

CHEM 1120- 16.6



[SPELL CARD]

- Equilibrium constant (K_c) is 24.0 at 200°C
- Initial presence of *cis*-stilbene is 0.850 mol/L



$$x = 0.816$$

	<i>cis</i> -stilbene	<i>trans</i> -stilbene
Initial (M):	0.850	0.000
Change (M):	- 0.816	+ 0.816
Equilibrium (M):	(0.850 - 0.816) = 0.034 M	0.816 M

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CHEM 1120- 16.7.1



[SPELL CARD]

The Reaction Quotient: Predicting the Direction of Change

For the gas phase reaction $aA + bB \rightleftharpoons cC + dD$,

the reaction quotient is as follows:

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad Q_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

It's the **exact same** functional form as K !If we *disturb* equilibrium, our new concentrations give us Q . The value of Q compared to K tells us how concentrations will slide back to equilibrium.

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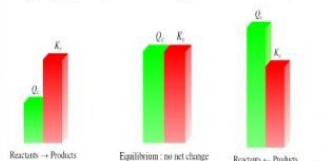
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[SPELL CARD]

The **reaction quotient** (Q_c) is calculated by substituting the **current or initial** concentrations of the reactants and products into the equilibrium constant (K_c) expression. If:

- $Q_c < K_c$ system proceeds from left to right to reach equilibrium
- $Q_c = K_c$ the system is at equilibrium
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium



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[SPELL CARD]

Solution We follow the preceding procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction for each 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

$$x = 0.393$$

	H_2	I_2	2HI
Initial (M):	0.500	0.500	0.000
Change (M):	- 0.393	- 0.393	+ 0.786
Equilibrium (M):	(0.500 - 0.393) = 0.107 M	(0.500 - 0.393) = 0.107 M	0.786 M

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CHEM 1120- 16.8.2



[SPELL CARD]

A trick for the 5%

$$\frac{\text{approximate } x}{\text{initial concentration}} \times 100 < 5\%$$

No one likes to do the same problem twice!

Look at initial concentration of reactants and compare to K . Typically if they are more than a factor of 10000 (10^4) different, the 5% rule will apply

If they are a factor of ~1000 different or less, it might be close

5% rule

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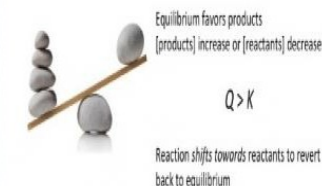
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CHEM 1120- 16.9.1



[SPELL CARD]

$$K = [\text{products}]/[\text{reactants}]$$



5% rule

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[SPELL CARD]

$$K = [\text{products}]/[\text{reactants}]$$

Equilibrium favors reactants
[reactants] increase or [products] decrease

$$Q < K$$

Reaction shifts towards products to revert back to equilibrium

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CHEM 1120- 16.9.3



[SPELL CARD]

Le Châtelier's Principle - Summary

Change	Shift Equilibrium	Change Equilibrium Constant
Concentration	yes	no
Pressure	yes*	no
Volume	yes*	no
Temperature	yes	yes
Catalyst	no	no

Dependent on relative moles of gaseous reactants and products

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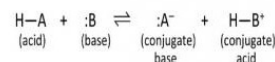
CHEM 1120- 17.3



[SPELL CARD]

Brønsted-Lowry Theory

- The Brønsted acid is an H^+ donor
- The Brønsted base is an H^+ acceptor
 - Structure of base **must** contain an atom with a **lone pair** of electrons
- In a Brønsted-Lowry acid-base reaction, the acid molecule donates an H^+ to the base molecule



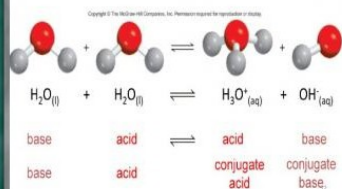
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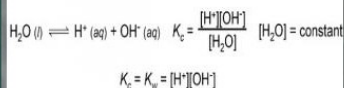
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Water can *autoionize*

- Can act as a water and a base in the same solution



The Ion Product of Water

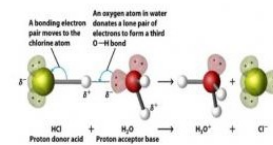


The *ion-product constant* (K_w) is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.

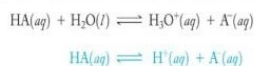
At 25°C
 $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$



- Memorize that these are strong acids
 - HCl , HBr , HI , HNO_3 , H_2SO_4 , & HClO_4
 - They completely ionize in water
- Memorize that these are strong bases
 - NaOH , $\text{Mg}(\text{OH})_2$, any Group IA/IIA bound to hydroxide

Acid Ionization Constant, K_a

- Acid strength is measured by the size of the equilibrium constant when the acid reacts with H_2O



- The equilibrium constant for this reaction is called the **acid ionization constant, K_a**
- The larger the K_a value, the stronger the acid

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



pH – A Measure of Acidity

$$\text{pH} = -\log[\text{H}^+]$$

Solution is

		At 25°C	
neutral	$[\text{H}^+] = [\text{OH}^-]$	$[\text{H}^+] = 1.0 \times 10^{-7}$	pH = 7
acidic	$[\text{H}^+] > [\text{OH}^-]$	$[\text{H}^+] > 1.0 \times 10^{-7}$	pH < 7
basic	$[\text{H}^+] < [\text{OH}^-]$	$[\text{H}^+] < 1.0 \times 10^{-7}$	pH > 7

$$\text{pH} \uparrow \quad [\text{H}^+] \downarrow$$



What is pOH?

- Another way of expressing the acidity/basicity of a solution is pOH
 - $\text{pOH} = -\log[\text{OH}^-]$
- If you know pOH, then you can determine $[\text{OH}^-]$
 - $[\text{OH}^-] = 10^{-\text{pOH}}$
 - $\text{pOH}_{\text{value}} = -\log(10^{-7}) = 7$
- $\text{pOH} < 7$ is basic; $\text{pOH} > 7$ is acidic; $\text{pOH} = 7$ is neutral



Relationship between pH and pOH

- $\text{pH} + \text{pOH} = 14.00$ at 25 °C
 - If you know pOH, you can determine pH
 - If you know pH, you can determine pOH

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$(-\log([\text{H}_3\text{O}^+][\text{OH}^-])) = -\log(1.0 \times 10^{-14})$$

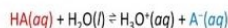
$$(-\log([\text{H}_3\text{O}^+])) + (-\log([\text{OH}^-])) = 14.00$$

$$\text{pH} + \text{pOH} = 14.00$$



Buffer solutions

- A **buffer** is a solution that contains significant amounts of
 - a weak acid or base,
 - its conjugate partner (HA and A^- or B^- and HB)



- The solution *resists changes* in pH
- A **weak acid (HA)** reacts with added base

$$\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^-$$
- A **weak base (B)** reacts with added acid

$$\text{B}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HB} + \text{H}_2\text{O}$$



An Acidic Buffer Solution

Must contain significant amounts of both a weak acid and its conjugate base

Adding a strong base to an acidic buffer:

- $$\text{NaOH}_{(aq)} + \text{HC}_2\text{H}_3\text{O}_2_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{NaC}_2\text{H}_3\text{O}_2_{(aq)}$$
- Added base is **neutralized** by weak acid component ($\text{HC}_2\text{H}_3\text{O}_2$) in the buffer
 - If the amount of NaOH added is less than the amount of acetic acid present, the pH change is small

Adding a strong acid to an acidic buffer:

- $$\text{HCl}_{(aq)} + \text{NaC}_2\text{H}_3\text{O}_2_{(aq)} \rightarrow \text{HC}_2\text{H}_3\text{O}_2_{(aq)} + \text{NaCl}_{(aq)}$$
- Added acid is **neutralized** by conjugate base component ($\text{NaC}_2\text{H}_3\text{O}_2$) in the buffer
 - If the amount of HCl is less than the amount of $\text{NaC}_2\text{H}_3\text{O}_2$ present, the pH change is small



Henderson-Hasselbalch Equation

Our solution contains:

Salt of a weak acid:



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Weak acid:



Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$



Preparing buffers

• Buffer Range:

- pH range where a given buffer can provide protection
- Buffer range = $\text{p}K_a \pm 1$

• Buffer Capacity:

- Quantity of acid / base that can be neutralized while maintaining pH within desired range
- To find an appropriate buffer, we find an acid where $\text{p}K_a$ of the acid \approx pH range of interest
- If $\text{p}K_a \approx \text{pH}$, what is $\log [\text{conjugate base}]/[\text{acid}]$?



Titrations

In a **titration**, a solution of accurately known concentration is gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Equivalence point – the point at which the reaction is complete

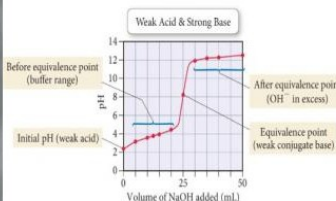
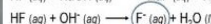
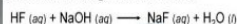
Indicator – substance that changes color at (or near) the equivalence point



Slowly add base to unknown acid UNTIL the indicator changes color



Weak Acid-Strong Base Titrations

 K_{sp} , the Solubility Product

- All ionic compounds dissolve in water to some degree
 - Many compounds have such **low** solubility in water that they are classified as **insoluble**
- The concepts of equilibrium can be applied to salts dissolving
 - Using the equilibrium constant K_{sp}
 - Relative solubilities in water can be determined



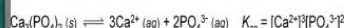
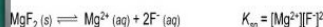
- The solubility product would be $K_{sp} = [M^{m+}]^a[X^{n-}]^b$



Solubility Equilibria



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \quad K_{sp} \text{ is the solubility product constant}$$



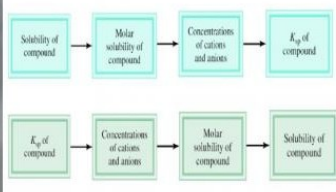
Dissolution of an ionic solid in aqueous solution:

$Q < K_{sp}$	Unsaturated solution	No precipitate
$Q = K_{sp}$	Saturated solution	
$Q > K_{sp}$	Supersaturated solution	Precipitate will form



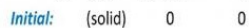
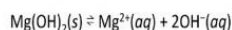
Molar solubility (mol/L) is the number of moles of solute dissolved in 1 L of a saturated solution.

Solubility (g/L) is the number of grams of solute dissolved in 1 L of a saturated solution.



Find molar solubility

$$K_{sp} \text{ of } \text{Mg(OH)}_2 \text{ is } 5.6 \times 10^{-12}$$

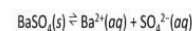


- "s" is like "x" from previous ICE problems
- We get $[\text{Mg}^{2+}]$ and $[\text{OH}^-]$ from ICE
- But "s" is a separate physical property – the **molar solubility**

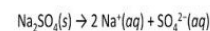


Factors affecting solubility

1) Common ion effect



- If we add common ion from another source:

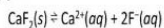


- Presence of "common ion" (SO_4^{2-}) will shift BaSO_4 equilibrium to the left (in first reaction), decreasing solubility.



Factors affecting solubility

2) pH



For insoluble salts containing basic anions, solubility increases as pH decreases.

- Add acid (H^+), reacts with basic anion:
 $\text{F}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{HF}(aq)$
- As F^- is consumed, CaF_2 equilibrium shifts right (in first reaction), solubility of CaF_2 increases.



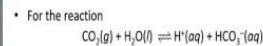
Precipitation

- Occurs when the concentrations of the ions exceed the solubility of the ionic compound
- Compare the reaction quotient, Q , for the current solution concentrations to K_{sp}
 - If $Q = K_{sp}$, the solution is saturated and no precipitation will occur
 - If $Q < K_{sp}$, the solution is unsaturated and no precipitation will occur
 - If $Q > K_{sp}$, the solution would be above saturation: The salt above saturation will precipitate



Heterogeneous Equilibria

- The concentrations of **pure solids** and **pure liquids** do not change during the course of a reaction
- Because their concentration doesn't change, solids and pure liquids are not included in the equilibrium constant expression



the equilibrium constant expression is as follows:

$$K_c = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$



Example

- $[\text{Cu}] = 8.96 \text{ g}/1 \text{ cm}^3 \times 1 \text{ mol}/63.55 \text{ g}$
 $= 0.141 \text{ mol}/\text{cm}^3$ or $141 \text{ mol}/\text{L}$
- The density is *intensive*
 - You cannot put solid copper "into" another material
 - Solids do not expand in volume to fill its container
- $[\text{Cu}]/[\text{Cu}]_s = \text{constant}$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant because their "concentrations" are always equal to their **activity** and thus cancel to a constant (typically equal to 1).