

سنتر فیو تشر

Subject:..... کیمیا، اعدادی

Chapter:..... (۲) الترمو

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* Adiabatic Expansion or Contraction of ideal gas :-

↳ Adiabatic = isolated
معزول = اديباتيكي

* Adiabatic change :- التغير الأديباتيكي

the process in which system doesn't gain or loss heat
النظام معزول يعني ان النظام لا يفقد او يكتسب أى حرارة

$$q_{in} = q_{out} = \text{Zero}$$

* 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 تغيير في درجة الحرارة

* Heat engine المحرك الحرارى

is device that convert heat into work

the heat engine can be characterize 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

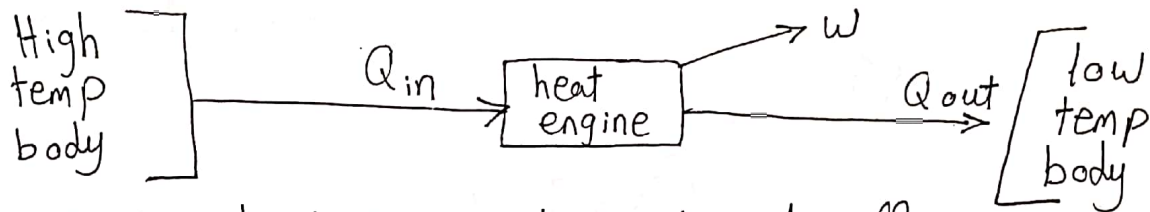
⇒ Second Law of thermodynamic

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 receive heat from reservoir and produce net amount of work
 مستحيل وجود آلة تحول Q إلى W بنسبة 100٪ أي لا توجد آلة كفاءتها 100٪

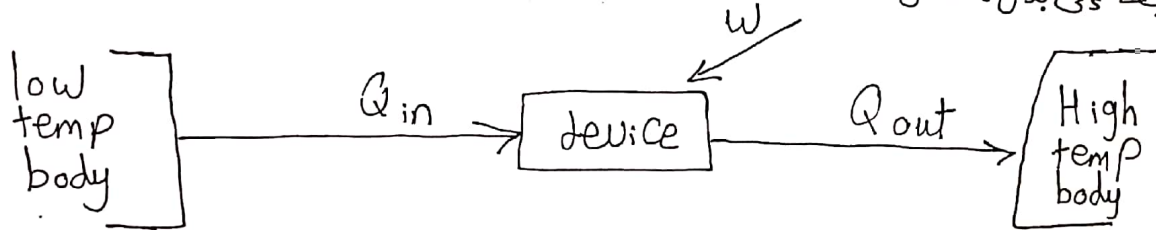


⇒ No heat engine have thermal efficiency 100%

→ 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 without doing work

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



* Thermal efficiency (η_{th}) % الكفاءة الحرارية

$$\text{thermal efficiency} = \frac{\text{Net work output}}{\text{Net heat input}} \quad \begin{matrix} \text{محصول الشغل الخارج} \\ \text{محصول الحرارة الداخلة} \end{matrix}$$

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

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

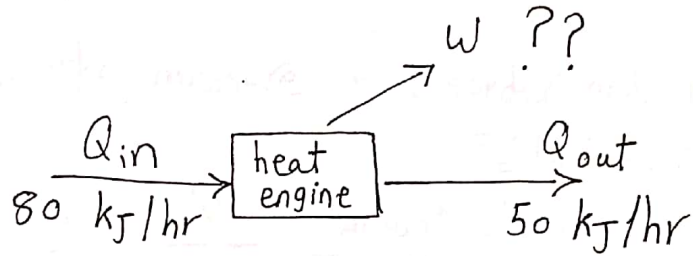
$$\eta_{th} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

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

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 furnace 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?



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

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

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 a minimum value

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

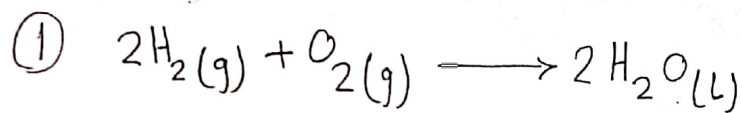
$$\text{Entropy (S)} = \frac{Q}{T} \quad \frac{\text{amount of heat}}{\text{temp in } ^{\circ}\text{K}}$$

$$\Delta S = S_2 - S_1$$

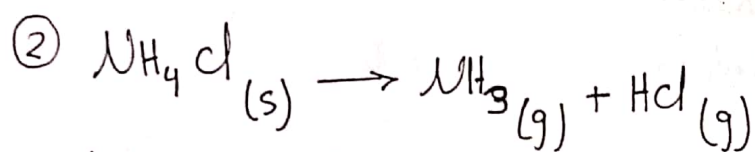
net change in entropy = entropy in final state - entropy in initial state

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

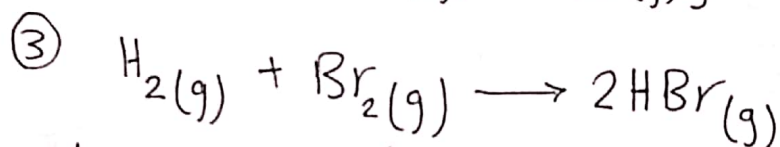
Example predict the value of entropy



$$\Delta S_{\text{total}} = 2S^{\circ}_{\text{H}_2\text{O}(\text{l})} - (2S^{\circ}_{\text{H}_2(\text{g})} + S^{\circ}_{\text{O}_2(\text{g})}) = -\text{ve}$$



$$\Delta S_{\text{total}} = [S^{\circ}_{\text{NH}_3(\text{g})} + S^{\circ}_{\text{HCl}(\text{g})}] - S^{\circ}_{\text{NH}_4\text{Cl}(\text{s})} = +\text{ve}$$



the same no. of molecules in reactant & product and molecules are diatomic, and we can't predict the value of ΔS



متفاعلات reactant

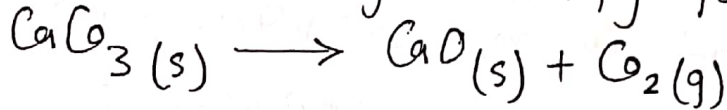
نواتج product

$$\Delta S_{rxn} = \sum n (\Delta S)_{product} - \sum n (\Delta S)_{reactant}$$

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

as S° is standard entropy of different substance from table

Example Calculate the change in entropy for the reaction



as $S_{CaCO_3}^\circ = 92.9 \text{ J/mol}^\circ\text{K}$

$S_{CaO}^\circ = 39.81 \text{ J/mol}^\circ\text{K}$

$S_{CO_2}^\circ = 213.6 \text{ J/mol}^\circ\text{K}$

$$\Delta S^\circ = \sum n S_{product}^\circ - \sum n S_{react}^\circ$$

$$= [S_{CaO}^\circ + S_{CO_2}^\circ] - [S_{CaCO_3}^\circ] = [39.81 + 213.6] - [92.9]$$

$$= 160.5 \text{ J/mol}^\circ\text{K}$$

(*)

$$S_{\text{solution}} > S_{\text{solvent} + \text{solute}}$$

بعد الذوبان قبل الذوبان

(*)

system ①

$$T_1 = 10^\circ\text{C}$$

system ②

$$T_2 = 100^\circ\text{C}$$

$$T_2 > T_1$$

$$S_2 > S_1$$

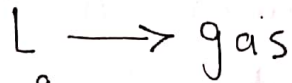
وذلك لأن زيادة درجة الحرارة تزداد طاقة التنشيط وطاقة الحركة للجزيئات المكونة للـ system

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

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

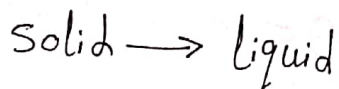
Example predict the value of entropy

1- When liquid vaporized or at vaporization التبخير



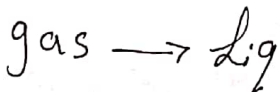
$$\Delta S = S_{\text{gas}}^{\circ} - S_{\text{liq}}^{\circ} = +ve$$

2- When solid is melted



$$\Delta S = S_{\text{liq}}^{\circ} - S_{\text{solid}}^{\circ} = +ve$$

3- When gas liquified



$$\Delta S = S_{\text{liq}}^{\circ} - S_{\text{gas}}^{\circ} = -ve$$

⊛ Relation between Entropy and Volume & pressure

→ Entropy increase as pressure decrease

$$S \propto \frac{1}{p} \quad \text{but} \quad p \propto \frac{1}{V}$$

$$\therefore S \propto V$$

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
 $\Delta T = \text{Zero}$

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

where ΔG is net change in free energy

ΔH is net change in enthalpy or heat content

T is absolute temperature

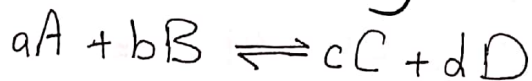
ΔS is net change in entropy

if $\Delta G < \text{Zero} \Rightarrow A + B \xrightleftharpoons[k_{-1}]{k_1} C + D$
 \Rightarrow Spontaneous reaction
in forward reaction

if $\Delta G = \text{Zero} \Rightarrow$ at equilibrium

if $\Delta G > \text{Zero} \Rightarrow$ & non-spontaneous reaction in forward direction
spontaneous reaction in opposite direction

(*) Standard Free energy ΔG° (at 1 atm & 25°C)



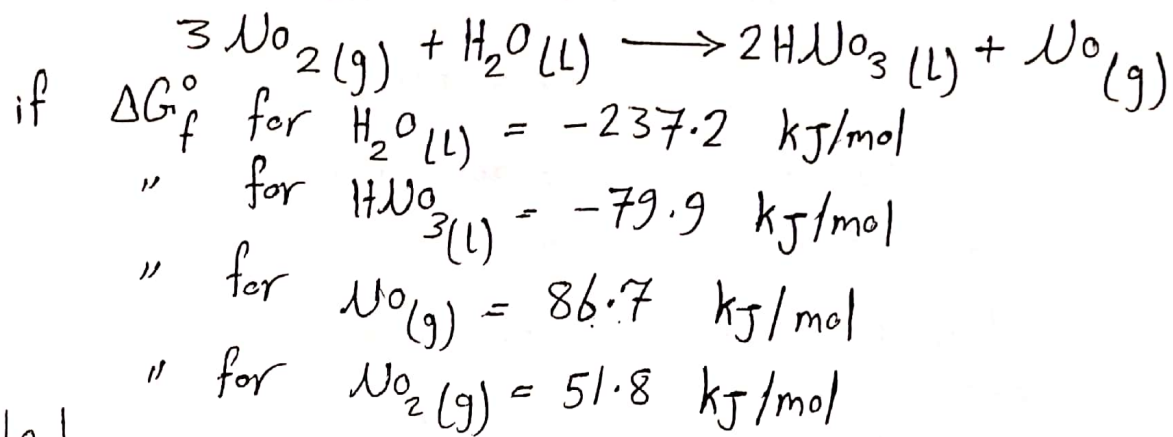
$$\Delta G^\circ_{\text{rxn}} = \sum n \Delta G^\circ_{\text{product}} - \sum n \Delta G^\circ_{\text{reactant}}$$

$$[c \Delta G^\circ_C + d \Delta G^\circ_D] - [a \Delta G^\circ_A + b \Delta G^\circ_B]$$

تعريف standard Free energy of formation for any element in its stable state at 1 atm & 25°C = Zero

Ex:- $G^\circ_{O_2} = \text{Zero}$ & $G^\circ_{H_2} = \text{Zero}$ & $G^\circ_{\text{Carbon}} = \text{Zero}$

Example:- Calculate ΔG° for the reaction

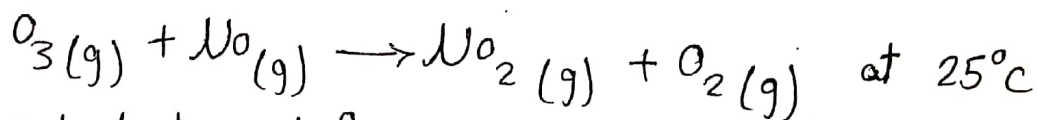


soln

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_{\text{product}}^\circ - \sum n \Delta G_{\text{reactant}}^\circ$$

$$\begin{aligned} & [2G_{\text{HNO}_3}^\circ + G_{\text{NO}}^\circ] - [3G_{\text{NO}_2}^\circ + G_{\text{H}_2\text{O}}^\circ] \\ & [2(-79.9) + 86.7] - [3(51.8) + (-237.2)] \\ & = 8.7 \text{ kJ/mol} \end{aligned}$$

Example:- Calculate ΔG° for the reaction



if $\Delta H^\circ = -199 \text{ kJ/mol}$, $\Delta S^\circ = -4.1 \text{ J/mol } ^\circ\text{K}$

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

$$\begin{aligned} \Delta G^\circ &= -199 \text{ kJ/mol} - (298 \times -4.1 \times 10^{-3} \text{ kJ/mol } ^\circ\text{K}) \\ &= -197.77 \text{ kJ/mol} \end{aligned}$$

(*) 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 الثابت العام للغازات = $8.314 \text{ J/mol}^\circ\text{K}$

Q is reaction quotient = $\frac{\text{حاصل ضرب تراكيز النواتج}}{\text{حاصل ضرب تراكيز المتفاعلات}}$

at equilibrium

$$\Delta G = \text{Zero}$$

$$\Delta G^\circ = -RT \ln k$$

as $Q = k$ equilibrium Constant

Example 1-

The equilibrium Constant for reaction $\text{AgBr(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq})$ is solubility product Constant $k_{sp} = 7.7 \times 10^{-13}$ at 25°C

Calculate ΔG for the reaction when $[\text{Ag}^+] = 1 \times 10^{-2} \text{ M}$ and $[\text{Br}^-] = 1 \times 10^{-3} \text{ M}$

Soln :-

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

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

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

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

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

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

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

$$\Delta G = +ve$$

\therefore non-spontaneous reaction

* At phase transition $\Rightarrow \Delta G = \text{Zero}$
 the system was at equilibrium
 i.e:- at boiling point or at the melting point

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

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

$$\therefore \Delta S = \frac{\Delta H}{T}$$

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

Example 1 - 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/mol

Soln:-

at Vaporization $\Delta G = \text{Zero}$

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

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

$$= 89.0 \text{ J/mol } ^\circ\text{K}$$

Example 2 Calculate the boiling point of Formic acid

HCOOH (l)

$\Delta H_f^\circ \text{ (kJ/mol)}$

$S^\circ \text{ (J/mol } ^\circ\text{K)}$

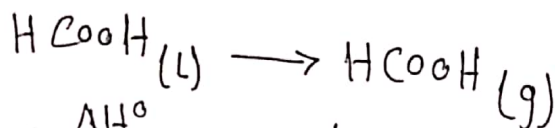
HCOOH (g)

-410

130

-363

Soln:-



$$\Delta H_{\text{rxn}}^\circ = \Delta H_g^\circ - \Delta H_l^\circ = -363 - (-410) = 47 \text{ kJ/mol}$$

$$\Delta S_{\text{rxn}}^\circ = \Delta S_g^\circ - \Delta S_l^\circ = 251 - 130 = 121 \text{ J/mol } ^\circ\text{K}$$

at boiling point $\Rightarrow \Delta G^\circ = \text{Zero}$

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

$$\text{boiling point (T)} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{47 \text{ J/mol} \times 10^3}{121 \text{ J/mol } ^\circ\text{K}} = 388.4 ^\circ\text{K}$$