# Lecture Notes H: Chemical Equilibrium I

## 1) *ΔG tells us whether a reaction is "spontaneous"*

How do we quantify the degree of spontaneity?

$$aA + bB \rightarrow cC + dD$$

## 2) *Law of Mass Action*

For a reaction: $aA + bB \rightarrow cC + dD$

Consider starting with 1 atm of $H_2$ and 1 atm of $I_2$. These will react according to the following reaction:

$$H_{2\,(g)} + I_{2\,(g)} \leftrightarrow 2HI_{(g)}$$

At equilibrium, you find 0.213atm each of $H_2$ and $I_2$ and 1.573 atm of $I_2$:

| | $H_{2\,(g)}$ + | $I_{2\,(g)}$ | $\leftrightarrow$ | 2 $HI_{(g)}$ |
|---|---|---|---|---|
| Initially | 1atm | 1atm | | 0 |
| At equilibrium | 0.213atm | 0.213atm | | 1.573atm |

If we then add 1atm of $I_2$ (raising it to 1.213 atm), the system will adjust and at equilibrium, the pressures will be as follows,

| | $H_{2\,(g)}$ + | $I_{2\,(g)}$ | $\leftrightarrow$ | 2 $HI_{(g)}$ |
|---|---|---|---|---|
| Initially | 0.213atm | 1.213atm | | 1.573atm |
| At equilibrium | 0.0612atm | 1.061atm | | 1.878atm |

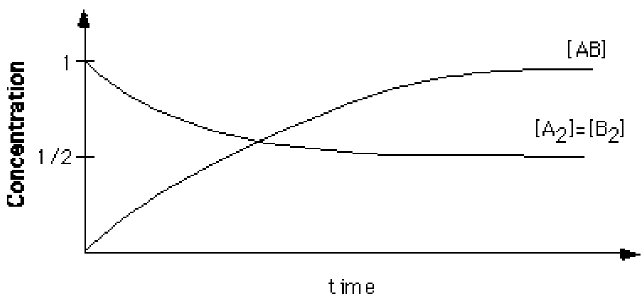
### 3) *The equilibrium constant*

$aA + bB \rightarrow cC + dD$

***Concept***

Consider the reaction: $A_2 + B_2 \leftrightarrow 2AB$

The reactants are mixed together and the following is a plot of the reactant and product concentrations with time:



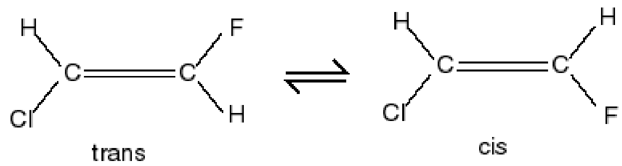

What is the value of the equilibrium constant?

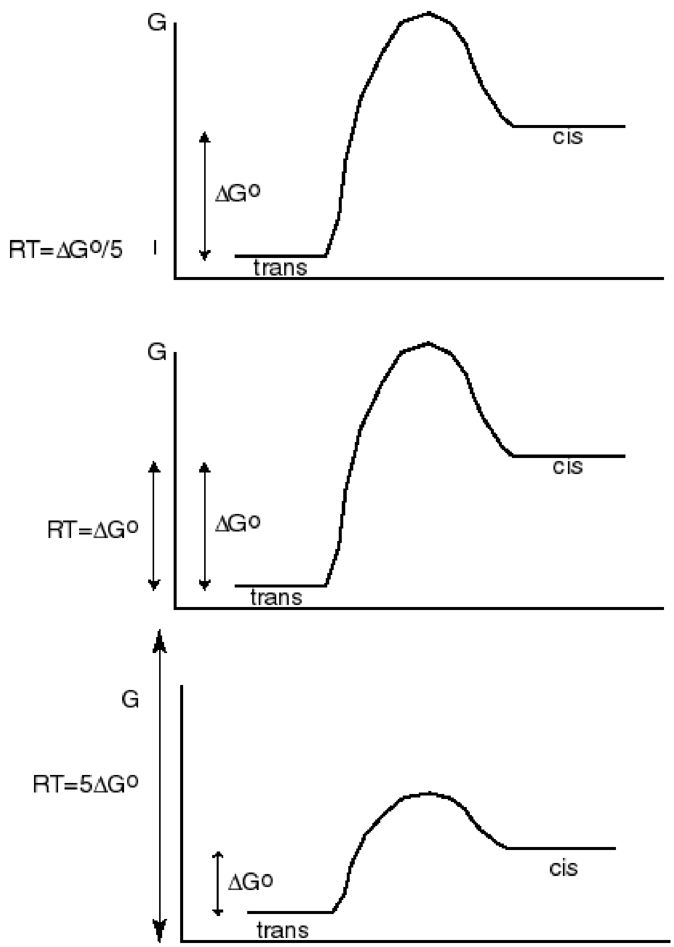
(A) 1/2 (B) 1 (C) 2 (D) 4

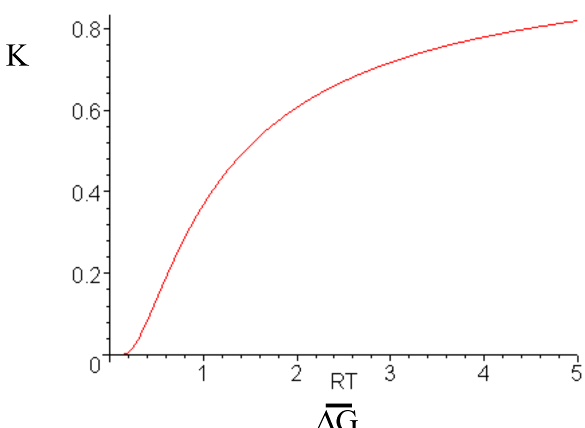
### 4) *Relation between the equilibrium constant and $\Delta G^o$.*

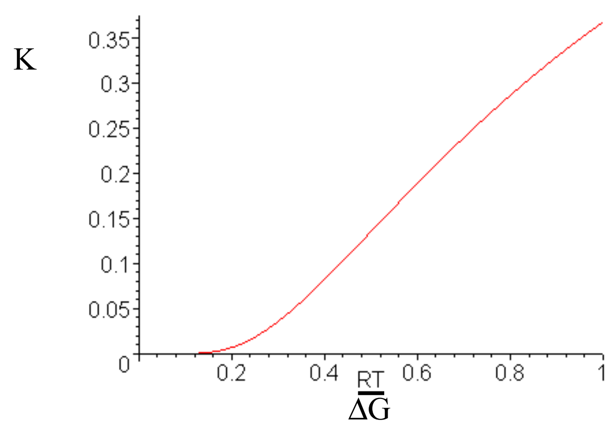
### *5) RT as "thermal energy"*

Consider an isomerization process:



***Concept***

The equilibrium constant for a certain reaction is 100. If the temperature is doubled, what happens to K (assuming that $\Delta G^o$ is independent of temperature)?

a) K stays the same b) new K=1000 c) new K= 10 d) new K= $100*e^2$

The equilibrium constant for a certain reaction is 0.01. If the temperature is doubled, what happens to K (assuming that $\Delta G^o$ is independent of temperature)?

a) K stays the same b) new K=0.0001 c) new K= 0.1 d) new K= $(1/100)*e^{-2}$

## *6) Properties of Equilibrium Constants:*

Consider the following reactions

$$A + 2B \leftrightarrow C$$

Multiply reaction coefficients by n

$$2A + 4B \leftrightarrow 2C$$

Reverse reaction

$$C \leftrightarrow A + 2B$$

Add two reactions

1) $A+B \leftrightarrow C$ $\Delta G_1$
2) $B+C \leftrightarrow D$ $\Delta G_2$
3) $A+2B \leftrightarrow D$ $\Delta G_3$

***Concept***

From a chemical handbook you find the equilibrium constants that give the concentrations of Iodine vapor above water and oil:

$I_2(\text{water}) \leftrightarrow I_2(g)$ $K_{water}$

$I_2(\text{oil}) \leftrightarrow I_2(g)$ $K_{oil}$

But you want the equilibrium constant for the partitioning of $I_2$ between water and oil

$I_2(\text{water}) \leftrightarrow I_2(\text{oil})$ $K$

You can obtain it as:

a) $K= K_{water}+K_{oil}$ b) $K= K_{water}K_{oil}$ c) $K= K_{water}/K_{oil}$ d) $K= K_{oil}/K_{water}$

## *7) Reaction Quotient*

When the mass action expression is not equal to K, its value is denoted Q.

$$aA + bB \rightarrow cC + dD$$

***concept***
Consider the reaction:

$N_2+3H_2 \leftrightarrow 2NH_3$

The equilibrium constant at 400°C is K=0.5.
Suppose we make a mixture with the following concentrations:

$[NH_3] = 1.0M$, $[N_2] = 1.0M$, $[H_2] = 1.0M$

In which direction will the reaction go?

a) $N_2+3H_2 \rightarrow 2NH_3$ b) $N_2+3H_2 \leftarrow 2NH_3$

### *8) Heterogenous Equilibrium (a reaction involving more than one phase)*

$$C(s) + CO_2(g) \leftrightarrow 2CO(g)$$

## Concept Test

Consider the equilibrium expression for the following reaction:

$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

Which of the following is true:

a) The ratio of $CaO(s)$ to $CaCO_3(s)$ will be the same in all samples of this solid.

b) The vapor pressure of $CO_2(g)$ above a mixture of $CaCO_3(s)/CaO(s)$ is independent of the relative amount of these two solids.

c) You need both $CaO(s)$ to $CaCO_3(s)$ to produce $CO_2(g)$.