Review - CHEM 142: Kinetics

title

Chemical Reactions

Consider a chemical reaction of the form A $\longrightarrow$ B.

1. The rate of a reaction tells you how many times a reaction happens in a certain amount of time.

2. if the reaction A $\longrightarrow$ B is first order, the the rate is proportional to the concentration of A:

$$\text{Rate} = k * [A]$$

   (a) From the differential rate law, we can find how the concentration of A and B as a function of time.

   (b) Since the rate is dependent of the concentration of A, once all of A is consumed, then we can say the reaction is complete (sometimes)

   However, this isn't the only type of reaction. There are also:

Reversible Reactions

1. If the reaction can happen both ways: A $\longrightarrow$ B and B $\longrightarrow$ A.

2. We write this as A $\rightleftharpoons$ B.

3. As you can expect, you'll have 2 different rates corresponding to their reactions - so you can find how the concentrations of A and B change with respect to time

These reactions will continue to happen until a time where the forward and reverse rates become equal to each other, and thus the concentrations no longer change AKA chemical equilibrium.
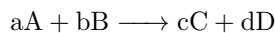
Definition 1 *Chemical Equilibrium*
Where forward and backward reaction rates become equal to each other and concentrations no longer change.
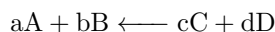
The goal of this class is to predict the concentrations of all species in equilibrium.

General Chemical Reactions

Consider a general **elementary** (reaction order is equal to the stoichiometric coefficient) chemical reaction:
Forward Reaction:
$$aA + bB \longrightarrow cC + dD$$

Backward Reaction:
$$aA + bB \longleftarrow cC + dD$$

Forward Rate:
$$\text{Forward Rate} = k_f[A]^a[B]^b$$

Backward Rate:
$$\text{Backward Rate} = k_b[C]^c[D]^d$$

Chemical Equilibrium (In Terms of Rates):

$$\text{Forward Rate} = \text{Backward Rate}$$
$$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

1   1

This essentially describes that rates at where chemical equilibrium happens. Solving for the stoichiometric constants k_f and k_b

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_b}$$

This gives us the stoichiometric coeffiencents for where equilibrium occurs. This gives us the constant that is dependent on temperature, and not concentration.

Example 1 *A scientist performs experiments at 500 C to study equilibrium concentrations of the ammonia synthesis reaction.*
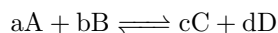
$$\mathrm{N_2\,(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3\,(g)}$$
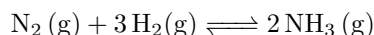
By finding the equilibrium coefficients for all 3 reactions from the previous equation:

$$\frac{[C]^c}{[A]^a[B]^b} = \frac{k_f}{k_b}$$

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{k_f}{k_b}$$

From this example (see class slides), we get the Law of Mass Action:

Definition 2 *Law of Mass Action*
For a reversible gas- or solution-phase chemical reaction

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

The ratio of concentrations K at equilibrium is constant (regardless of inital concentrations) at a given temperature, where K is defined as

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

For gas phase reactions, we also use partial pressures instead of concentrations to describe the chemical equilibrium.
The pressure-based equilibrium constant is:

$$K_P = \frac{\left(\frac{P_C}{P_0}\right)^c \left(\frac{P_D}{P_0}\right)^d}{\left(\frac{P_A}{P_0}\right)^a \left(\frac{P_B}{P_0}\right)^b}$$

Where $P_0 = 1$ atm as the reference temperature.

Statement 1 *The equilibrium concentrations themselves **DO** depend on the inital concentrations are. However the ratio of equilibrium concentrations **DO NOT** depend on the inital conditions.*

However, using concentrations doesn't exactly make the units work out perfectly - so we use the "activities" of the molecular species instead of their concentrations. For ideal gases and molecules in solution, the activity is equal to the concentration divided by a reference concentration c_0, which by common convention 1 molar.

$$a_A = \frac{[A]}{c_0}$$

$$a_B = \frac{[B]}{c_0}$$

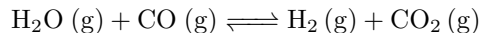$$a_C = \frac{[C]}{c_0}$$

$$a_D = \frac{[D]}{c_0}$$

One thing to note is that even though we continue to write the equilibrium constant in form:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

We actually mean to write the equilibrium constant in form:

$$K = \frac{[a_C]^c[a_D]^d}{[a_A]^a[a_B]^b}$$

Example 2 *The reaction*

$$H_2O \text{ (g)} + CO \text{ (g)} \rightleftharpoons H_2 \text{ (g)} + CO_2 \text{ (g)}$$

Has the equilibrium constant $K = 4$ at 800K. What will the equilibrium concentrations be if you put 1 mole of H_2O and 1 mole of CO into a container of volume 1L at that temperature?

Due to stoichiometry, $[H_2O] = [CO]$, $[H_2] = [CO_2]$, $[H_2O] + [CO] + [H_2] + [CO_2] = 2\,M$

1. Due to how these these 2 chemicals have the same stoichiometric coefficients (they both have 1), they will always have the same amount at all times.

2. The total number of molecules you should have should always be the same.

   (a) Since in both forward and backward reactions, you have 2 molecules being transformed into 2 other molecules.

However, you need the law of mass action in order to find the equilibrium concentrations to act as the fourth equation which you can use to solve for them!
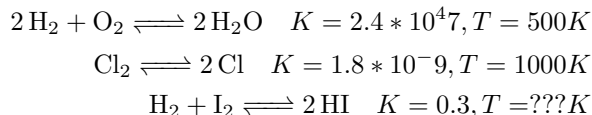
1. Since we're given K = 4 and we're trying to find the equilibrium concentrations:

$$K = \frac{[H_2][CO_2]}{[H_2O][CO]}$$
$$4 = \frac{[H_2][CO_2]}{[H_2O][CO]}$$
$$4 = \frac{[H_2]^2}{[H_2O]^2}$$
$$[H_2] = 2[H_2O]$$

2. Note that since we're given that $[H_2O] = [CO]$ and $[H_2] = [CO_2]$, we can replace [CO] and [CO$_2$] so we can simplify the law of mass action.

3. Given that we know $[H_2O] + [CO] + [H_2] + [CO_2] = 2\,M$, let replace [CO] and [CO$_2$]

$$[H_2O] + [CO] + [H_2] + [CO_2] = 2\,M$$
$$[H_2O] + [H_2O] + 2\,[H_2O] + 2\,[H_2O] = 2\,M$$
$$6\,[H_2O] = 2\,M$$
$$[H_2O] = \frac{1}{3}M$$

Equilibrium is reached when the forward and reverse reactions occur at the same rate, so there is no net change in the concentrations of reactants and products. However, where this balancing point occurs can be different for each reaction:

$$2\,H_2 + O_2 \rightleftharpoons 2\,H_2O \quad K = 2.4 * 10^4 7, T = 500K$$
$$Cl_2 \rightleftharpoons 2\,Cl \quad K = 1.8 * 10^-9, T = 1000K$$
$$H_2 + I_2 \rightleftharpoons 2\,HI \quad K = 0.3, T = ???K$$

For a general chemical reaction in which the number of gas-phase molecules changes by Δn:

$$K_C = (\frac{P_0}{c_0RT})^{\Delta N} K_P \quad K_P = (\frac{c_0RT}{P_0})^{\Delta N} K_c$$

3

Activities and Heterogeneous Equilibrium

For ideal gases and molecules in solution, the activity is equal to the concentration divided by a reference concentration $c_0 = 1M$

$$a_A = \frac{[A]}{c_0}$$
$$= \frac{[A]}{1}$$

For solids and pure liquids, the activity is simply equal to 1.

Example 3 *What is K for the thermal decomp. for calcium carbonate to calcium oxide and carbon dioxide?*

$$\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$$
$$K = \frac{a_{CaO}a_{CO_2}}{a_{CaCO_3}}$$
$$= a_{CO_2} = \frac{\text{CO}_2}{1M}$$

Note - this shows us that the equilibrium constant is depentent on the gas molecules and independent on the others.

Manipulating Equilibrium Constants

Example 4 *Ammonia Synthesis Reaction*

$$\text{N}_2 + 3\,\text{H}_2 \rightleftharpoons 2\,\text{NH}_3 \quad K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$
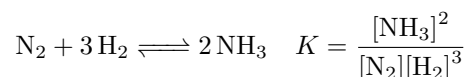
Swapping reactants and products
Note - swapping reactants and products gives the inverse of the equilibrium constant.

$$2\,\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\,\text{H}_2 \quad K^f = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

Example 5 *Multi-step formulation of nitrogen dioxide:*

$$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\,\text{NO} \quad K_1 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$
$$2\,\text{NO} + \text{O}_2 \rightleftharpoons 2\,\text{NO}_2 \quad K_2 = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$
$$\text{N}_2 + 2\,\text{O}_2 \rightleftharpoons 2\,\text{NO}_2 \quad K = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = K_1 K_2$$

Note - When adding reactions, multiply equilibrium constants.

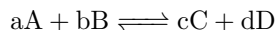**Example 6** *Multiplying first step reaction by 3:*

$$3\,\text{N}_2 + 3\,\text{O}_2 \rightleftharpoons 6\,\text{NO} \quad K = \frac{[\text{NO}]^6}{[\text{N}_2]^3[\text{O}_2]^3} = K_1^3$$

Note - when multiplying a reaction by a number n, raise the equilibrium constant to the n-th power.

The Reaction Quotient Q

We've seen from the law of mass action:

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

The concentrations in **in chemical equilibrium** satisify:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

However, what if you're not in chemical equilibrium? We can calculate the reaction quotient Q:

$$Q = \frac{[C]_0^c[D]_0^d}{[A]_0^a[B]_0^b}$$

This represents what has to happen to reach equilibrium.

Definition 3 *Reaction Quotient (Q)*
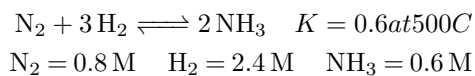
$$Q = \frac{[C]_0^c[D]_0^d}{[A]_0^a[B]_0^b}$$

1. *If $Q < K$, there is not enough product or too much reactant compared to equilibrium. The system will shift "toward the right" AKA the system will be biased to have more forward reactions happening relative to backward reactions.*

2. *If $Q > K$, there is too much product/too little reactant compared to equilibrium. The system will shift "toward the left" ALA the system will be biased to have more backward reactions happening relative to forward reactions.*

3. *If $Q = K$, the system is in equilibrium.*

for ICE Table - as many columns as there are species in chemical reaction: I - Inital: represents inital concentrations in M C - Change: represents stoichiometric coefficients multiplied by x moles of molecules E - Equilibrium: Represents inital value added with change value

Quizzes

1. First quiz opens 4/5/2023 and is open between 3PM and Midnight and can be found on Canvas.

2. Only online resources allowed is Canvas quiz page itself and the online textbook.

3. Will need to have something to write on and scientific calculator.

4. Also **will not cover the lecture on the day the quiz is on**. But does cover previous lectures.

Example 7 *Ammonia synthesis reaction:*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad K = 0.6 \, at \, 500C$$
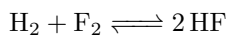$$N_2 = 0.8\,M \quad H_2 = 2.4\,M \quad NH_3 = 0.6\,M$$

Finding Q from inital concentrations:

$$Q = \frac{[C]_0^c[D]_0^d}{[A]_0^a[B]_0^b}$$
$$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3}$$
$$Q = \frac{[0.6]_0^2}{[0.8]_0[2.4]_0^3}$$

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Example 8 *Hydrogen Flouride Reaction and ICE Table*

$$H_2 + F_2 \rightleftharpoons 2\,HF$$

3 moles of each species is added to a 1.5 L flask. K = 115. Find equilibrium concentrations.

1. Finding Inital Concentrations:

$$[H_2] = \frac{3\,M}{1.5\,L} = 2\,M \quad [F_2] = \frac{3\,M}{1.5\,L} = 2\,M \quad [HF] = \frac{3\,M}{1.5\,L} = 2\,M$$

2. Create ICE Table

X	$[H_2]$ +	$[F_2]$	$\rightleftharpoons [2HF]$
I	1	2	0
C	-x	-x	2x
E	1 - x	2 - x	2x

3. Write Equilibrium Expression:

$$K = \frac{[HF]^2}{[H_2][F_2]}$$
$$= \frac{[2\,x]^2}{[1\text{-x}][2\text{-x}]}$$

4. Solve for x:

$$K = \frac{[2\,x]^2}{[1\text{-x}][2\text{-x}]}$$
$$= K(1-x)(2-x) = (2x)^2$$
$$= 2K - Kx - 2Kx + Kx^2 =$$
$$= (K-4)x^2 - 3Kx + 2K = 0, \quad a = (K-4) \quad b = -3K \quad c = 2K$$

5. Plugging in K for a, b, and c and finding X via quadratic equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
$$x = \frac{345 \pm \sqrt{345^2 - 4(111 * 230)}}{2(111)}$$
$$x_1 = 2.14 \quad x_2 = 0.968$$

6. However, we are x = 2.14 cannot be solution as the equilibrium concentration for H_2 is $1 - x$! Thus the solution is x = 0.968.

7. Calculating Equilibrium Concentrations:

$$[H_2] = (1\text{-}0.968)\,M = 0.032\,M$$
$$[F_2] = (2\text{-}0.968)\,M = 1.032\,M$$
$$[HF] = (2 \cdot 0.968)\,M = 1.936\,M$$

8. Checking Results (Optional)

$$K = \frac{[HF]^2}{[H_2][F_2]}$$
$$= \frac{1.936^{\,2}}{0.032 \cdot 1.032}$$
$$= 113 \approx K$$

Example 9 *Decomposition of Nitrosyl Chloride*

$$2\,\text{NOCl} \rightleftharpoons 2\,\text{NO} + \text{Cl}_2 \quad K = 1.6 * 10^-5@35C$$
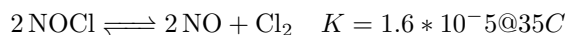
Walter White adds 1 mol NOCl into a 2L flask, what are the equilibrium concentrations?

1. Finding Inital Concentrations:

$$[\text{NOCl}] = \frac{3\,\text{M}}{1.5\,\text{L}} = 2\,\text{M} \quad [\text{F}_2] = \frac{3\,\text{M}}{1.5\,\text{L}} = 2\,\text{M} \quad [\text{HF}] = \frac{3\,\text{M}}{1.5\,\text{L}} = 2\,\text{M}$$

2. Create ICE Table

X	$[2NOCl] \rightleftharpoons [2NO] + [Cl_2]$		
I	0.5	0	0
C	-2x	2x	x
E	0.5 - 2x	2x	x

3. Write Equilibrium Expression:

$$K = \frac{[\text{NO}]^2[\text{CL}_2]}{[\text{NOCl}]^2}$$
$$= \frac{(2\,\text{x})^2\text{x}}{(0.5-2\,\text{x})^2}$$
$$= \frac{4\,\text{x}^3}{(0.5-2\,\text{x})^2}$$

4. Solve for x:

$$K = \frac{4\,\text{x}^3}{(0.5-2\,\text{x})^2}$$
$$= 4x^3 - 4Kx^2 + 2Kx - 0.25K = 0$$

5. However, you get a cubic function here which makes things much harder to solve for X! We've seen that the equilibrium constant is very small, so we should expect to the equilibrium position to be far to the left, and x to be small.
   Lets simplify $0.5 - 2x \approx 0.5$ (Small X Approximation) and try again.

6. Write Equilibrium Expression:

$$K = \frac{[\text{NO}]^2[\text{CL}_2]}{[\text{NOCl}]^2}$$
$$= \frac{(2\,\text{x})^2\text{x}}{(0.5)^2}$$
$$= \frac{4\,\text{x}^3}{0.25}$$
$$K = 16x^3$$

7. Solving for X:

$$K = 16x^3$$
$$\rightarrow x = \left(\frac{K}{16}\right)^{1/3}$$
$$\rightarrow x = 0.01$$

8. Calculating Equilibrium Concentrations:

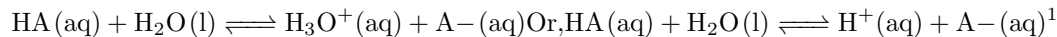$$[\text{H}_2] = (2\text{-}0.01)\,\text{M} = 0.48\,\text{M}$$
$$[\text{F}_2] = (2 \cdot 0.01)\,\text{M} = 1.032\,\text{M}$$
$$[\text{HF}] = (2 \cdot 0.968)\,\text{M} = 1.936\,\text{M}$$

9. Checking Results (Optional)

$$K = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$$
$$= \frac{1.936^{\,2}}{0.032 \cdot 1.032}$$
$$= 113 \approx K$$

Strong and Weak Acids

Acid dissociation reaction:

$$\text{HA (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+ \text{(aq)} + \text{A}- \text{(aq)} \quad \text{Or,} \quad \text{HA (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{A}- \text{(aq)}^1$$
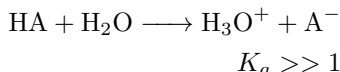
The equilibrium constant is also called the "acid dissociation constant" and is written as K_a:

$$K_a = \frac{[\text{H}_3\text{O}]\,[\text{A}-]}{[\text{HA}]}$$

For strong acids, they dissociate completely, and thus when we compute K_a gives us ∞; indicating equilibrium is "to the right".

$$\text{HA} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{A}^-$$
$$K_a \gg 1$$

For weak acids, they do not completely dissociate, and we will still have some HA left over. Computing K_a will give us a number that is less than 1 indicating equilibrium is "to the left"

$$\text{HA} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{A}^- + \text{HA}$$
$$K_a < 1$$
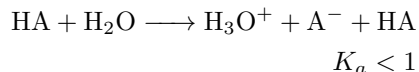
Example 10 *What is the hydronium concentration of a 0.2M solution of hydrochloric acid (HCl) in equilibrium.*

1. Since HCl is a strong acid and completely dissociates, we will have a reaction:

$$\text{HA} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{A}^-$$
$$[\text{H}_3\text{O}^+] = [\text{HCl}]_0 = 0.2\,\text{M}$$
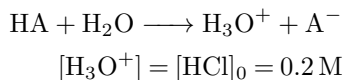
Example 11 *What is the hydronium concentration of a 0.2M solution of nitrious acid (*HNO_2*) in equilibrium with* $K_a = 4 * 10^{-4}$

1. You must make a ICE table to find it!

X	$[HNO_2] +$	$[H_2O] \rightleftharpoons$	$[H_3O^+] +$	$[NO_2^-]$
I	0.2	-	0	0
C	-x	-	x	x
E	0.2 - x	-	x	x

2. Creating K_a

$$K_a = \frac{[\text{H}_3\text{O}]\,[\text{A}-]}{[\text{HA}]}$$
$$K_a = \frac{x^2}{0.2 - x}\text{Then applying small x approximation}$$
$$= \frac{x^2}{0.2}$$
$$x = \sqrt{0.2K_a} = \sqrt{0.2 * 4 * 10^{-4}}$$
$$x = 0.009$$
$$[\text{H}_3\text{O}^+] = 0.009$$
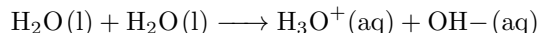
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3. Checking approximation

$$\text{Error} = \frac{x}{0.2}$$
$$= \frac{0.009}{0.2}$$

Error = 4.5%   Error within 5%, acceptiable to use small x approximation!

Water Autoionizaztion

Water undergoes acid dissociation with itself. This is called autoionization:

$$H_2O\,(l) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + OH-\,(aq)$$

The equilibrium constant in this case is also called the "water autodissociation constant" and is written as K_w. This is a measure for how acidic water is.
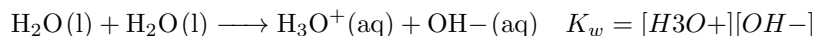For pure water at room temperature (25C):[2]

$$[H_3O^+] = 10^-7M$$
$$[OH-] = 10^-7M$$
$$K_w = 10^-14$$

Multiple Simultaneous Equilibria

Water autoionization:

$$H_2O\,(l) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + OH-\,(aq) \quad K_w = [H3O+][OH-]$$

Acid dissociation:

$$HA + H_2O \longrightarrow H_3O^+ + A^- \quad K_a = \frac{[H_3O]\,[A-]}{[HA]}$$
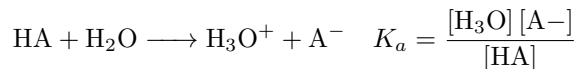
In order to find the equilibrium concentrations, we have to solve for ALL things like $[H_3O^+]$ and $[OH-]$ using both equilibrium constants at the same time.
This can be done, but is complicated to do so - instead, we'll do a simple shortcut:

Example 12 *What is the hydronium concentration of a 0.2M solution of nitrious acid (*HNO_2*) in equilibrium with* $K_a = 4 * 10^-4$

We found that $[H_3O^+] = 0.009$M from the dissociation of the nitrious acid. Water autoionization also adds additional hydronium ions, but only 10^-7M, a miniscule amount relative to the acid dissociation.
For these cases, we can igniore the contribution from the water autoionization.

The power of Hydrogen

The concentration of protons (or hydronium ions) is an important property of aqueous solutions. It's often quite small, and is often convenient to express it in a different from that yields more "convenient" numbers:
(AKA pH scale)

$$pH = -log_{10}[H^+] \quad [H^+] = 10^{-pH}$$

Where:

1. p stands for $-log_1 0$

2. $[H^+]$ represents the concentration of H^+ in Molar

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[2]There is no such thing as perfectly "pure" water - it constantly fluxuates between slightly basic and slightly acidic

Note that pH represents the "inverse order of magnitude" of the hydronium concentration. Which means:
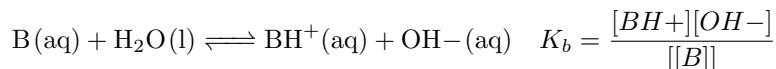
1. The smaller the pH, the more "acidic" a solution is. (Such as HCl and lemon juice)

2. The greater the pH, the more "basic" a solution is. (Such as baking soda or household ammonia)

**Example 13** *What is the pH of a 0.5M solution of acetic acid CH_3COOH, a weak acid with $K_a = 1.8*10^-5$?*

$$CH_3OOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3OO-\,(aq) + H_3O^+\,(aq)$$
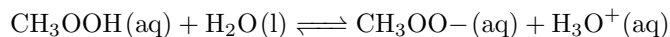
Strong and Weak Bases

Base hydrolysis reaction:

$$B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH-\,(aq) \quad K_b = \frac{[BH+][OH-]}{[[B]]}$$

In this situation, the equilibrium constant is also called the "base ionization constant" and is written as K_b.
Adding a base to water increases the concentration of hydroxide ions.
For strong bases, they are good at grabbing protons, and thus when we compute K_b gives us ∞; indicating equilibrium is "to the right".

$$B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH-\,(aq)$$
$$K_a \gg 1$$
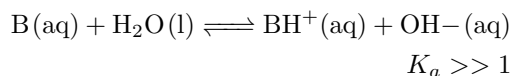
For weak bases, they don't act as well at grabbing protons, and we will still have some B left over. Computing K_b will give us a number that is less than 1 indicating equilibrium is "to the left"

$$B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH-\,(aq) + B\,(aq)$$
$$K_a < 1$$
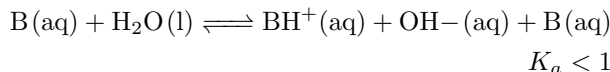
Example 14 *What is the hydroxidde concentration of a 0.1M solution of NaOH (sodium hydroxide), a strong base?*

$$NaOH\,(aq) \rightleftharpoons Na^+\,(aq) + OH-\,(aq)$$
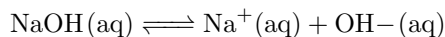
However, this doesn't even look like a base hydrolysis reaction! However, when we break it down further, we can show that this is still a hydrolysis reaction:

$$Na^+\,(aq) + OH-\,(aq) + H_2O\,(l) \rightleftharpoons Na^+\,(aq) + OH-\,(aq) + H_2O\,(l)$$
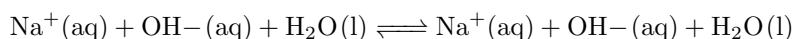
In this case, Na+ is a spectator ion.

Example 15 *What is the hydroxide concentration of a 0.1M solution of ammonia (NH_3) witha weak base where $K_b = 1.8 * 10^-5$?*

1. Writing reaction:

2. Creating ICE Table:

X	$[NH_3] + [H_2O] \rightleftharpoons [NH_3^+] + [OH^-]$		
I	0.1	0	0
C	-x	x	x
E	0.1-x	x	x

3. Writing K_b

$$K_b = \frac{[NH_4^+][]}{}$$

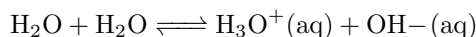4. Solving for x

5. Is our small-x approximation appropiate?

$$\frac{x}{0.1} = 1.3\% < 5\% \quad \text{Is acceptiable}$$

6. Can we ignore autoionization of water?

$$0.0013 >> 10^-7 \quad \text{Can ignore autoionization}$$

Relationship between pH and pOH

The water autoionization reaction:

$$H_2O + H_2O \rightleftharpoons H_3O^+(aq) + OH-(aq)$$

Guarantees that whenever the system is in equilibrium,

$$K_w = [H_3O^+][OH-]$$

Let's take $-log_10$ of both sides:

$$log_10(K_w) = log_10([H_3O^+][OH-])$$
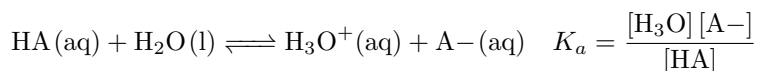$$= -log_10([H_3O^+]) - log_10([OH-])$$
$$= pH + pOH$$

For water at 25C, $K_w = 10^-14$ and therefore

$$pH + pOH = 14 \quad \text{(at room temperature)}$$

Conjugate Acids and Bases

Acid Dissociation Reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A-(aq) \quad K_a = \frac{[H_3O][A-]}{[HA]}$$

A^- can accept a proton and turn into HA, so it is a base - the conjugate base of HA.

$$A-(aq) + H_2O(l) \rightleftharpoons HA(aq) + H_2O(l) \quad K_b = \frac{[HA][OH-]}{[A-]}$$
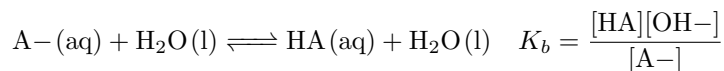
Now what if we take the product of the acid dissociation constant K_a and the base ionization K_b for a conjugate acid/base pair?

$$K_a K_b = \frac{[H_3O][A-]}{[HA]} \frac{[HA][OH-]}{[A-]} = K_w$$

Important parts about conjugate acids and bases!!!

1. Acids that are stronger than H_3O have conjugate bases that are weaker than H_2O. This makes sense as that we have to have Ka and Kb ALWAYS equal to 14 (or a constant!), thus the higher Ka, the lower Kb must be in order to compensate.

2. Acids that are weaker than water have conjugate bases that are stronger than OH^-

3. Acids that are weaker than H_3O^+ and stronger than OH^- have conjugate bases that have strengths somewhere in between the two cases above.

Example 16 *At 25C, the accid dissociation constant for acetic acid CH_3COOH is $K_a = 1.8 * 10^-5$. What is the pH of a 0.35M solution of acetate CH_3COO^-?*

1. Writing out reaction:

2. Creating ICE Table:

X	$[CH_3COO^-] + [H_2O] \rightleftharpoons [CH_3COOH] + [OH^-]$		
I	0.35	0	0
C	-x	x	x
E	0.35-x	x	x

3. Writing K_b

$$K_b = \frac{[CH_3COOH][OH-]}{CH_3COO^-}$$

4. Solving for x

5. Is our small-x approximation appropiate?[3]

$$\frac{x}{0.35} = 0.004\% < 5\% \quad \text{Is acceptiable}$$

6. Can we ignore autoionization of water?

$$1.4 * 10^-5 >> 10^-7 \quad \text{Can ignore autoionization}$$

7. Finding pH and pOH

General form of finding concentration for ANY weak acid with an inital concentration of "c" M and given Ka

1. Writing out reaction:

2. Creating ICE Table:

X	$[HA] + [H_2O] \rightleftharpoons [H^+] + [A^-]$		
I	c	0	0
C	-x	x	x
E	c-x	x	x

3. Writing K_a

$$K_a = \frac{[H^+][A-]}{HA}$$
$$K_a = \frac{x^2}{c - x}$$

4. Solving for x (assuming small x approximation)

$$K_a = \frac{x^2}{c - x}$$
$$K_a = \frac{x^2}{c}$$
$$K_a(c) = x^2$$
$$x = \sqrt{K_a * c}$$

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[3]Double check small x approximation error by dividing the x concentration by inital concentration - this will give you the error
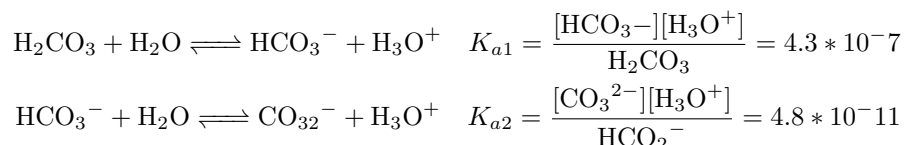
5. Now that we have x in terms of K_a and c, we can find the minimum concentration to find where small x approximation can apply - Solving for x in our error check:

$$\frac{x}{c} = 0.05\%$$

$$\frac{\sqrt{K_a * c}}{c} = 0.05$$

$$\left(\frac{\sqrt{K_a * c}}{c}\right)^2 = 0.05^2$$

$$\frac{K_a * c}{c^2} = 0.025$$

$$\frac{K_a}{c} = 0.025$$

$$c = \frac{K_a}{0.025}$$

1. As acid concentration increases H_3O^+ increases, pH decreases, and percent dissociated decreases We quantify this through the use of the pKa constant, where the acid is 50% dissociated when pH = pKa

2.

Polyprotic Acids

Some acids can donate more than 1 proton, for example carbonic acid H_2CO_3. There are multiple equilibria to consider simultaneously:

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad K_{a1} = \frac{[HCO_3-][H_3O^+]}{H_2CO_3} = 4.3 * 10^-7$$

$$HCO_3^- + H_2O \rightleftharpoons CO_{32}^- + H_3O^+ \quad K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{HCO_2^-} = 4.8 * 10^-11$$

With each step, the equilibrium constant decreases.
Calculating equiulibrium concentrations is possible, but difficult due to multiple equilibria. But we can make qualitative predictions:

1. At high pH, the acid will be completely dissociated

2. At low pH, the acid will not be dissociated at all.

This leads to a graph where we can plot the theoretical concentrations of each compound as a function of the pH

Acid-Base Properties of Salts

What happens when you add ions to water?

Example 17 *When adding chloride ions to water, the following is in principle possible:*

$$Cl^- + H_2O \rightleftharpoons HCl + OH^-$$
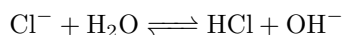
1. However, this doesn't happen since HCl is a strong acid, and Cl- is a very weak base - and doesn't have enough strength to pull the hydrogen ions - so the equilibrium lies far to the left. **This means that adding anions of strong acids have no effect on pH.**

2. Similarly, this is true when doing it for strong bases - adding cations for strong bases have no effect on pH

3. Thus generally, **Adding the conjugate bases/acids of strong acids/bases have no effect on pH**

4. **However**, this isn't true for when we do the opposite! Adding the conjugate bases/acids of **weak** acids/bases DO have a effect on pH

Chapter 8: Applications of ... Ion Solutions
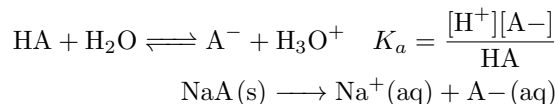
Common Ion Solutions

We know that pure water has a pH of 7 at room temperature. So far, we have studied how the pH changes if you add either acid or base to water. For example:

1. A 0.01M solution of sodium hydroxide, a strong base, has a pH of 12 through:

$$pOH = -log_{10}(0.01) = 2$$
$$pH = 14 - pOH$$
$$pH = 12$$

2. A 0.5M solution of acetic acid, a weak acidm, has a pH of 2.52.

3. a 0.5M solution of sodium acetate, a salt containing the weak base acetate, has a pH of 9.22.
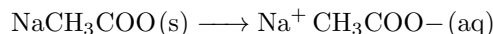
What happens if you add both a weak acid and its conjugate base to water, for example by adding a salt?
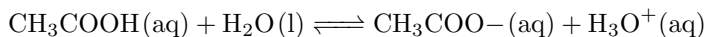
$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad K_a = \frac{[H^+][A-]}{HA}$$
$$NaA(s) \longrightarrow Na^+(aq) + A-(aq)$$

1. Both the acid and the salt generate A^- - it is a common ion.

2. If we look at this step according to Le Chatelier's principle, you'll be adding acetate ions, disturbing equilibrium. Since we have additional acetate anions and hydronium cations, you'll shift the reaction to the left in order to return to equilibrium.

Example 18 *What is the pH of a solution that is 0.5M acetic acid(CH_3COOH, $Ka = 1.8*10^-5$) and 0.5M sodium acetate ($NaCH_3COO$)?*

1. Sodium acetate dissolves completely:

$$NaCH_3COO(s) \longrightarrow Na^+ CH_3COO-(aq)$$

2. Solve acetic acid dissocation equilibrium:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO-(aq) + H_3O^+(aq)$$

3. Creating ICE table:

X	$[NaCH_3COO] + [H_2O] \rightleftharpoons [CH_3COO^-] + [H_3O]$		
I	0.5	0.5	0
C	-x	x	x
E	0.5-x	0.5+x	x

4. Solving for hydronium concentration (x)

From this, we have considered solutions containing a weak acid and its conjugate base:

1. Ex - A solution that is 0.5M in acetic acid and in sodium acetate has a pH of 4.74 (this is between 2.52 and 9.22)

2. The present of the (conjugate?) base inhibits the dissociation of the acid

 Now, what if we add a strong base (or strong acid) to this solution?

Example 19 *A solution that is 0.5M acetic acid(CH_3COOH, $Ka = 1.8 * 10^{-5}$) and 0.5M sodium acetate ($NaCH_3COO$) has a pH of 4.74. How does the pH change if we add 0.01 mol of sodium hydroxide to 1L of this solution?*

1. Sodium hydroxide dissolves completely:

$$NaOh(s) \longrightarrow Na^+(aq) + OH-(aq)$$
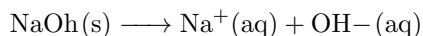
2. Hydroxide is a strong base that will "steal" protons. These will come from the strongest acid available - acetic acid.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO-(aq) + H_3O^+(aq)$$
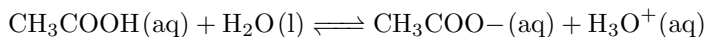
3. Since hydroxide is stuch a strong base, the reaction will go to completion - and we can use basic stoichiometry to calculate the resulting concentrations:

X	$[CH_3COOH]$	$+$	$[H_2O]$	$\leftrightharpoons$	$[CH_3COO^-]$	$+$	$[H_3O^+]$
I	0.49				0.51		0
C	-x				x		x
E	0.49-x				0.51+x		x

4. Finding K_a

$$K_a = \frac{(0.51 + x)(x)}{(0.49 - x)} \quad \text{small-x approximation}$$

$$K_a \approx \frac{(0.51 + x)(x)}{(0.49)}$$

$$x = \frac{0.49}{0.51} K_a = 1.73 * 10^{-5}$$

$$pH = 4.76$$

5.

From this, it's very strange that adding a strong base to a common ion solution will change the pH by only 0.02! From this we get that:

1. It is difficult to change the pH of a solutionm containing signifficant amounts of weak acid and its conjugate base.

2. Such solution resists changes in pH - this is called a **buffered solution** or just "buffer"

3. This is very important for applications requiring a constant pH (examples include blood)

Buffered Solutions

Recap - How do buffers maintain a nearly constant pH?

1. We start with a solution with similar (read: roughly equal) amounts of weak acid and its conjugate base

2. Their equilibrium is governed by:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad K_a = \frac{[H^+][A-]}{HA} \quad [H_3O^+] = Ka\frac{[HA]}{[A-]}$$
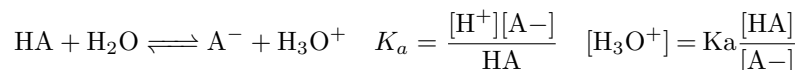
3. Adding strong bases to weak acids leads to them being neutralized by the weak acid, and turning into their conjugate base.

   (a) If we add OH^-, then HA is converted to A^- If the amount of OH- is much less than that of HA and A-, then the ratio [HA]/[A-] changes by very little. AKA the pH changes very little.

   (b) If we add H^+, then A^- is converted to HA. If the amount of H^+ is much less than that of HA and A^-, then the ratio of $[HA]/[A-]$ changes very little. AKA the pH changes very little.

Henderson-Basselbalch Equation

[4] In the final step, we considered the equilibrium position of the weak acid dissocation:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad K_a = \frac{[H^+][A-]}{HA}$$
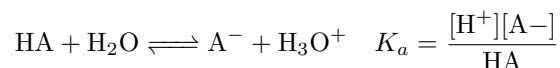
Once you know the equilibrium concentrations of HA and A^-, you can calculate concentration of hydronium and then pH:

$$pH = pKa + log_{10}\frac{[A-]}{[HA]}$$

THIS ONLY APPLIES IF A- is the conjugate base of HA!

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[4]Be careful! Tricky as there are situations in which this section doesn't count for