporization ΔS_{vap}
if HI has boiling point of $-35.4 \, °C$ and its ΔH_{vap} is $21.16 \, kJ/m_o$

<u>Soln :-</u>

at vaporization ΔG = Zero

$$\Delta H = T\Delta S$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{21.16 \; kJ/mol}{-35.4 + 273}$$

$$= 89.0 \; J/mol \, °k$$

<u>Example 1</u> Calculate the boiling point of Formic acid

	ΔH_f^o (kJ/mol)	S^o (J/mol °k)
H COOH (l)	-410	130
H COOH (g)	-363	251

<u>Soln :-</u>

$$H COOH_{(l)} \longrightarrow H COOH_{(g)}$$

$$\Delta H^o_{rxn} = \Delta H^o_g - \Delta H^o_L = -363 - (-410) = 47 \; kJ/mol$$
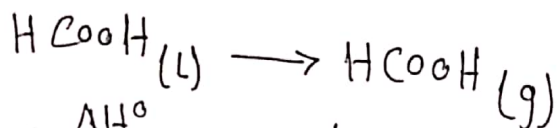
$$\Delta S^o_{rxn} = \Delta S^o_g - \Delta S^o_L = 251 - 130 = 121 \; J/mol°K$$

at boiling point $\longrightarrow$ ΔG^o = Zero

$$\therefore \Delta H^o = T \Delta S^o$$

$$\text{boiling point } (T) = \frac{\Delta H^o}{\Delta S^o} = \frac{47 \; J/mol \times 10^3}{121 \; J/mol°k} = 388.4 \, °k$$