

Free energy and chemical equilibrium

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

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

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 ΔG° and $RT \ln Q$.
- For a given reaction at temp T the value of ΔG° is fixed but that of $RT \ln Q$ is not.

❖ We have two special cases

Case 1

ΔG° 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 $RT \ln Q$ will become positive enough to match the negative ΔG° in magnitude.

Case 2

ΔG° 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 $RT \ln Q$ will become negative enough to match the positive ΔG° in magnitude.

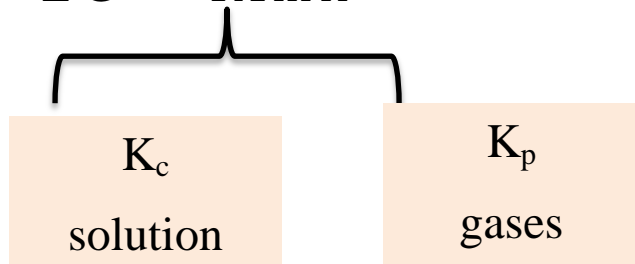
At equilibrium:

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

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

$$\therefore 0 = \Delta G^\circ + RT \ln K$$

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



- This equation relates the equilibrium constant to the standard free energy change " ΔG° " rather than actual free energy change " ΔG ".
- Larger the K , The more negative ΔG° .
- ΔG° 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° and K

Relation between ΔG° and K as Predicted by the Equation $\Delta G^\circ = -RT \ln K$

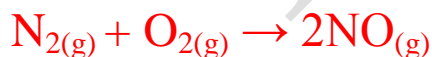
K	$\ln K$	ΔG°	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

Note that

- 1) Sign of ΔG and not that ΔG° that determine the direction of reaction spontaneity.
- 2) Sign of ΔG° only tells us the relative amount of product and reactants when equilibrium is reached.
- 3) Sign of ΔG° 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 monitoring مراقبة the concentrations of all reacting species.

Example 1

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

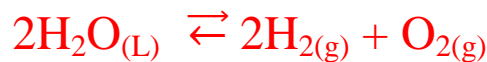


∴ The equilibrium constant $K_p = \frac{P^2_{\text{NO}}}{P_{\text{N}_2} + P_{\text{O}_2}} = 4 * 10^{-31}$

- 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.



$$\begin{aligned}\Delta G^\circ_{rxn} &= [2\Delta G^\circ F(\text{H}_2) + \Delta G^\circ F(\text{O}_2)] - [2\Delta G^\circ F(\text{H}_2\text{O})] \\ &= [2 * 0 + 0] - [2 * -237.2] \\ &= 474.4 \text{ KJ/mol}\end{aligned}$$

$$\Delta G^\circ_{rxn} = -RT \ln K_p$$

$$474.4 \text{ KJ/mol} * 1000 = - (8.314 * (25+273) \ln K_p)$$

$$\therefore \ln K_p = -191.5$$

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

Example 3

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



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.6 * 10^{-10}$$

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

$$\Delta G^\circ = - 8.314 * (25+273) \ln 1.6 * 10^{-10}$$

$$= 5.6 * 10^4 \text{ J/mol}$$

$$= 56 \text{ KJ/mol}$$

Example 4

The equilibrium constant (K_p) for the reaction



is 0.113 at 298K, which corresponds to a standard free energy change of 5.40 KJ/mol. In a certain experiment, the initial pressures are $P_{\text{NO}_2} = 0.122 \text{ Atm}$ and $P_{\text{N}_2\text{O}_4} = 0.453 \text{ Atm}$.

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

$$K_p = 0.113 \quad T = 298\text{K} \quad \Delta G^\circ = 5.7\text{KJ/mol} \quad P_{\text{NO}_2} = 0.122 \text{ Atm}$$

$$P_{\text{N}_2\text{O}_4} = 0.453 \text{ Atm}$$

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

$$\Delta G = (5.4 * 10^3) + (8.314 * 298) \ln \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

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

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

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

Because $\Delta G < 0$

\therefore The net reaction proceeds from left to right to reach equilibrium.

Choose

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

- A) ΔG , $RT \ln Q$ C) ΔG° , ΔG
B) ΔG° , $RT \ln Q$ D) $RT \ln Q$, ΔG°

2) When ΔG° is large negative, then ΔG is.....

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

3) When ΔG° is large positive, then ΔG is.....

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

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

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

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

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

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

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

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

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

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

7) Larger the equilibrium constant, ΔG° be.....

A) more positive

C) zero

B) more negative

D) infinity

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

A) ΔG°

C) $RT \ln Q$

B) ΔG

D) $\ln Q$

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

A) ΔG°

C) $RT \ln Q$

B) ΔG

D) $\ln Q$

10) The sign of determine the direction of reaction spontaneity

A) ΔG°

C) $RT \ln Q$

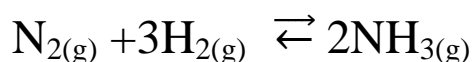
B) ΔG

D) $\ln Q$

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

- | | |
|---------------------|---------------|
| A) ΔG° | C) $RT \ln Q$ |
| B) ΔG | D) $\ln Q$ |

12) The equilibrium constant at 427°C for the reaction



Calculate the value of ΔG° for the reaction under these condition

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

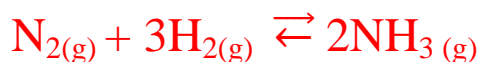
Solution

$$T = 427 + 273 = 700^\circ\text{K}$$

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

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

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



$$\Delta G^\circ_f (\text{NH}_3)_{(g)} = -16.6\text{KJ/mol}$$

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

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

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

D) 2.60

Solution

$$T = 25 + 273 = 298 \text{ }^\circ\text{K}$$

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

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

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

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

14) for the reaction $2\text{C "graphite"} + \text{H}_{2(\text{g})} \rightarrow \text{C}_2\text{H}_{2(\text{g})}$

$\Delta G^\circ = +209.2 \text{ KJ/mol}$ at 25°C .

If $P(\text{H}_2) = 100 \text{ Atm}$, $P(\text{C}_2\text{H}_2) = 0.1 \text{ Atm}$

Calculate ΔG for this reaction.

A) $+207.8 \text{ KJ/mol}$

C) $+192.1 \text{ KJ/mol}$

B) $+226.3 \text{ KJ/mol}$

D) $+17.3 \text{ KJ/mol}$

Solution

$$T = 25 + 273 = 298 \text{ }^\circ\text{K}$$

$$K_p = \frac{P(\text{C}_2\text{H}_2)}{P(\text{H}_2)} = \frac{0.1}{100} = 1 * 10^{-3}$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln K_p \\ &= 209.2 * 10^3 + (8.314 * 298 * \ln 10^{-3}) = 192.1 \text{ KJ/mol} \end{aligned}$$

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



$$\Delta G^\circ = -28.5\text{KJ/mol}$$

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

C) 1.2

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

D) $1 * 10^5$

Solution

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

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

$$\ln K_p = 11.5$$

$$K_p = e^{11.5}$$

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