Reversible Reactions & Equilibrium

Reversible Reactions

- Reactions are spontaneous if ΔG is negative.
- $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ + energy
- If ΔG is positive the reaction happens in the opposite direction.
- $2H_2O(g)$ + energy $\rightarrow 2H_2(g) + O_2(g)$
- $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ + energy

Equilibrium

$A + B \rightleftharpoons C + D$

- When I first put reactants together the forward reaction starts.
- Since there are no products there is no reverse reaction.
- As the forward reaction proceeds the reactants are used up so the forward reaction slows.
- The products build up, and the reverse reaction speeds up.

Equilibrium

- Eventually you reach a point where the reverse reaction is going as fast as the forward reaction.
- This is dynamic equilibrium.
- The rate of the forward reaction is equal to the rate of the reverse reaction.
- The concentration of products and reactants may not be the same, **but stay constant**, but the reactions are still running.

Equilibrium

- Equilibrium position- how much product and reactant there are at equilibrium.
- Shown with the double arrow.
- $\leftharpoondown\!\!\!\!\longrightharpoonup$ Reactants are favored
- $\longleftharpoondown\!\!\!\!\rightharpoonup$ Products are favored
- Catalysts speed up both the forward and reverse reactions so don't affect equilibrium position.

Measuring Equilibrium

- At equilibrium the concentrations of products and reactants are constant, NOT EQUAL.
- We can write a constant that will tell us where the equilibrium position is.
- K_{eq} = equilibrium constant
- $K_{eq} = \dfrac{[\text{Products}]^{\text{coefficients}}}{[\text{Reactants}]^{\text{coefficients}}}$
- Square brackets [ ] means concentration in molarity (moles/liter)

Writing Equilibrium Expressions

- General equation
  $aA + bB \rightleftharpoons cC + dD$
- $K_{eq} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$
- Write the equilibrium expressions for the following reactions.
- $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$
- $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

Calculating Equilibrium

- K_{eq} is the equilibrium constant, it is only effected by temperature.
- **Only Aqueous ions and gases are included in the K_{eq} expression.**

Write the equilibrium expression for the reaction:

$NH_2OH_{(aq)} + H_2O_{(l)} \leftrightarrow NH_3OH^+{}_{(aq)} + OH^-{}_{(aq)}$

Calculating Equilibrium

- Calculate the equilibrium constant for the following reaction.
  $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$
  if at 25ºC there 0.15 mol/L of N_2, 0.25 mol/L of NH_3, and 0.10 mol/L of H_2.

Answer = 4.17×10^2

What Does K_{eq} Tell Us?

$aA + bB \rightleftharpoons cC + dD$

- $K_{eq} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$
- If $K_{eq} > 1$ Products are favored
- If $K_{eq} < 1$ Reactants are favored

K_{eq} Worksheets

LeChâtelier's Principle

Regaining Equilibrium

LeChâtelier's Principle

- If something is changed in a system at equilibrium, the system will respond to relieve the stress.
- The Equilibrium will be shifted
- Three types of stress are applied.
  - Concentration
  - Pressure on a Gas
  - Temperature

Changing Concentration

- If you add reactants (or increase their concentration).
- The forward reaction will speed up.
- More product will form.
- Equilibrium "*Shifts to the right*"

$$A + B \rightarrow C + D$$

Stress of Adding Reactants. The equilibrium system will react against this, removing reactants by the formation of additional products through chemical reaction. The reaction will proceed to the right.

Changing Concentration

- If you add products (or increase their concentration).
- The reverse reaction will speed up.
- More reactant will form.
- Equilibrium "*Shifts to the left*"

$$A + B \leftarrow C + D$$

Stress of Adding Products. The equilibrium system will react against this, removing products by chemical reaction to form additional reactants. The reaction will proceed to the left (in reverse).

Changing Concentration

- If you remove products (or decrease their concentration).
- The forward reaction will speed up.
- More product will form.
- Equilibrium "*Shifts to the right*"

$$A + B \rightarrow C + D$$

Stress of Removing Products. The equilibrium system will react against this, removing reactants to form products by chemical reaction. The reaction will proceed to the right.

Changing Concentration

- If you remove reactants (or decrease their concentration).
- The reverse reaction will speed up.
- More reactant will form.
- Equilibrium "*Shifts to the left*".

$$A + B \leftarrow C + D$$

Stress of Removing Reactants. The equilibrium system will react against this, removing products by chemical reaction to form additional reactants. The reaction will proceed to the left (in reverse).

Changes in Pressure

- As the pressure increases the reaction will shift in the direction of the least gases.
- At high pressure, it's like increasing the "effective conc" of the side with the most moles of gas:
- $2H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$

Changes in Pressure

- As the pressure decreases the reaction will shift in the direction of the most gases.
- At low pressure, it's like decreasing the amount of the side with the most moles of gas:

$$2H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

Changes in Concentration & Pressure

- Changes in Concentration and Pressure cause the equilibrium to shift until equilibrium is reestablished.
- These changes DO NOT change the value of the Equilibrium Constant, $K_{eq.}$

Changing Temperature

- Reactions either require or release heat.
- Change in Temperature shifts the equilibrium & changes the value of K_{eq}.
- Endothermic reactions go faster at higher temperature.
- Exothermic go faster at lower temperatures.

How Come??

Changing Temperature in an Endothermic Reaction

$$A\ +\ B\ +\ Q \Leftrightarrow C\ +\ D$$

- Raising the temperature is analogous to increasing "Q" thus driving the endothermic reaction to the products side.
- K_{eq} will increase

Changing Temperature in an Exothermic Reaction

$$A\ +\ B \Leftrightarrow C\ +\ D\ +\ Q$$

- Raising the temperature increases "Q" thus driving the exothermic reaction to the reactants side.
- K_{eq} will decrease

Summary of Le Chatelier

1. An increase in concentration on one side of an equation favors or drives the reaction to the opposite side.
   - adding reactants favors products
   - adding products favors reactants
   - K_{eq} remains the same
2. An increase in temperature favors or drives an endothermic reaction forward to products.
   - K_{eq} is increased

Summary of Le Chatelier

3. An increase in temperature drives an exothermic reaction backwards to reactants.
   - Keq is decreased
4. An increase in pressure drives a reaction from the higher moles of gas, towards the side with fewer moles of gas.
   - K_{eq} does not change
5. Adding a catalyst does not alter the relative amounts of reactant and product. Forward reaction happens more easily and so does the reverse reaction. Equilibrium is only reached faster.

Le Chatelier's Worksheets

Equilibrium ICE

What the heck is it?

What is ICE?

$$aA + bB \rightleftharpoons cC + dD$$

- The ICE Method allows us to calculate the equilibrium concentration of each reactant & product in an equilibrium reaction
- Knowing the Equilibrium concentrations, we can calculate K_{eq} for the same reaction

What is ICE?

- What does ICE mean?

  I → Initial conditions at experiment start

  C → Change as system adjusts and reaches equilibrium

  E → Equilibrium

Probably better explained through a problem …

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

1. A solution prepared has an initial concentrations of $[H_2]$ = 2.0 M and $[N_2]$ = 0.66M. The final concentration of $[NH_3]$ = 0.8 M. What are the equilibrium concentrations, and calculate K_{eq}?

The Solution:

	$3H_2(g)$	$+ N_2(g)$	$\rightleftharpoons 2NH_3(g)$
Initial conc	2 (Given)	0.66 (Given)	0
Change in conc	-3x	-x	+ 2x
Eqm. Conc.			0.8 (Given)

Don't forget K_{eq}

$$K_{eq} = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.8)^2}{(0.8)^3(.26)} = 4.81$$

Probably better explained through a problem …

1. A solution prepared has an initial concentration [NOCl] = 2.0 M, and an equilibrium concentration of [NO] = 0.66M. What are the equilibrium concentrations, and calculate K_{eq}.

The Solution:

Balanced Eqn (given)	$2\ NOCl$ ↔	$2\ NO$ +	Cl_2
Initial conc	2 (Given)	0	0
Change in conc	-2x	+ 2x	+ x
Eqm. Conc.		0.66(Given)	

Don't forget K_{eq}

$$K_{eq} = \frac{[NO]^2\,[Cl_2]}{[NOCl]^2} = \frac{(0.66)^2\,(0.33)}{(1.34)^2} = 0.08$$

One more type … I promise!

Given the equilibrium reaction:

$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)}$, where $K_{eq} = 0.26$

Before the reaction begins, the concentrations of $CO_{2(g)}$ and $H_{2(g)}$ are 0.3M. Determine the equilibrium concentrations of all reactants and products.

Balanced Eqn (given)	$CO_{2(g)}$ +	$H_{2(g)}$ ↔	$CO_{(g)}$ +	$H_2O_{(g)}$
Initial conc	0.3M	0.3M	0	0
Change in conc	-x	-x	+ x	+ x
Eqm. Conc.	0.3 - x	0.3 - x	x	x

Answer: 0.3 – 0.10 = 0.2M   0.10M   0.10M

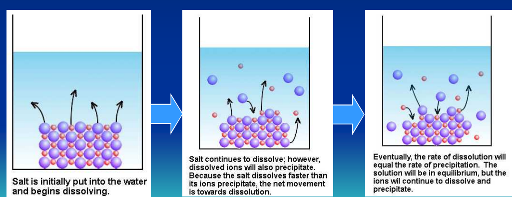
The Solubility-Product Constant K_{sp}

What is K_{sp}?

- It is used to quantitate solid substances that usually considered insoluble in water.
- For K_{sp}, we will consider a saturated solution of the insoluble substance that is in contact with some undissolved solid.
- Important points to consider are:
  - Some of the solid does dissolve. Not very much, but enough.
  - The substance dissociates upon dissolving.
  - There exists an equilibrium between the undissolved solid and the solvated ions.

What is K_{sp}?

– Some of the solid does dissolve.
– The substance dissociates upon dissolving.
– There exists an equilibrium between the undissolved solid and the solvated ions.



What is K_{sp}?

- Our first example is silver chloride, AgCl. When it dissolves, it dissociates like this:

  $AgCl_{(s)} \Leftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$
- An equilibrium expression can be written:

  $K_{eq} = [Ag^+] [Cl^-] / [AgCl]$
- The "molar concentration" of solid AgCl is constant.

  $K_{eq} [AgCl] = [Ag^+] [Cl^-]$
- Since K_{eq} [AgCl] is a constant, we replace it with a single symbol, K_{sp}:

  $K_{sp} = [Ag^+] [Cl^-]$

Write the K_{sp} Expression for These

1) $AlPO_4$
2) $BaSO_4$
3) $Sn(OH)_2$
4) $Cu_3(PO_4)_2$
5) CuCN
6) AgBr
7) $AgNO_3$

Calculating Solubilities

- Knowing the K_{sp}, we can calculate the solubility of the substance

Here's an example:

- For the dissociation of $Sn(OH)_2$:

  $Sn(OH)_{2(s)} \Leftrightarrow Sn^{2+}_{(aq)} + 2\ OH^-_{(aq)}$
- The K_{sp} expression is: $K_{sp} = [Sn^{2+}] [OH^-]^2$
- The K_{sp} for $Sn(OH)_2$ is 5.45×10^{-27}
- Calculate the solubility of the $Sn(OH)_2$?

What do We Know?

$Sn(OH)_{2(s)} \Leftrightarrow Sn^{2+}_{(aq)} + 2\ OH^-_{(aq)}$

- $K_{sp} = [Sn^{2+}] [OH^-]^2$
- $K_{sp} = 5.45 \times 10^{-27}$

Answer

- $K_{sp} = [Sn^{2+}] [OH^-]^2$
- $5.45 \times 10^{-27} = (x) (2x)^2$
- $x = 1.11 \times 10^{-9}$ M ***(This is the Solubility)***
- The Conc of $Sn^{2+} = x = 1.11 \times 10^{-9}$ M
- $OH^- = 2x = 2(1.11 \times 10^{-9}\ M) = 2.22 \times 10^{-9}$ M

Try Another??

- Calculate the solubility of $Fe(OH)_3$.
- The Ksp = 2.64×10^{-39}

Answer:

- $Fe(OH)_{3(s)} \Leftrightarrow Fe^{3+}_{(aq)} + 3\ OH^-_{(aq)}$
- $Ksp = [Fe^{3+}] [OH^-]^3$
- $2.64 \times 10^{-39} = (x) (3x)^3$
- $27x^4 = 2.64 \times 10^{-39}$
- $x = 9.94 \times 10^{-11}$ M

One more … a bit tougher …

- Calculate the solubility of Ag_3PO_4.
- The Ksp = 8.88×10^{-17}

Answer:

- $Ag_3PO_4 \Leftrightarrow 3\,Ag^+ + PO_4^{3-}$
- Ksp = $[Ag^+]^3\,[PO_4^{3-}]$
- $8.88 \times 10^{-17} = (3x)^3\,(x)$
- $27x^4 = 8.88 \times 10^{-17}$
- $x = 4.26 \times 10^{-5}$ M

What are the concentrations of Ag^+ & PO_4^{3-}?

- $Ag^+ = 3 \times 4.26 \times 10^{-5}$ M
- $PO_4^{3-} = 1 \times 4.26 \times 10^{-5}$ M

The K_{sp} Worksheet