Free energy and chemical equilibrium

❖ There is a relationship between ΔG and ΔGº which can be derived from thermodynamics.

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

R → gas constant "8.314 J/K.mol"

T → absolute temp of the reaction.

Q → reaction quotient.

❖ From this relationship we see that :

- ΔG depend on ΔGº and RTln Q.
- For a given reaction at temp T the value of ΔGº is fixed but that of RTln Q is not.

❖ We have two special cases

Case 1

ΔG^o large negative.

$\therefore$ $\Delta G \rightarrow$ is also negative.

Net reaction will proceed from left to right.

Until a significant amount of product has been formed.

At that points, the RTln Q will become positive enough to match the negative ΔG^o in magnitude.

Case 2

ΔG^o large positive.

$\therefore$ $\Delta G \rightarrow$ is also positive.

Net reaction will proceed from right to left.

Until a significant amount of reactant has been formed.

At that points, the RTln Q will become negative enough to match the positive ΔG^o in magnitude.

At equilibrium:

$\Delta G = 0$, $Q = K$ → equilibrium constant.

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

$\therefore\ 0 = \Delta G^{o} + RT\ln K$

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

K_c	K_p
solution	gases

- This equation relates the equilibrium constant to the standard free energy change " ΔG^{o} " rather than actual free energy change " ΔG ".
- Larger the K, The more negative ΔG^{o}.
- ΔG^{o} is a constant for a particular reaction at a given temperature.
- ΔG varies with the reaction and become zero at equilibrium.

❖ Three possible relations between ΔG^{o} and K

Relation between D*G*° and *K* as Predicted by the Equation D*G*=-*RT* ln *K*

K	ln *K*	ΔG°	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

Note that

1) Sign of ΔG and not that ΔGº that determine the direction of reaction spontaneity.

2) Sign of ΔGº only tells us the relative amount of product and reactants when equilibrium is reached.

3) Sign of ΔGº don't tells us the direction of the net reaction.

4) If K is very large or very small , It's very difficult to measure the value by monitoringمراقبة the concentrations of all reacting species.

Example 1

The formation of nitric oxide from molecular oxygen and nitrogen at 25ºC.

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$

∴The equilibrium constant $K_P = \frac{P^2NO}{PN2+PO2} = 4 * 10^{-31}$

- The small value of K_p means that the concentration of NO at equilibrium will be Low.

Example 2

Calculate the equilibrium constant K_p for the following reaction at 25°C.

$$2H_2O_{(L)} \rightleftarrows 2H_{2(g)} + O_{2(g)}$$

$$\Delta G°rxn = [2\Delta G°F(H2) + \Delta G°F(O2)] - [2\Delta G°F(H2O)]$$
$$= [2 * 0 + 0] - [2 * \ -237.2]$$
$$= 474.4 \text{ KJ/mol}$$

$$\Delta G°rxn = -RT \ln Kp$$

474.4 KJ/mol * 1000 = - (8.314 * (25+273) ln Kp)

$\therefore \ln Kp = \ -191.5$

$K_p = e^{-191.5} = 7 * 10^{-84}$

Example 3

Using the solubility product of silver chloride at 25°C ($1.6 * 10^{-10}$) to calculate ΔG° for the process.

$$AgCl_{(s)} \rightleftarrows Ag^+_{(aq)} + Cl^-_{(aq)}$$

$$Ksp = \ [Ag^+][Cl^-] = 1.6 * 10^{-10}$$

$$\Delta G° = -RT \ln Ksp$$

Δ G° = - 8.314 * (25+273) ln $1.6 * 10^{-10}$

$= \ 5.6 * 10^4 J/mol$

= 56 KJ/mol

Example 4

The equilibrium constant (K_p) for the reaction

$$N_2O_{4(g)} \rightleftarrows 2NO_{2\,(g)}$$

is 0.113 at 298K , which corresponds to a standard free energy change of 5.40 KJ/mol . in a certain experiment , the initial pressure are P_{NO2} = 0.122 Atm and P_{N2O4} = 0.453 Atm.

Calculate ΔG for the reaction at these pressures and predict the direction of the net reaction toward equilibrium.

Kp = 0.113 T = 298K ΔGº = 5.7KJ/mol P_{NO2} = 0.122 Atm

P_{N2O4} = 0.453 Atm

$$\Delta G = \Delta G° + RT \ln Qp$$

$$\Delta G = (5.4 * 10^3) + (8.314 * 298) \ln \frac{P^2NO2}{PN2O4}$$

$$\Delta G = (5.4 * 10^3) + (8.314 * 298) \ln \frac{(0.122)^2}{(0.453)}$$

$$\Delta G = -3.06 * 10^3 J/mol$$

$$= -3.06 \text{ KJ/mol}$$

Because ΔG < 0

∴The net reaction proceeds from left to right to reach equilibrium.

Choose

1) For the relation ($\Delta G = \Delta G^o + RT\ln Q$) The value of ……. is fixed but that of …… is not.

A) ΔG , $RT\ln Q$
B) ΔG^o, $RT\ln Q$
C) ΔG^o , ΔG
D) $RT\ln Q$,ΔG^o

2) When ΔG^o is large negative, then ΔG is……..

A) positive
B) negative
C) zero
D) infinity

3) When ΔG^o is large positive, then ΔG is……..

A) positive
B) negative
C) zero
D) infinity

4) When ΔG^o is large negative, the Net reaction will proceed from …….. to………

A) Left to right
B) right to Left
C) a or b according to the state
D) none of them

5) When ΔG^o is large positive, the Net reaction will proceed from …….. to……….

A) Left to right
B) right to Left
C) a or b according to the state
D) none of them

6) Which relation from the following is true at equilibrium.

A) $\Delta G = \Delta G^\circ + RT \ln Qp$

B) $\Delta G^\circ = \Delta G + RT \ln Qp$

C) $\Delta G = -RT \ln Qp$

D) $\Delta G^\circ = -RT \ln Qp$

7) Larger the equilibrium constant , ΔGº be……..

A) more positive

B) more negative

C) zero

D) infinity

8) …… is constant for a particular reaction at a given temp.

A) ΔGº

B) ΔG

C) $RT \ln Q$

D) $\ln Q$

9) …….. Varies with the reaction and become zero at equilibrium.

A) ΔGº

B) ΔG

C) $RT \ln Q$

D) $\ln Q$

10) The sign of ……… determine the direction of reaction spontaneity

A) ΔGº

B) ΔG

C) $RT \ln Q$

D) $\ln Q$

11) The sign of ……… tells us the relative amount of product and reactants when equilibrium is reached.

A) ΔG^o
B) ΔG
C) $RT \ln Q$
D) $\ln Q$

12) The equilibrium constant at 427ºC for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

Calculate the value of ΔGº for the reaction under these condition

A) -33KJ/mol
B) 54KJ/mol
C) -54KJ/mol
D) 33KJ/mol

Solution

T = 427 + 273 = 700ºK

$\Delta G^o = - RT \ln Q$

$$= - 8.314 * 700 * \ln 9.4 * \frac{10^{-5} J}{mol} = 53.9 * \frac{10^{3} J}{mol} = 54 KJ/mol$$

13) determine The equilibrium constant (K_p) at 25ºC for the reaction

$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3\,(g)}$

$\Delta G^o f\ (NH_{3)(g)} = -16.6 KJ/mol$

A) $1.52 * 10^{-6}$

B) $6.60 * 10^{-3}$

C) $8.28 * 10^{-2}$

D) 2.60

Solution

T = 25 + 273 = 298 ºK

$\Delta G^o = - RT \ln Kp$

$2 * -16.6 * 10^3 = - 8.314 * 298 * \ln Kp$

$$\ln Kp = \frac{16.6 * 10^3 * 2}{8.314 * 298} = 13.4$$

$$Kp = e^{13.4} = 6.6 * 10^5$$

14) for the reaction 2C "graphite" + $H_{2(g)} \rightarrow C_2H_{2(g)}$

$\Delta G^o = +209.2$ KJ/mol at 25ºC .

If $P(H_2) = 100$Atm , $P(C_2H_2) = 0.1$Atm

Calculate ΔG for this reaction.

A) +207.8 KJ/mol

B) +226.3 KJ/mol

C) +192.1 KJ/mol

D) +17.3 KJ/mol

Solution

T = 25 + 273 = 298 ºK

$$Kp = \frac{P(C2H2)}{P(H2)} = \frac{0.1}{100} = 1 * 10^{-3}$$

$\Delta G = \Delta G^o + RT \ln Kp$

$= 209.2 * 10^3 + (8.314*298*\ln 10^{-3}) = 192.1$KJ/mol

15) determine The equilibrium constant (K_p) at 25ºC for the reaction

$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2\,(g)}$

$\Delta G^o = -28.5 KJ/mol$

A) $2.9 * 10^{-60}$

B) $1 * 10^{-4}$

C) 1.2

D) $1*10^5$

Solution

$$\Delta G^o = -RT \ln Kp$$

$$-28.5 * 10^3 = -8.314 * 298 * \ln Kp$$

$$\ln Kp = 11.5$$

$$Kp = e^{11.5}$$

$$= 9.9 * 10^4 = 1 * 10^5$$