Chapter 15 – Equilibrium

Equilibrium in Chemical Reactions

Let's look back at our hypothetical reaction from the kinetics chapter.

\[ A + 2B \rightarrow C \]

Why doesn't the concentration of \( A \) ever go to zero?

What if we waited longer?

What is happening here?

In reality, a better way to represent our reaction would be...

\[ A + 2B \rightleftharpoons C \]

Equilibrium – Some Reactions are Reversible

\[ \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \]

Tells us there is more than one reaction taking place.

Will there be more reactants or more products at equilibrium?

Reversible Reactions & Equilibrium

1. Fwd worker breaks reactant in two, sends pieces down the line....

2. Rev worker takes the two pieces, puts back together. Sends back....
   However, it takes REV worker twice as long to put the pieces together....

How will the amounts of products and reactants change over time?

Reversible Reactions & Equilibrium

As the workday progresses.....

1. Because the fwd and rev workers are working at different rates, over time, there will be a build-up of products

2. Since the REV worker is being overwhelmed with more products, the foremen sends in help!!!

Reversible Reactions & Equilibrium

Eventually...

5. Because there are now two REV workers, they together they work at the same rate as the FWD worker

From this point on, the amounts of reactants and products will stay the same...they are in dynamic equilibrium

Once dynamic equilibrium is reached, the amounts of reactants and products DO NOT CHANGE.

The reaction appears to have stopped, but the forward and reverse reaction are taking place at the same rate.
Experimental Evidence of Equilibrium

INITIAL  FINAL

Notice that although each trial started with a different ratios of reactant/products, the "ratio" of concentrations of reactants/products at equilibrium will be the same.

Equilibrium Constant – K

The quantitative measure of "how far" a reaction proceeds is represented by a constant, K.

\[ \text{K} = \frac{[\text{Products}]}{[\text{Reactants}]} \text{ at equilibrium} \]

\[ \text{Rate} = \text{k}_\text{fwd} \text{[Reactants]} - \text{k}_\text{rev} \text{[Products]} \]

For the following reaction, we can determine the rate laws since it is an elementary step:

\[ 2\text{A} + \text{B} \rightarrow \text{C} + 2\text{D} \]

\[ \text{K}_\text{eq} = \frac{[\text{C}][\text{D}]^2}{[\text{A}]^2[\text{B}]} \text{ at equilibrium} \]

We can determine K experimentally by measuring concentrations of reactants and products at equilibrium.

Equilibrium Constant and concentration – \( K_c \)

For gaseous species and gases we can use concentration in our constant

\[ K_c = \frac{[\text{Products}]}{[\text{Reactants}]} \text{ at equilibrium} \]

\[ \text{K}_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^2} \text{ at equilibrium} \]

\[ \text{K}_c = \frac{0.0172 \text{M}}{0.00140 \text{M}} = 12.3 \]

K values and equilibrium concentration practice

Oxygen gas can be converted into ozone based on the following reaction:

\[ 3\text{O}_2(g) = 2\text{O}_3(g) \]

• If the equilibrium concentration of \( \text{O}_2 \) is 0.50M and \( \text{O}_3 \) is 2.2x10^{-8} M, determine the value of the equilibrium constant, \( K_c \)

\[ K_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^2} = \frac{(2.2\times10^{-8})^2}{0.50^2} = 3.9\times10^{-13} \]

• If the equilibrium concentration of \( \text{O}_2 \) is 0.10M, what would be the equilibrium concentration of \( \text{O}_3 \)?

\[ K_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^2} = \frac{(0.10)^2}{3.9\times10^{-13}} = 2.6\times10^8 \text{ M} \]
Heterogeneous Equilibria

How do we deal with reactions that have different states of matter within the same reaction? For example:

$\text{Fe(OH)}_2(s) \rightarrow \text{Fe}^{2+}(aq) + \text{OH}^{-}(aq)$

$K = \frac{[\text{Fe}^{2+}][\text{OH}^{-}]}{[\text{Fe(OH)}_2]}$

A solid or liquid does not change concentration. Although a gas can be represented by $K_p$, how do we represent solids? Well, there's no need to calculate it since it will not change even if you change the amount do we. So, we take it out of the $K_p$ expression.

$K'[\text{Fe(OH)}] = [\text{Fe}^{2+}][\text{OH}^{-}]$

Pure liquids and solids are not represented in the equilibrium expression.

So for the following equation...

$\text{CO}_2(g) \rightarrow 2\text{CO}(g)$

$K = \frac{[\text{CO}_2]}{[\text{CO}]^2}$

...solid carbon will not be a part of the equilibrium expression.

And for the following equation...

$\text{H}_2(aq) + \text{OH}^{-}(aq) \rightarrow \text{H}_2\text{O}(aq)$

$K = \frac{1}{[\text{H}_2][\text{OH}^{-}]}$

...liquid H$_2$O will not be a part of the equilibrium expression.

The Relationship between $K_c$ and $K_p$

The relationship between $K_c$ and $K_p$ is determined by the following equation:

$$K_p = K_c \left(\frac{RT}{mol\ gas\ products - mol\ gas\ reactants}\right)^n$$

For example, the following reaction:

$2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$

has a $K_p$ of $4.09 \times 10^{-1}$ at 300 K. To determine $K_p$, we can use:

$$K_p = \left(\frac{RT}{mol\ gas\ products - mol\ gas\ reactants}\right)^n = \frac{4.98 \times 10^{1}}{2} = 4.98 \times 10^{0}$$

When the number of moles of gas are the same on both sides of the equation, $K_c = K_p$

Equilibrium Constant and Pressure – $K_p$

Just as we can have an equilibrium constant based on pressure of products and reactants ($K_p$), we can also use partial pressures when dealing with gases.

$$K_p = \left(\frac{P_{\text{products}}}{P_{\text{reactants}}}\right)^{n}$$

For example, the following reaction:

$\text{aA} + \text{bB} \rightarrow \text{cC} + \text{dD}$

$K_p = \left(\frac{P_{\text{cC}}/P_{\text{dD}}}{{P_{\text{aA}}}^{a}{P_{\text{bB}}}^{b}}\right)^{n}$

Relationships between related $K$'s

Remember that for the reaction:

$\text{aA} + \text{bB} \rightarrow \text{cC} + \text{dD}$

We have:

$$K_p = \left(\frac{P_{\text{cC}}/P_{\text{dD}}}{{P_{\text{aA}}}^{a}{P_{\text{bB}}}^{b}}\right)^{n}$$

But what about the reverse reaction? When we deal with reversible reactions, we can write it any direction we choose.

Since we have written the equation in reverse, products and reactants are switched. Thus, $K$ is different.

$$K_p = \left(\frac{P_{\text{aA}}}{P_{\text{bB}}}\right)^{a}$$

$$K_p = \left(\frac{P_{\text{cC}}}{P_{\text{dD}}}\right)^{b}$$

$$K_p = \left(\frac{P_{\text{cC}}/P_{\text{dD}}}{{P_{\text{aA}}}^{a}{P_{\text{bB}}}^{b}}\right)^{-1}$$

$$K_p = \frac{1}{K_p}$$

Reaction Quotient and Equilibrium Constant

What do we do when we know the concentration of reactants before equilibrium (or before we mix them to perform a reaction)? Do we have an expression that can quantify this?

$$Q = \left(\frac{P_{\text{cC}}}{P_{\text{dD}}}\right)^{b}$$

The expression can be used to check if a reaction is moving left or right under equilibrium.

$$Q = \left(\frac{P_{\text{cC}}/P_{\text{dD}}}{{P_{\text{aA}}}^{a}{P_{\text{bB}}}^{b}}\right)^{-1}$$

$$Q = \frac{1}{K_p}$$

Notice that the ratio of the concentrations of products to reactants is the inverse of the equilibrium constant.
Le Chatelier’s Principle

When an equilibrium is disturbed, the reaction will proceed in the direction that reestablishes an equilibrium.

\[ \text{N}_2\text{O}_5(s) \rightleftharpoons 2\text{NO}_2(g) \]

Decrease in volume

A certain reaction has a balanced equation of \( \text{A} \rightleftharpoons 2\text{B} + 3\text{C} \). After placing 6.00M \( \text{A} \) in reaction vessel @ 1000K, the reaction begins. During the reaction, the reactant decreased by 1.33M. What are the equilibrium concentrations and what is \( K_e \)?

\[ \text{Initial} \quad \begin{array}{c|c|c|c} \text{A} & \text{B} & \text{C} \\ \hline \text{6.00M} & \text{0M} & \text{0M} \end{array} \]

\[ \text{I.C.E. Table} \]

\[ [\text{A}]_e = \frac{[\text{A}]}{[\text{B}][\text{C}]^3} \]

Le Chatelier’s Principle

Only reactants and/or products that are part of the equilibrium equation, will affect equilibrium.

\[ \text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq) \]

Exothermic reactions (\( \Delta H < 0 \))

Endothermic reactions (\( \Delta H > 0 \))

Equilibrium is established and stable

Equilibrium is established or unstable

Le Chatelier’s Principle

What happens when an equilibrium is disturbed? Once it is disturbed, it will shift toward reactants or products to return to equilibrium.

\[ \begin{array}{c|c|c|c} \text{Increase the amount of a} & \text{Decrease the amount of a} & \text{Decrease the amount of a} & \text{Increase the amount of a} \\ \text{reactant} & \text{product} & \text{reactant} & \text{product} \\ \begin{array}{c} \text{A} + \text{B} + \text{C} + \text{D} \quad Q < K \\ \text{A} + \text{B} + \text{C} + \text{D} \quad Q > K \end{array} & \begin{array}{c} \text{A} + \text{B} + \text{C} + \text{D} \quad Q < K \\ \text{A} + \text{B} + \text{C} + \text{D} \quad Q > K \end{array} \end{array} \]

To make a reaction shift toward products

\( -\text{Decrease the amount of product} \)

\( -\text{Increase the amount of reactant} \)

\( -\text{Increase the amount of product} \)
Determining Change from Initial and Equilibrium Values

Gas A is put in a reaction flask and heated to 40.0°C until it changes to gas B in a 3-to-2 ratio. Before the reaction, gas A had a partial pressure of 1.00atm. At the end of the reaction, after it has cooled gas A had a partial pressure of 0.40atm. Determine the equilibrium pressure of gas B and determine Kc for the reaction.

- Write the balanced equation
- Plug in what we know
- Since we don't know the change, we can substitute with a variable x (temporarily).
- We can actually work backward from equilibrium.

Calculating Equilibrium Concentration using K

A certain reactant "A" manages to produce a product "B" at room temperature in a 2-to-1 ratio. If you started with 3.33M "A", what will be the concentration of both "A" and "B" at equilibrium if Kc = 1.11x10⁻³?

- Write the balanced equation
- Plug in what we know
- Since we don't know the change, we can substitute with a variable x.
- Equilibrium is just the initial plus the change
- Substitute equilibrium concentrations

Calculating Equilibrium Concentration using K – Perfect Squares

The reaction between H₂ and I₂ produces HI. Assume 0.100mol of H₂ and 0.100 mol of I₂ are placed into a 1.00L container. The gas react and are allowed to reach equilibrium. Calculate the equilibrium concentration of all the gases. Kc for the reaction at 443°C is 50.5.

- Write the balanced equation
- Plug in what we know
- Since we don't know the change, we can substitute with a variable x.
- Equilibrium is just the initial plus the change
- Substitute equilibrium concentrations

Calculating Equilibrium Concentration using K – Quadratic Formula

We can calculate equilibrium concentrations if we know initial concentrations and the equilibrium constant, Kc.

If we start with an initial concentration of N₂O₃, 5.0M before decomposition, how much NO₂ will there be at equilibrium? Kc for the reaction is 4.6x10⁻³.

- Write the balanced equation
- Plug in what we know
- Since we don't know the change, we can substitute with a variable x.
- Equilibrium is just the initial plus the change
- Substitute equilibrium concentrations

General form of a Quadratic

ax² + bx + c = 0

Quadratic Formula

-b ± √b² - 4ac

2a
Calculating Equilibrium Concentration using $K$ – Quadratic Formula

$$\begin{align*}
-0.0046 & = \frac{(0.0244)^2}{2(4)} \\
x & = 0.075
\end{align*}$$

This value for $x$ does not make "chemical sense" because you cannot have negative concentrations.

$\left[\text{NO}_2\right] = 5.06M$ 
$\left[\text{NO}_3\right] = 2x$ 
$\left[\text{H}_2\text{O}_4\right] = 4.9M$ 
$\left[\text{H}_4\text{O}_4\right] = 0.15M$

Double check by working backward:

$\text{Slightly off because of approximation, but O.K.}$

Calculating Equilibrium Concentration using $K$ – Simplifying Assumptions

$2\text{H}_2\text{S} \rightleftharpoons 2\text{H}_2 + \text{S}_2$

Initial: 
$\left[\text{H}_2\text{S}\right] = 0.0250M$ 
$\left[\text{H}_2\right] = 0M$ 
$\left[\text{S}_2\right] = 0M$

Change: 
$-2x$ 
$+2x$ 
$+x$

Equilibrium: 
$\left[\text{H}_2\text{S}\right] = 0.0244M$ 
$\left[\text{H}_2\right] = 5.94x10^{-4}M$ 
$\left[\text{S}_2\right] = 2.97x10^{-4}M$

Is our approximation appropriate? 
Calculate what percentage $x$ is of your original $[\text{H}_2\text{S}]$. If it is 5% or smaller, it is O.K.

$2.97x10^{-4} \times 100 = 1.19\%$ 
Our approximation is appropriate.

Let’s make some simplifying assumptions. For example, since $K$ is so small, I'm going to assume that the change in $x$ will be small also. So…

This value for $x$ does not make "chemical sense" because you cannot have negative concentrations.

Calculating Equilibrium Concentration using $K$ – Simplifying Assumptions

Consider the decomposition of $\text{H}_2\text{S}$ to give $\text{H}_2$ and $\text{S}_2$. If $K_c = 1.67x10^{-7}$ at 800°C, determine the equilibrium concentrations for all gases if the initial amount of $\text{H}_2\text{S}$ is 0.0250M.

At this point, you had better know which steps to take!!!

$$
\begin{align*}
K_c & = \frac{[\text{H}_2][\text{S}_2]}{[\text{H}_2\text{S}]} \quad 1.67x10^{-7} \\
(2x)^2 & = 0.0250 - 2x
\end{align*}
$$

This looks like it is going to be a cubic function; 3rd degree polynomial!!! That is: 
$$ax^3 + bx^2 + cx + d = 0$$
I don't feel like solving this!!! Although you can do this via a graphing calculator (which you can't use on an exam, of course….) or using successive approximations.

Let’s make some simplifying assumptions. For example, since $K$ is so small, I’m going to assume that the change in $x$ will be small also. So…

$\left[\text{NO}_2\right]_{\text{eq}} = 0.15M$

$\left[\text{H}_2\text{S}\right]_{\text{eq}} = 0.0250M - 2x$

$\left[\text{H}_2\text{O}_4\right]_{\text{eq}} = 4.9M$

Consider the decomposition of $\text{H}_2\text{S}$, to give $\text{H}_2$ and $\text{S}_2$. If $K_c = 1.67x10^{-7}$ at 800°C, determine the equilibrium concentrations for all gases if the initial amount of $\text{H}_2\text{S}$ is 0.0250M.