

(61)

Subject: / /

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

If we increased the temp. of the furnace 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 oxidized.

* The Van't 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 \hat{P}_A , \hat{P}_B by Isotherm reversible change.

So the free energy change involved in changing partial pressure

$P_A > P_B \rightarrow \hat{P}_A > \hat{P}_B$

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

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

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

Subject:

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

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

* So the Free energy change in the reaction so

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

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

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

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

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

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

Above equation known as the van't Hoff isotherm.

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

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

(63)

Subject: _____

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:

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

→ $\Delta G = -RT \ln K_p = \Delta G^\circ$

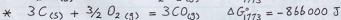
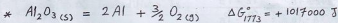
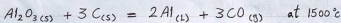
وبنفس
الطريقة

→ $\Delta G = -RT \ln K_c = \Delta G^\circ$

ΔG°
the standard
free energy
change.

* ملاحظة: استخدام التفاعلات بحالتها القياسية الموجودة يعطي نتائج في الحالة القياسية وهنا من الواضح أنه لا توجد إمكانية لجعل التفاعل تلقائياً
● المثال التالي

Ex. In the reaction:



- ① this reaction spontaneously or not?
- ② If the reaction is not spontaneously, change it to spontaneously?

Sol: ① $\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ$
 $\Delta G^\circ = +1017000 - 866000$
 $\Delta G^\circ = 151000 \text{ J}$

Subject: _____

$$\therefore \Delta G_{1773} = +151000 + RT \ln \frac{P_{CO}^3 \cdot C_{AI}}{C_{Fe_2O_3} \cdot C_C^3} \quad \text{at } \ln 1 = 0$$

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

② If we reduce the partial pressure of carbon monoxide gas in the system by placing the reactants in a vacuum 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,

$$\textcircled{1} \frac{P_C \cdot P_D}{P_A \cdot P_B} < \frac{\hat{P}_C \cdot \hat{P}_D}{\hat{P}_A \cdot \hat{P}_B}$$

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

$$\textcircled{2} \frac{P_C \cdot P_D}{P_A \cdot P_B} = \frac{\hat{P}_C \cdot \hat{P}_D}{\hat{P}_A \cdot \hat{P}_B} \quad \text{at equilibrium } \Delta G = 0$$

$$\textcircled{3} \frac{P_C \cdot P_D}{P_A \cdot P_B} > \frac{\hat{P}_C \cdot \hat{P}_D}{\hat{P}_A \cdot \hat{P}_B}$$

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