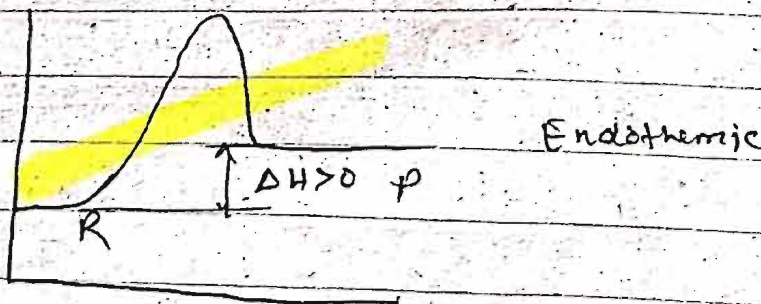
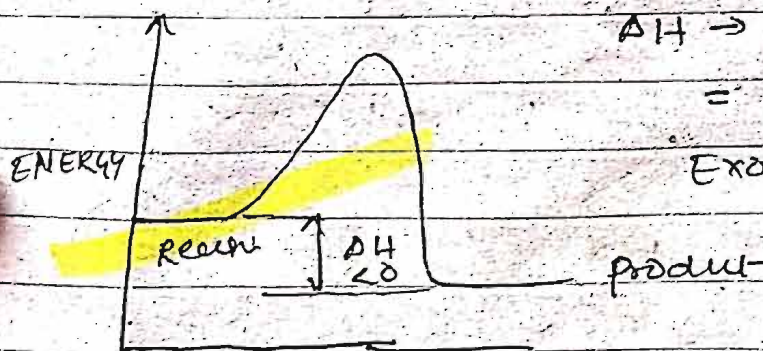


Q Temperature and pressure effect of chemical Reaction

- ✓ for endothermic reaction $(X, K) \uparrow$ with $\uparrow T$
- ✓ " Exothermic " $(X, K) \downarrow$ with $\uparrow T$
- ✓ Eq. Constant K is the $f(T)$
- ✓ " Compression is the $f(T, P, \text{inerts} \dots)$

Type of rxn	Exothermic	Endothermic
Energy	Released	Absorbed
Relative energy of reactant and product	Energy of reactant greater than energy of product	Energy of reactant less than energy of product
Sign of ΔH	Negative	Positive



$$H = U + PV$$

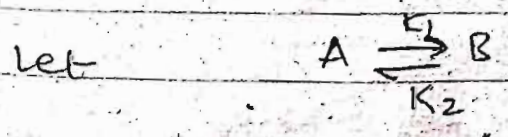
Heat of rxn (also known as enthalpy of rxn) is the change in the enthalpy of a chemical reaction that occurs at a constant pressure.

It is a thermodynamic unit of measurement useful for calculating the amount of energy per mole either released or produced in a rxn.

$$\Delta H_{rxn} = (\sum H_f)_{product} - (\sum H_f)_{reactant}$$

~~Statement of rxn~~

Reversible rxn - Takes place in both forward & backward direction.



for constant volume rxn system

$$(-r_A) = - \frac{dC_A}{dt} = k_1 C_A - k_2 C_B$$

let $x \text{ & } R \approx 1$

$$-r_A \text{ will be } = k_1 C_A - k_2 C_B$$

& we know that

$$r_A = - \frac{1}{\nu} \frac{dN_A}{dt}$$

So, what is the maximum conversion we can achieve from the rxn.

And so we know

$$X_A = 1 - \frac{N_A}{N_{A0}} \quad \begin{array}{l} \text{Final moles of Component A} \\ \text{Initial moles of Component A} \end{array}$$

for irreversible rxn

$$N_{A \text{ min}} = 0$$

$$X_{A \text{ max}} = 1 \quad \text{for irreversible}$$

for reversible

$$N_{A \text{ minimum}} = N_{A \text{ at equlib}}$$

Equilibrium Conversion

$$X_{A \text{ eq max}} = 1 - \frac{N_{A \text{ eq}}}{N_{A0}} \quad (1)$$

So, in reversible rxn we can't achieve 100% conversion.

at eq. the net amount

$$N_{A \text{ eq}} = \text{const}$$

$$\frac{dN_A}{dt} = 0$$

$$(-r_A) = 0$$

so at eq. $-r_A = k_1 C_{A \text{ eq}} - k_2 C_{B \text{ eq}} = 0$

$$k_1 C_{A \text{ eq}} = k_2 C_{B \text{ eq}}$$

$$\frac{k_1}{k_2} = \frac{C_{B \text{ eq}}}{C_{A \text{ eq}}} \quad (2)$$

for CVRS

$$C_B = C_{B0} + \frac{\Delta}{a} C_{A0} X_A$$

$$C_{B \text{ eq}} = 0 + 1 C_{A0} X_{A \text{ eq}} \quad \text{for given rxn}$$

$$C_{B \text{ eq}} = C_{A0} X_{A \text{ eq}} \quad \text{or} \quad C_{A \text{ eq}} = C_{A0} (1 - X_{A \text{ eq}})$$

use eq. (2)

$$\frac{K_1}{K_2} = \frac{X_{A \text{ eq}}}{1 - X_{A \text{ eq}}}$$

Eq. Constant

$$\text{or } K = \frac{X_{A \text{ eq}}}{1 - X_{A \text{ eq}}}$$

$$\text{or } X_{A \text{ eq}} = \frac{K}{1 + K}$$

$$\text{or } K \uparrow \Rightarrow X_{A \text{ eq}} \uparrow \quad \#$$

$$K \downarrow \Rightarrow X_{A \text{ eq}} \downarrow \quad \#$$

As we know

$$\Rightarrow K = \frac{-\Delta G^\circ}{RT}$$

eff of temp

$$\frac{\partial \ln K}{\partial T} = \frac{\partial}{\partial T} \left[\frac{-\Delta G^\circ}{RT} \right]$$

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_{\text{rxn}}^\circ}{RT^2} \quad \text{--- van't Hoff eq.}$$

on integration

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta H_{\text{rxn}}^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

for endothermic rxn

$$\Delta H_{\text{rxn}}^\circ > 0$$

$$\text{as } T \uparrow \Rightarrow K \uparrow \Rightarrow X_{A \text{ eq}} \uparrow$$

2 for exothermic rxn

$$\Delta H_{rxn} < 0$$

$$\text{as } T \uparrow \Rightarrow K \downarrow = X_{eq} \downarrow$$

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

eff of pressure

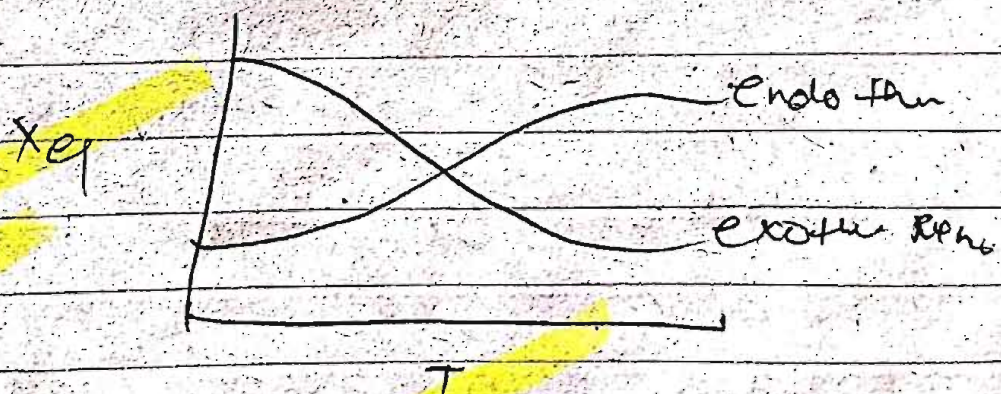
$$\frac{\partial \ln K}{\partial p} = \frac{\partial}{\partial p} \left[\frac{-\Delta G^\circ}{RT} \right]$$

eq. con. is independent on pressure

$$\text{As we know } K_2 = K_1 \exp \left[\frac{\Delta H_{rxn}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$



$$X_{eq} = \frac{K}{1+K} = \frac{\exp f(T)}{1 + \exp f(T)}$$



from eq. (4) & (5)

$$\Delta H^\circ = RT^2 \left[\frac{d \ln K_p}{dT} \right]$$

$$\boxed{\frac{\Delta H^\circ}{RT^2} = \frac{d(\ln K_p)}{dT}}$$

Van't Hoff eq.

Std. heat of Reaction

The std. heat of rxn (ΔH_r° or ΔH°) is the heat of rxn (i.e. enthalpy change resulting from rxn) when both the reactant & product are in their std. state (pure state at 25°C and 1 atm)

Std. heat of rxn from heat of formation of individual component (Reactant & product)

The std. heat of rxn (ΔH_r°) can be calculated from the data of std. heat of formation of the reactant material as follows

Consider the rxn



The std. heat of rxn for above rxn can be calculated by using

$$\Delta H_R^\circ = \sum \Delta H_f^\circ(P) - \sum \Delta H_f^\circ(R)$$

$$= [r \Delta H_{fR}^\circ + s \Delta H_{fS}^\circ] - [a \Delta H_{fA}^\circ + b \Delta H_{fB}^\circ]$$

std. heat of rxn from heat of combustion of individual component (Reactant & Product).

The std. heat of rxn i.e. the heat of rxn at 25°C (298 K) and 1 atm pressure can also be calculated from the data of std. heat of combustion of the reacting material as follow.

$$\Delta H_R^\circ = \sum \Delta H_c^\circ(\text{Reactant}) - \sum \Delta H_c^\circ(\text{Product})$$

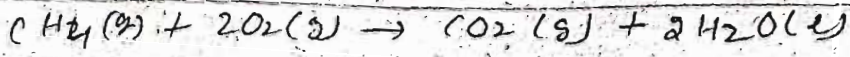
$$= (a \Delta H_{cA}^\circ + b \Delta H_{cB}^\circ) - (r \Delta H_{cR}^\circ + s \Delta H_{cS}^\circ)$$

Important definition

Enthalpy of formation: Amount of heat absorbed or released when 1 mole of a compound is formed by its constituent element in their free natural state.

Enthalpy of Combustion: Amt. of heat absorbed or released when 1 mole of a compound is combusted (completely) in excess of air (O₂)

$\Delta H_c \rightarrow -ve$



$$\Delta H_r = -090105$$