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if we put a steel ingot into furance the system would approach equilibrium by reducing any iron oxide present to Iron.

If we increased the temp. of the furance to 1000 °c the

$\frac{P_{CO}}{P_{CO_2}} < \frac{P'_{CO}}{P'_{CO_2}}$ & in order to reach equilibrium the iron would be oxidizod.

★ The Vant Hoff Isotherm :-

for the reaction :- $A + B = C + D$

we will consider this chemical reaction involving the ideal gases A, B, C & D, the reaction at constant temp. T

& initially we have one mole each of A & B at partial pressure P_A & P_B.

change their partial pressure to the equilibrium value P'_A, P'_B by Isotherm reversible change.

So the free energy change involved in changing partial pressure $P_A, P_B \rightarrow P'_A, P'_B$.

$$\therefore \Delta G_1 = RT \ln \frac{P'_A}{P_A} + RT \ln \frac{P'_B}{P_B}$$

*If the system is at equilibrium there are no free energy change.

ملاحظة :- عندما يكون النظام في حالة التوازن فان ($\Delta G = 0$) وهذا ينطبق على حالة التبخر والإنصهار.

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& 1 mole of each the gases (C & D) change from their partial pressure. $P'_C , P'_D \longrightarrow P_C , P_D$

$$\therefore \Delta G_2 = RT \ln \frac{P_C}{P'_C} + RT \ln \frac{P_D}{P'_D}$$

* So the free energy change in the reaction :-

$$\therefore \Delta G = \Delta G_1 + \Delta G_2$$

$$\therefore \Delta G = RT \ln \frac{P'_A}{P_A} + RT \ln \frac{P'_B}{P_B} + RT \ln \frac{P_C}{P'_C} + RT \ln \frac{P_D}{P'_D}$$

$$\therefore \Delta G = RT[\ln P'_A - \ln P_A] + RT[\ln P'_B - \ln P_B] + RT[\ln P_C - \ln P'_C] + RT[\ln P_D - \ln P'_D]$$

$$\therefore \Delta G = RT \ln \frac{P'_A \cdot P'_B}{P'_C \cdot P'_D} + RT \ln \frac{P_C \cdot P_D}{P_A \cdot P_B}$$

$$\therefore \Delta G = -RT \ln \frac{P'_C \cdot P'_D}{P'_A \cdot P'_B} + RT \ln \frac{P_C \cdot P_D}{P_A \cdot P_B}$$

$$\therefore \Delta G = -RT \ln K_P + RT \ln \frac{P_C \cdot P_D}{P_A \cdot P_B}$$

Above equation Known as the van't hoff isotherm.

* If the concentration of the reactants are used as in the case of solid & liquid.

$$\therefore \Delta G = -RT \ln K_C + RT \ln \frac{C_C \cdot C_D}{C_A \cdot C_B}$$

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Note :. if P_A, P_B, P_C & P_D are equal to 1 atom pressure that is the reactants & products are in their standard states.

where :.

$$\ln \frac{P_C \cdot P_D}{P_A \cdot P_B} = \ln 1 = 0$$

$\therefore \rightarrow$ $\Delta G = -RT \ln K_P = \Delta G^\circ$

وبنفس الطريقة $\rightarrow$ $\Delta G = -RT \ln K_c = \Delta G^\circ$

ΔG° the standard free energy change.

*ملاحظة :. إستخدام المتفاعلات بحالتها القياسية الموجودة يعطي نواتج في الحالة القياسية وهنا من الواضح أنه لاتوجد إمكانية لجعل التفاعل تلقائي للمثال التالي •

Ex :. In the reaction :.

$$Al_2O_{3(s)} + 3C_{(s)} = 2Al_{(L)} + 3CO_{(g)} \quad \text{at } 1500\,°C$$

* $Al_2O_{3(s)} = 2Al + \frac{3}{2}O_{2(g)}$ $\Delta G^\circ_{1773} = +1017000$ J

* $3C_{(s)} + \frac{3}{2}O_{2(g)} = 3CO_{(g)}$ $\Delta G^\circ_{1773} = -866000$ J

① this reaction sponteneously or not ?

② If the reaction is not sponteneously, change it to sponteneously?

Sol. ① $\Delta G^\circ = \Delta G^\circ_1 + \Delta G^\circ_2$

$\Delta G^\circ = +1017000 - 866000$

$\Delta G^\circ = 151000$ J

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$$\because \Delta G_{1773} = +151000 + RT \ln \frac{P_{CO}^3 \cdot C_{Al}^2}{C_{Al_2O_3} \cdot C_c^3} \quad , \ln 1 = 0$$

$$\therefore \Delta G_{1773} = +151000 \text{ J}.$$

② If we reduce the partial pressure of carbon monoxide gas in the system by placing the reactants in a vaccum unit.

$$\Delta G = 151000 + RT \ln p_{co}^3$$

P_{co} atm	ΔG «J»
1	+ 151000
10^{-1}	+ 49000
10^{-2}	− 52700
10^{-3}	− 154400
10^{-4}	− 256100
10^{-5}	− 357700

So :

① $\frac{P_c \cdot P_D}{P_A \cdot P_B} < \frac{P'_c \cdot P'_D}{P'_A \cdot P'_B}$

the equilibrium constant ΔG must be negative & the reaction will proceed from left to right.

② $\frac{P_c \cdot P_D}{P_A \cdot P_B} = \frac{P'_c \cdot P'_D}{P'_A \cdot P'_B}$ at equilibrium $\Delta G = 0$

③ $\frac{P_c \cdot P_D}{P_A \cdot P_B} > \frac{P'_c \cdot P'_D}{P'_A \cdot P'_B}$

ΔG is positive & the reaction will proceed from right to left.