Ch. 17b Additional Aqueous Equilibria

- Chapter 17a situations basically only involved one solute: strong or weak acid; strong or weak base; or ionic salt
- Real solutions often have >1 solute
  - ⇒more complex equilibria, pH calculations
  - ⇒extra solute impacts degree to which first chemical dissociates

3 general multi-solute situations:

1. buffers: weak acid and weak base mixture, to which strong acid or base may be added
2. titration: mixing acid and base, at least one of which is normally strong
3. partially soluble solids: impact of pH or other salts on solubility

17.7,8 Buffer solutions: resist change in pH when either acid or base added

- Crucial in nature: blood pH, lake pH, etc. must be tightly controlled.
- Blood: pH ≈7.40 ± 0.05
  - o pH < 7.35 → acidosis pH > 7.45 → alkalosis
- The body needs a system for keeping the blood at the target pH, and protecting it from the extreme pH disruption that could result from addition of acid or base
- Many cellular processes likewise depend on precise control of pH
- Buffers provide protection against the addition of H^+ or HO^-

1. Unbuffered: Find pH

a. 1.0 L pure water

b. 1.0 L water + 0.1 mol HCl

c. 1.0 L water + 0.1 mol NaOH

Point: In an unbuffered, unprotected solution, a small addition of strong acid or base can cause a massive and dangerous shift in pH.

A. Reaction of strong acid with weak base. Background Facts:

•While it reacts only slightly with water, a weak acid reacts **almost completely** with strong base

•While it reacts only slightly with water, a weak base reacts **almost completely** with strong acid

WB + water: $NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + HO^{\ominus}$ $K = 1.8 \times 10^{-5}$

WB + SA: $NH_3 + HCl \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$ $K = 1.8 \times 10^{+9}$

WA + water: $HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus}$ $K = 6.8 \times 10^{-4}$

WA + SB: $HF + NaOH \rightleftharpoons H_2O + NaF$ $K = 6.8 \times 10^{+10}$

1. Key: Strong acid $H^{\oplus}$ can be consumed by weak base.

- Strong acid is replaced by weak acid HCl (SA) in, $NH_4^{\oplus}$ (WA) out

2. Strong base $HO^{\ominus}$ can be consumed by weak acid

- The strong base is replaced by weak base NaOH (SB) in, NaF (WB) out

B. Buffer Action: A buffer system contains both a weak acid (to neutralize any added $OH^{\ominus}$) and a weak base (to neutralize any added $H^{\oplus}$)

- normally the weak acid and weak base are conjugates
- normally they are present in approximately equal quantities, but not always

1. **Since a strong acid reacts with a weak base to produce a weak acid, addition of strong acid results in a weak increase in acidity rather than a strong increase**
2. **Since a strong base reacts with a weak acid to produce a weak base, addition of strong base results in a weak increase in basicity rather than a strong increase**

C. The pH of buffer solutions: Ka, pKa, H^+, pH

1. Formula

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

rearrange: $$\boxed{pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}}$$ "**Henderson-Hasselbalch Equation**"

$pK_a = -\log K_a$
$K_a = 10^{-pK_a}$

Practical note: **the base/acid ratio can be entered in moles/moles** or in **molarity/molarity**, whichever is easier and more accessible
• since the volume is common to both base and acid

2. Some Practical Simple Stuff

a. **A buffer pH depends on:**
   1. **pK_a which depends on K_a (weak acid strength)**
   2. **Base/acid ratio**

b. If you have a target pH that you want for a solution, choose an acid with the appropriate K_a and pK_a

c. **If the base/acid ratio = 1, then $pH = pK_a$**

- **This is a helpful reference: basically the $pH \approx pK_a$, adjusted to the basic or acidic side of pK_a depending on whether you have more of the base or of the acid**
   - a. **More base than acid: → pH number is higher (more basic) than pK_a**
   - b. **Less base than acid: → pH number is lower (more acidic) than pK_a**

d. **Adding base** increases the weak base/weak acid ratio, and **makes the pH more basic**

e. **Adding acid** decreases the weak base/weak acid ratio, and **makes the pH more acidic**

C. Buffer Capacity: determined by the quantity of weak acid/base
-dictates how much strong acid/base is consumed before buffer exhausted
-if more strong acid(base) is added than there is weak base(acid), the capacity is exceeded.

Consider 1.0 L water. Determine the pH's for the following solutions.

1. A solution with 0.5 moles of HF? (K_a for HF = 6.8×10^{-4})

Scenario

2. A solution with 0.5 moles of NaF?

Scenario

3. A solution with 0.5 moles of HF and 0.5 moles of NaF? (K_a for HF = 6.8×10^{-4})

Scenario

4. A solution with 0.5 moles of HF and 0.5 moles of NaF, to which 0.1 moles of HCl is added?

Scenario

5. A solution with 0.5 moles of HF and 0.5 moles of NaF, to which 0.1 moles of NaOH is added?

Scenario

Tips:

1. Diagnose the scenario
2. **For a buffer, use Henderson-Hasselbalch equation**
3. **When strong acid or base is added to a buffer, write out the reaction that would occur with the strong acid or base on the left side, and then work out the ICE change.**

D. Creating/Recognizing a Buffer

-must have or end up with **weak acid/weak base** pair

1. Mix some weak acid with it's conjugate weak base (most common)

HF, NaF H_3PO_4, NaH_2PO_4 $NaHSO_4$,Na_2SO_4 CH_3COOH, CH_3COONa NH_4Cl, NH_3

2. Start with only one of conjugate pair, but create some of the other by adding less than an equivalent amount of strong acid or strong base to create the other (harder to recognize)

Begin	Add(1/2 as much)	Result
Weak Acid	Strong Base	weak acid + conj base
Weak Base	Strong Acid	weak acid + conj base

Ex 1:	HF	+	NaOH	$\rightleftharpoons$	H_2O	+	NaF
I	0.4 moles		0.20 moles				0
C							
E							

Ex 2:	NH_3	+	HCl	$\rightleftharpoons$	$NH_4^+Cl^-$
I	0.6 mol		0.3 mol		0
C					
E					

Note: doesn't work if you add <u>too much</u> strong acid/base:

Ex 3 (failure):	NH_3	+	HCl	$\rightleftharpoons$	$NH_4^+Cl^-$
I	0.6 mol		0.6 mol		0
C					
E					

Buffer Recognition Practice

1. Which combos would make a buffer solution?

a. HF, KF

b. NH_4Cl, NH_3

c. HCl (0.2 M), NaN_3 (0.4 M)

d. HCl (0.2 mol), NaN_3 (0.1 M)

e. HN_3, NaCl

f. KF, NaF

g. KF, NaOH

h. HF, HCl

i. NH_3, KF

j. HF (0.2 mol), NaOH (0.1 mol)

Key: a) two acids don't work b) two bases don't work
c) an acid and a base is required d) tricky: strong and weak mixtures react, sometimes resulting in a buffer combination (both weak acid and weak base, examples c and j), but sometimes not, depending on ratios (example d)

2. Which could be added to 0.4 mol Na^+CN^- to give a buffer?

a. HCN

b. 0.2 mol HCl

c. 0.2 mol NaOH

d. 0.5 mol HCl

3. Which could be added to 0.4 mol H_3PO_4 to give a buffer?

a. NaH_2PO_4

b. 0.2 mol NaOH

c. 0.4 mol NaOH

d. 0.2 mol HCl

e. KCl

E. Simple Buffer Calcs

a. find pH Logic: $K_a \rightarrow pK_a \rightarrow pH$
b. find K_a Logic: $pH \rightarrow pK_a \rightarrow K_a$
c. solve for quantity of acid or base needed for target pH
Logic: pH and $pK_a \rightarrow$ base/acid ratio → needed quantity to achieve that ratio

$$\boxed{pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}}$$

"Henderson-Hasselbalch Equation"

- remember: mole/mole ration works as well as molarity/molarity ratio for base/acid

1. **Finding pH**. Find pH for buffer 0.12 M HNO_2, 0.16M $NaNO_2$ $K_a(HNO_2) = 4.5 \times 10^{-4}$

2. **Finding pK_a**. $[HA] = 0.11$ M $[NaA] = 0.13$ M. What is K_a for HA if pH = 5.18?

3. **Finding quantity of acid or base**. How many grams of NaF (42 g/mol) should be added to 612 mL solution of 0.4 M HF ($K_a = 6.8 \times 10^{-4}$) to produce a buffer solution in which pH = 3.10?

Logic:

F. pH Changes after Strong Acid or Strong Base is added to a Buffer Solution

(note: the following is written in terms of adding strong acid. Use analogous strategy for addition of strong base)

1. Write out the reaction of the added strong acid with the buffer's weak base
2. Make out an ICE-type table to show how the quantities of weak base and weak acid change as a result of the reaction
   a. Remember that a strong acid basically reacts completely with the weak base
   b. It's often best to do the ICE in terms of moles rather than molarity
   c. The "E" at the end is really the "End" of the acid-base reaction. It may not represent equilibrium
3. **Assess the situation at the end of the ICE analysis. 3 Scenarios**
   a. Are both weak acid and weak base present?
   - buffer situation → Use HH equation

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}}$$

   b. Is only weak acid left? (the strong acid exhausted the weak base?)
   - weak acid situation → use Ch. 17a procedure.
   - Be sure your weak acid is in terms of molarity, and factors in the combined volumes

$$[\mathrm{H}^{\oplus}] = \sqrt{K_a \times [\text{weak acid}]}$$

   c. **Is strong acid as well as weak acid left?** (The strong acid exhausted the buffer's weak base, and you still have some strong acid left over?)
   - Strong acid situation
   - Be sure your strong acid is in terms of molarity, and factors in the combined volumes

$$[\mathrm{H}^{\oplus}] = [\text{strong acid}]$$

Note: Scenario "a" is when the buffer capacity is not exhausted, and you still have a buffer situation at the end. **Scenario's "b" and "c" both represent cases where the buffer capacity is exhausted**, and you do **not** have a buffer scenario at the end of the reaction.

Problems

Given a 1.0 L solution that is initially 0.2 M in both HF and KF, assess the situation and find the pH after the following acids or bases are added.

a. 0.1 mol HCl added Assess:

Reaction:

I

C

E

Problems

Given a 1.0 L solution that is initially 0.2 M in both HF and KF, assess the situation and find the pH after the following acids or bases are added.

b. 0.1 mol NaOH added Assess:

Reaction:

I

C

E

c. 1.0 L of 0.20-M HCl added Assess:

Reaction:

I

C

E

E

d. 1.5 L of 0.20-M mol NaOH added Assess:

Reaction: Web answer key has error on this one, fix

I

C

E

E

17.10 Acid-Base Titration

1. An acid and a base are mixed, at least one being strong
2. "**equivalence point**" or "**end point**:" equal moles of acid/base
3. Indicator often used to turn color, or pH meter used to give "titration curve"
4. pH meter often used. (Lab will use both pH meters and color indicators)
5. **Unlike buffer, pH changes sharply near endpoints**

A. Endpoint Situations: Qualitative, Non-Math Version

Acid In	Base In	Conjugate Acid Out	Conjugate Base Out	Endpoint Outcome	Endpoint pH	Example
Strong Acid	Strong Base	Non-acid	Non-base	Neutral	pH = 7.0	1
Strong Acid	Weak Base	Weak acid	Non-base	Weakly acidic	pH < 7.0	2
Weak Acid	Strong Base	Non-acid	Weak base	Weakly basic	pH > 7.0	3

Example		Endpoint pH
1	HCl + NaOH →	
2	HCl + NaCN →	
3	HF + NaCN →	

1. Would the pH at endpoint be acidic, basic, or neutral when titrated with NaOH?

a. HCN

b. HNO_3

c. HF

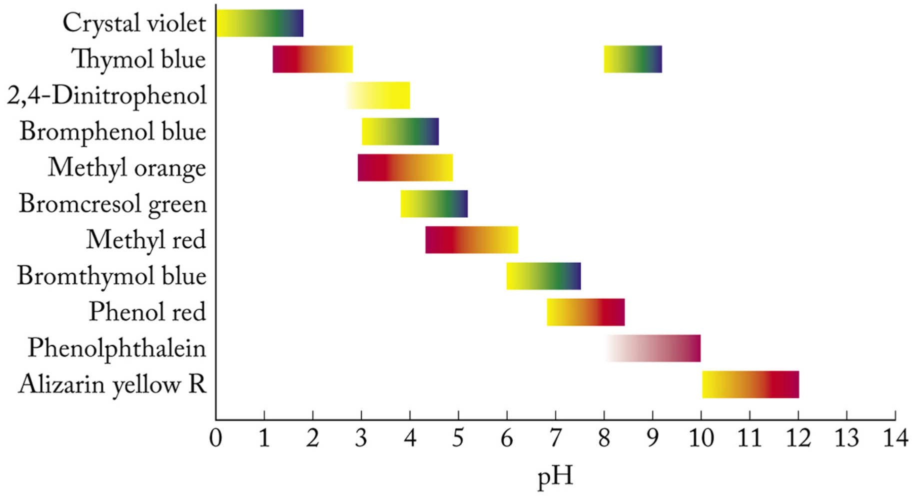
2. Would pH at endpoint be acidic, basic, or neutral when titrated with HCl?

a. NaOH

b. NaF

Some Indicators, and Where they Change pH

- **Phenolphthalein is by far the most famous and common**
- Most have a limited range over which they turn color. You’re either on the acid side (one color) or base side (different color). But you can’t tell exactly which pH you’re at.
- “Universal Indicator” has a mixture, so that your color changes from pH 4 to 5 to 6 etc.
- Note for Organic Lab future: ☺ Indicators and pH paper only work in aqueous solvents



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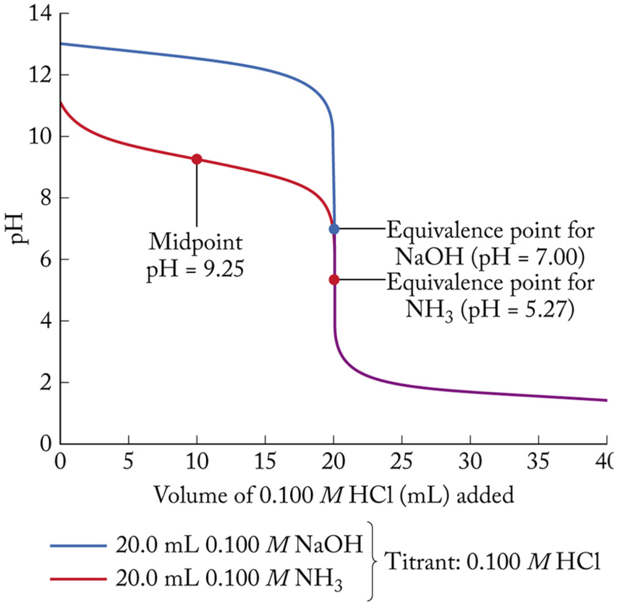
Sample Titration Curves



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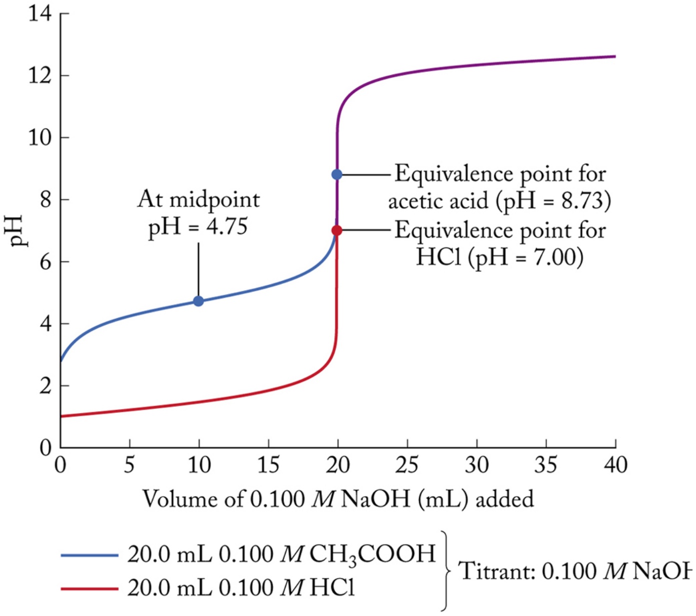

***Chemistry: The Science in Context* 3/e Figure 17.18**
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Notes:

1. Sharp pH change near endpoints
2. Mark the character of original chemical (SA, WA, SB, WB), and what was added (SB or SA)
3. Midpoint starting from WA or WB: Buffer! pH = pK_a
4. Buffer capacity exhausted at endpoint
5. pH at Equivalence point: 7 for SA/SB titrations, but not when starting from WA or WB

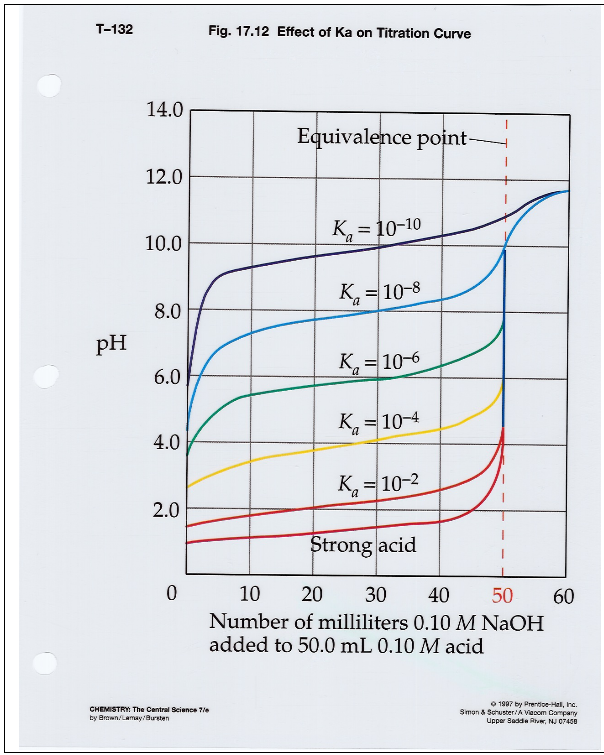
B. Calculation of pH at the **Endpoint=Equivalence Point** for a Titration

- Review: at endpoint equal moles of acid and base have been added. At least one of them was a strong acid or base, and possibly both.
- Three Possible Scenarios

Acid In	Base In	Endpoint Outcome	Endpoint pH	pH Strategy
Strong Acid	Strong Base	Neutral	pH = 7.0	None needed, pH = 7
Strong Acid	Weak Base	Weak acid	pH < 7.0	$K_a \rightarrow [H^+] \rightarrow$ pH
Weak Acid	Strong Base	Weak base	pH > 7.0	$K_a \rightarrow K_b \rightarrow [OH^-] \rightarrow$ pOH → pH

Problem: What is the pH after 40 mL of 0.10-M NaOH is added to 20 mL of 0.20-M HClO? (The K_a for HClO = 3.0×10^{-8})

C. Titration Curves: a plot of how pH changes as strong acid is added to a solution of base, or as a strong base is added to a solution of acid


T–132 Fig. 17.12 Effect of Ka on Titration Curve

CHEMISTRY: The Central Science 7/e by Brown/Lemay/Bursten

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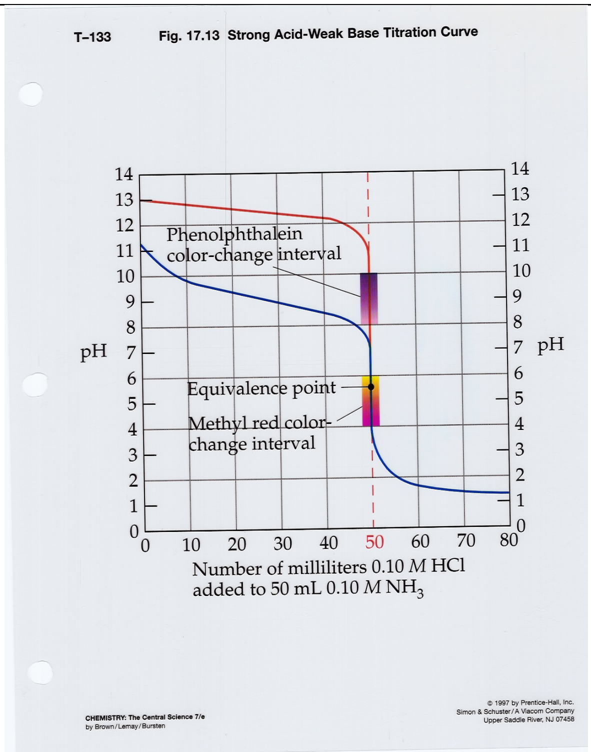
T–133 Fig. 17.13 Strong Acid-Weak Base Titration Curve

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2 Key Diagnostic features:

1. Initial pH
   - Acidic or basic? Strong or weak?
   - This reflects what you started with, before you titrate it with the strong acid or base.

Initial pH	$pH < 2$	$2 < pH < 7$	$7 < pH < 12$	$12 < pH$
Initial acid/base				

2. The endpoint/equivalence point pH
   - Acidic, neutral, or basic?
   - **If the equivalence point is pH=7, then both the acid and the base involved were STRONG**
   - If the equivalence point is NOT pH=7, then either the acid or the base involved in the titration was WEAK

Odds n ends

1. Endpoint pH is where pH changes most steeply, rapidly
2. When a weak acid is titrated by a strong base, the titration involves an extended "buffer zone" prior to the end-point, during which the pH change is rather gradual
   a. Prior to the endpoint, some of the weak acid is converted to weak base, so a conjugate weak acid/weak base buffer situation exists.
   b. The analogous situation happens when a weak base is titrated by a strong acid
3. When a weak acid "HA" is titrated by a strong base, at the half-way point (half-way to the end-point), half of the original weak acid HA is converted to its weak conjugate base A^-
   - At this point, the $pH = pK_a$ (see HH-equation when [base]/[acid] = 1)
   - The analogous situation happens when a weak base is titrated by a strong acid

Problems

1. An initial pH = 1.3 and an equivalence point of 7 corresponds to a titration curve in which a __

__________________________ is added to a __________________________.

2. An initial pH = 9.3 and an equivalence point of 4.7 corresponds to a titration curve in which a

__________________________ is added to a __________________________.

D. Titration Calculations Involving Endpoint/Equivalence Point

Key: At equivalence point, moles acid = moles base

- know one ⇒ know other

Applications

1. Find volume required
2. Determine unknown concentrations
3. Determine unknown grams

Problems

1. What volume of 0.12 M NaOH is needed to titrate 36 mL of 0.14 M HCl to its endpoint?

2. When 42 mL of aqueous HCl is titrated by 0.10 M NaOH, it takes 25 mL of the NaOH solution to reach the endpoint. What is the [HCl] of the original solution?

3. How many grams of KOH (56 g/mol) would it take to neutralize 86 mL of 1.2 M HNO_3?

E. General pH Strategy: Finding the pH after Acid or Base is added to a solution

- Whether it be to a buffer solution, a strong acid solution, a weak acid solution, a strong base solution or a weak base solution prior to the new addition
- The strategy is similar to when we added acid or base to a buffer

1. Write out the acid-base reaction
    - It helps to recognize which species are acidic or basic or neutral, and weak or strong
2. Calculate the initial moles
    - Number of moles = molarity x volume (in Liters)
3. Use ICE to determine post-reaction ("E") moles
4. **Assess the post-reaction situation, based on what's left at the end**
5. Solve the pH problem from there

	Post-Reaction Situation		
1	Strong acid only	$[H^+] = [SA]$	
2	Strong acid plus weak acid	$[H^+] = [SA]$	Ignore WA, which makes insignificant contribution
3	Strong base only	$[HO^-] = [SB]$	
4	Strong base plus weak base	$[HO^-] = [SB]$	Ignore WB, which makes insignificant contribution
5	Weak acid only	$[H^+] = \sqrt{K_a x[WA]}$	Qual: pH < 7
6	Weak base only	$[HO^-] = \sqrt{K_b x[WB]}$	Qual: pH > 7 May need to find K_b from K_a
7	Weak acid plus weak base	$pH = pK_a + \log \frac{[base]}{[acid]}$	Buffer solution
8	No acid or base; only neutral salts	pH = 7.0	

- For many of these, it will be necessary to calculate molarities
- To do this, make sure that you factor in the total, combined volume

Key: Recognizing the Final Situation!!

Strong base added to weak acid. (Strong acid/weak base combinations would be analogous.)
What is the situation and what is the pH after:

A. **Equal Base**: 20 mL of 0.10 M NaOH is added to 20 mL of 0.10 M HClO? (Ka = 3.0×10^{-8})

B. **Excess Base**: 20 mL of 0.10 M NaOH is added to 10 mL of 0.10 M HClO?

C. **Excess Acid**: 20 mL of 0.10 M NaOH is added to 30 mL of 0.10 M HClO? (Ka = $3.0 * 10^{-8}$)

F. What Happens when a Strong Acid is Added to a Weak Acid? Addition of strong acid to a weak acid solution. (Analog would be strong base to weak base)

1. **Weak Acid Prior to Addition of Strong Acid:** A solution has 1 L of 0.40 M acetic acid ($K_a = 1.80 \times 10^{-5}$). Find the pH and [$CH_3COO^-$]

Ex: $HA \rightleftharpoons H^+ + A^-$

I

C

E

2. **Weak Acid then Addition of Strong Acid:** Suppose 0.10 moles of HCl is added to the above solution (assume no change in volume). Find the pH and [CH_3COO^-]

Ex: $HA + \quad \rightleftharpoons H^+ + A^-$

I

C

E

Notice:

1. **The strong acid dominates the pH**
2. **When a weak acid is in water by itself, then $[H^+] = [A^-]$**
3. **But when strong acid was added (as an additional source of $[H^+]$,) $[H^+] >> [A^-]$**
4. **The equilibrium constant still applies. With $[H^+]$ up, $[A^-]$ goes down, ala LeChatelier's principle**

17.9 Solubility Equilibria for Ionic Compounds: K_{sp}

- The solubility of ionic compounds is a big deal, from kidney stones to drinking water to stalagtites and stalagmites

A. K_{sp} "Solubility Product Constant"

- **In a "saturated solution," insoluble solid is in equilibrium with aqueous ions**
- Easy to write K expressions, since aqueous ions appear but solid starting chemical doesn't

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ K=

I

C

E (doesn't matter,
not in K!!)

B. Various K_{sp} setups, depending on Formulas and Number of Cations/Anions Produced. Assuming no other source of ions other than from the solid itself.

1. $AgCl(s) \rightleftharpoons$ K =

2. $Zn(OH)_2(s) \rightleftharpoons$ K =

3. $ScCl_3(s) \rightleftharpoons$ K =

4. $Al_2(SO_4)_3(s) \rightleftharpoons$ K =

Points:

1. Manipulating equations with x^3 or x^4 is common!
2. **While the solid itself doesn't appear in the K expression, the value of "x" does tell how many moles/L of the original solid can dissolve.**
    - If you know how many moles/Liter of product solute is present, you know how many moles/Liter of parent solid actually dissolves

C. Technical note: often K_{sp} problems end up with x^3 or x^4 type terms. What does this mean and how do I solve them?

- Ex 1: $x^3 = 100$ meaning: x times x times x = 100. Or, $x = 100^{1/3}$ ($x = 4.64$)
    - Calculator: find your calculator's $\sqrt[x]{y}$ key, enter 100 for "y" and 3 for "x"
    - In other words, solve as $x = \sqrt[3]{100}$
    - On my Texas Instruments Calculator (yours may differ):
        - enter 100 first
        - click the $\sqrt[x]{y}$ key second
        - enter 3 third

- Ex 2: $0.26^3 = x$ meaning: 0.26 times 0.26 times 0.26 = x. ($x = 0.0176$)
    - Calculator: find your calculator's y^x key, enter 0.26 for "y" and 3 for "x"
    - On my Texas Instruments Calculator (yours may differ, x^y for Casio?):
        - enter 0.26 first
        - click the y^x key second
        - enter 3 third

Calculator Practice

x equals

1. $x^3=125$
    - enter 125
    - click the $\sqrt[x]{y}$ key
    - enter 3
2. $x^3=200$
3. $x^4=12.7$

x equals

4. $12^3=x$
    - enter 12
    - click the y^x key
    - enter 3
5. $8^4=x$
6. $3.2^3=x$

D. Definitions

1. **"Solubility": g/L of solid that dissolves**
2. **"Molar solubility": mol/L of solid that dissolves**

- For problems, always be aware of whether you're dealing with g/L or mol/L

E. Interconverting Solubility and K_{sp}: Calculations

1. Working from K_{sp} to solubility:

K_{sp} $\rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

2. Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

Working from K_{sp} to solubility:

$K_{sp} \rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

1. $PbCl_2$ (278 g/mol) $PbCl_2\,(s) \rightleftharpoons$ K =

$K_{sp}=1.6 \times 10^{-5}$

a. Calculate $[Pb^{2+}]$ and $[Cl^-]$ for a saturated solution of $PbCl_2$.

b. Calculate molar solubility (mol/L) for $PbCl_2$

c. Calculate mass solubility (g/L) for $PbCl_2$

d. What mass of $PbCl_2$ (278 g/mol) would dissolve in 140 mL?

Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

1. Find K_{sp} for CaF_2 whose molar solubility is 2.1×10^{-4} mol/L.

Molar solubility plus stoichiometry tells us what ion concentrations are, from which K can be found.

2. $BaCO_3$ (197g/mol) has a solubility of 0.014 g/L. Find K_{sp} for $BaCO_3$.

17.9,17.7 Factors that affect Solubility of Ionic Compounds (LeChatelier's Principle)

A. pH Factor: If anion is basic, (weakly or strongly), => solubility increases at low pH (high $[H^+]$)

1. Via selective removal of anion (product side)
2. Many basic anions: OH^-, F^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} etc.
3. Few non-basic anions (the strong acid big-6!): Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-

Question: In Which of the following will adding Acid Impact Solubility?

Example 1: $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

Add acid:

By selective removal of $[OH^-]$,
$Q < K$, so ala LeChatelier,
solid $Cu(OH)_2$ keeps dissolving,
and $[Cu^{2+}]$ keeps rising

Notice: In pure water, when $Cu(OH)_2$ dissolves $[HO^-] = 2\,[Cu^{2+}]$
But when acid is added (low pH), $[HO^-] \neq 2\,[Cu^{2+}]$

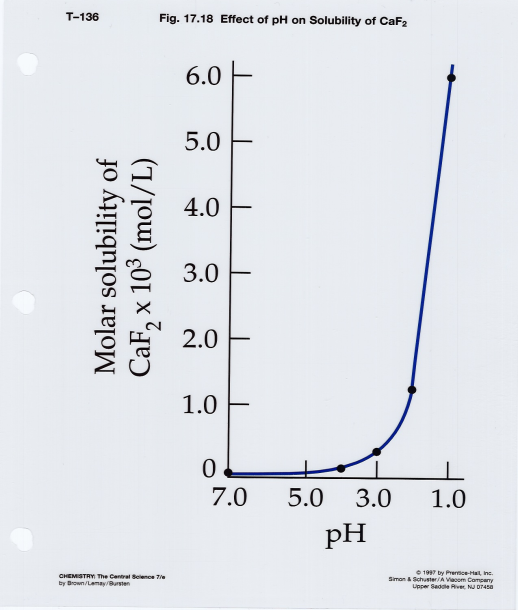
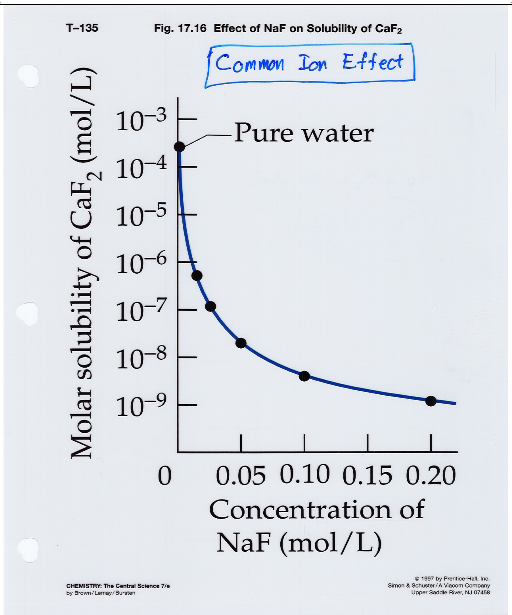
Example 2: $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$ $K=[Pb^{2+}][F^-]^2$

Add acid:

Example 3: $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$ $K=[Pb^{2+}][Br^-]^2$

Add acid:

Notice:

pH Effect on CaF_2 (fluoride is a basic anion)	**Common Ion Effect on CaF_2** (fluoride from NaF is the "common ion")
	

Example: $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

- Adding H^+ (reducing pH) raises solubility from 10^{-3} to >6, (factor of over a thousand
- Adding F^- reduces solubility from 10^{-3} to 10^{-9} (factor of a million)
- In terms of LeChatelier's Principle, H^+ is a product ion remover (shift equilibrium to the right), while NaF is a product ion source (shifts equilibrium to the left).

B. Common Ion Effect (17.7): A "common ion" DECREASES solubility. (LeChatelier)

Example: $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

	Additive	Equilibrium Shift Response	Impact on:		Ratio of $[Ba^{2+}]$ to $[SO_4^{2-}]$	Impact on Solubility of $BaSO_4$
1	Add $Ba^{2+}(aq)$ (for example, $Ba(NO_3)_2$)		$[SO_4^{2-}]$		$[Ba^{2+}]$ $[SO_4^{2-}]$	
2	Add SO_4^{2-} (aq) (for example, Na_2SO_4)		$[Ba^{2+}]$		$[Ba^{2+}]$ $[SO_4^{2-}]$	

Notes:

1. If Ba^{2+} or SO_4^{2-} is added as a common ion from a different source, that pushes the equilibrium to left, so solubility decreases
2. Case 1, where $Ba(NO_3)_2$ was added:
   a. The barium ion concentration $[Ba^{2+}]$ is dominated by the fully soluble $[Ba(NO_3)_2]$ source
   b. Simplifying assumption allows the contribution "x" from $BaSO_4$ to be ignored
   c. As a result, solving for $[SO_4^{2-}]$ and thus the molar solubility of $BaSO_4$ under these conditions becomes easy.

Equilibrium Calculations when a "Common Ion" is Present: Way Easier!

When a known concentration of a common ion is present, you can easily:

1. **Calculate molar concentrations of ions**
2. **Calculate molar solubility of the solid**

Example **WITHOUT common ion**:

1. What is the molar solubility of $BaSO_4$ when added to regular water?

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$$

Example **WITH common ion**:

2. What is the molar solubility of $BaSO_4$ in the presence of 0.10-M $Ba(NO_3)_2$?

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$$

I

C

E (doesn't matter)

Example **WITH common ion**:

3. What is the molar solubility of $BaSO_4$ in the presence of 0.50-M Na_2SO_4?

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$$

I

C

E (doesn't matter)

How would the solubility of the salts be affected?

Q's: 1. Is there a common ion? 2. Is there a basic anion that might be impacted by pH?

	Added $Ca(NO_3)_2$	Added NaF	Added HNO_3	More soluble at Low or High pH?
1. CaF_2				
2. $CaCO_3$				
3. $Ca(OH)_2$				
4. ZnF_2				
5. $PbCl_2$				
6. AgI				
7. $ZnSO_4$				

Example **WITHOUT common ion**:
8. What is molar solubility of AgBr ($K_{sp}=3.3x10^{-13}$) in a solution with 0.20 M NaBr (which of course dissolves fully)?

I

C

E (doesn't matter)

Example **WITH common ion**:
9. What would AgBr solubility be without NaBr present? ($K_{sp}=3.3x10^{-13}$)

I

C

E (doesn't matter)

Calculating Solubility for Metal Hydroxides, given pH.

- Any ionic formula with a basic anion is more soluble under acidic conditions. (LeChatelier)
- With metal hydroxide, knowing pH enables easy quantitative solubility calculations
- Essentially when you know pH, you can know [HO^-],which simplies the math

10. Determine molar solubility for $Mg(OH)_2$ ($K_{sp}=1.5 \times 10^{-11}$) at the following pH's:

Equation:

a. pH=12.00

b. pH=6.00

pH can define the concentration of hydroxide

C. Complex Ion Formation (not for test, but lab relevant)

- many Lewis bases can <u>increase</u> the solubility of a solid by <u>irreversible removal</u> of a product cation
- NH_3, ^-CN common

$$\begin{tikzcd} CuBr(s) \arrow[r, shift left] & Cu^+(aq) + Br^-(aq) \arrow[l, shift left] \arrow[d, "4\ NH_3"] \\ & Cu(NH_3)_4^+ \end{tikzcd}$$

$K = 5.3 \times 10^{-9}$

- Selective, irreversible removal of the copper ion via ammonia complexation drives the equilibrium in the right direction.
    - Thus, the solubility of the original solid increases.

General pH Strategy: Finding the pH after Acid or Base is added to a solution

- Whether it be to a buffer solution, a strong acid solution, a weak acid solution, a strong base solution or a weak base solution prior to the new addition
- The strategy is similar to when we added acid or base to a buffer

1. Write out the acid-base reaction
   - It helps to recognize which species are acidic or basic or neutral, and weak or strong
2. Calculate the initial moles
   - Number of moles = molarity x volume (in Liters)
3. Use ICE to determine post-reaction ("E") moles
4. Assess the post-reaction situation, based on what's left at the end
5. Solve the pH problem from there

	Post-Reaction Situation		
1	Strong acid only	$[H^+] = [SA]$	
2	Strong acid plus weak acid	$[H^+] = [SA]$	Ignore WA, which makes insignificant contribution
3	Strong base only	$[HO^-] = [SB]$	
4	Strong base plus weak base	$[HO^-] = [SB]$	Ignore WB, which makes insignificant contribution
5	Weak acid only	$[H^+] = \sqrt{K_a x[WA]}$	Qual: pH < 7
6	Weak base only	$[HO^-] = \sqrt{K_b x[WB]}$	Qual: pH > 7 May need to find K_b from K_a
7	Weak acid plus weak base	$pH = pK_a + \log \frac{[base]}{[acid]}$	Buffer solution
8	No acid or base; only neutral salts	pH = 7.0	

- For many of these, it will be necessary to calculate molarities
- To do this, make sure that you factor in the total, combined volume

Key: Recognizing the Final Situation!!

APPENDIX
Table of Solubility Product Constants (K_{sp} at 25° C)

Bromides	$PbBr_2$	6.3×10^{-6}		Iodides	PbI_2	8.7×10^{-9}
	$AgBr$	3.3×10^{-13}			AgI	1.5×10^{-16}
Carbonates	$BaCO_3$	8.1×10^{-9}		Oxalates	BaC_2O_4	1.1×10^{-7}
	$CaCO_3$	3.8×10^{-9}			CaC_2O_4	2.3×10^{-9}
	$CoCO_3$	8.0×10^{-13}			MgC_2O_4	8.6×10^{-5}
	$CuCO_3$	2.5×10^{-10}		Phosphates	$AlP0_4$	1.3×10^{-20}
	$FeCO_3$	3.5×10^{-11}			$Ba_3(P0_4)_2$	1.3×10^{-29}
	$PbCO_3$	1.5×10^{-13}			$Ca_3(P0_4)_2$	1.0×10^{-25}
	$MgCO_3$	4.0×10^{-5}			$CrP0_4$	2.4×10^{-23}
	$MnCO_3$	1.8×10^{-11}			$Pb_3(P0_4)_2$	3.0×10^{-44}
	$NiCO_3$	6.6×10^{-9}			Ag_3P0_4	1.3×10^{-20}
	Ag_2CO_3	8.1×10^{-12}			$Zn_3(P0_4)_2$	9.1×10^{-33}
	$ZnCO_3$	1.5×10^{-11}		Sulfates	$BaS0_4$	1.1×10^{-10}
Chlorides	$PbCl_2$	1.7×10^{-5}			$CaS0_4$	2.4×10^{-5}
	$AgCl$	1.8×10^{-10}			$PbS0_4$	1.8×10^{-8}
Chromates	$BaCrO_4$	2.0×10^{-10}			Ag_2S0_4	1.7×10^{-5}
	$CaCrO_4$	7.1×10^{-4}		Sulfides	CaS	8×10^{-6}
	$PbCrO_4$	1.8×10^{-14}			CoS	5.9×10^{-21}
	Ag_2CrO_4	9.0×10^{-12}			CuS	7.9×10^{-37}
Cyanides	$Ni(CN)_2$	3.0×10^{-23}			FeS	4.9×10^{-18}
	$AgCN$	1.2×10^{-16}			Fe_2S_3	1.4×10^{-88}
	$Zn(CN)_2$	8.0×10^{-12}			PbS	3.2×10^{-28}
Fluorides	BaF_2	1.7×10^{-6}			MnS	5.1×10^{-15}
	CaF_2	3.9×10^{-11}			NiS	3.0×10^{-21}
	PbF_2	3.7×10^{-8}			Ag_2S	1.0×10^{-49}
	MgF_2	6.4×10^{-9}			ZnS	2.0×10^{-25}
Hydroxides	$AgOH$	2.0×10^{-8}		Sulfites	$BaS0_3$	8.0×10^{-7}
	$Al(OH)_3$	1.9×10^{-33}			$CaS0_3$	1.3×10^{-8}
	$Ca(OH)_2$	7.9×10^{-6}			Ag_2S0_3	1.5×10^{-14}
	$Cr(OH)_3$	6.7×10^{-31}				
	$Co(OH)_2$	2.5×10^{-16}				
	$Cu(OH)_2$	1.6×10^{-19}				
	$Fe(OH)_2$	7.9×10^{-15}				
	$Fe(OH)_3$	6.3×10^{-38}				
	$Pb(OH)_2$	2.8×10^{-16}				
	$Mg(OH)_2$	1.5×10^{-11}				
	$Mn(OH)_2$	4.6×10^{-14}				
	$Ni(OH)_2$	2.8×10^{-16}				
	$Zn(OH)_2$	4.5×10^{-17}				

Ch. 14 Thermodynamics and Direction of Reactions

Product Favored Processes that Proceed Spontaneously (14.1)

- Chemical events can be strongly product favored, reactant favored, or in some cases in equilibrium

Examples

Product-Favored Chemistry Examples	Other Examples of Spontaneous Events
1. H_2O (s) → H_2O (l) at 50°	1. Ball falling
2. 2Na + Cl_2 → 2NaCl + heat	2. Desk getting messy
3. Gasoline + O_2 (+ spark) → CO_2 + H_2O + heat	3. Forgetting first semester chemistry…
4. NaCl (s) in water → NaCl (aq)	

Reactant Favored Chemistry Examples	Other Examples of Non-Spontaneity
1. H_2O (s) ← H_2O (l) at -50°	4. Automobile self-assembly
2. $2H_2O$ ← $2H_2$ + O_2	5. Learning organic chemistry

1. Product-favored events may be slow at room temperature, but a catalyst or spark can initiate them so that once started, they can **continue spontaneously**, without requiring continuous energy input
   - Once started, they are self-sustaining
   - The reason they may not start on their own is because of activation barriers
2. Reactant-favored chemical events require **continuous energy input** from the outside
3. Most (but not all) product-favored processes are **exothermic**
4. Most (but not all) reactant-favored processes are **endothermic**
5. The spontaneity of chemical events may depend on temperature

Probability and Reactions

Facts

1. Exothermic processes usually product favored
2. Some highly favorable processes are not exothermic:
   - Expansion of gas into vacuum
   - Heat/energy transfer from something hot to cold
   - The mixing of colored liquids
   - NaCl dissolving in water’
   - My desk gets messy, your chemistry knowledge gets disordered

Fact: Common to **All** Favorable Chemical Events: An Increase in the **Disorder** of **Energy or Matter**

1. Dispersal of energy
   a. Exothermic processes: disperse energy to the surrounding
      - Chemicals → surroundings (small # particles → large # particles)
      - Eating candy bar: concentrated energy → energy dispersed through body → energy dispersed outside of body

   b. More probable for energy to be dispersed than concentrated in small number of particles

2. Dispersal of matter
   a. Concentrated matter tends to disperse (gases filling a room or filling a vacuum; sodium chloride dissolving in water; colored liquids mixing….)
   b. More probable for matter to be dispersed than concentrated in a small space
      - More probable for matter to be dispersed than highly organized

3. Dispersal of matter usually involves dispersal of energy, so in either case 1 or case 2, dispersal of energy results
   - Chemists often recognize the dispersal/disorganization of atoms as being inherently favorable, but the underlying reason is really the corresponding but less obvious dispersal of chemical energy

1. **If both energy and atoms are more dispersed ⇒ product favored**
2. **If neither energy and atoms are more dispersed ⇒ reactant favored**
3. **If one of energy or atoms is more dispersed but the other is less dispersed ⇒ ????**

Energy dispersal: **enthalphy** issue	Atoms dispersal: **entropy** issue

"Entropy" = S = Amount of Disorder

1. Each chemical has a finite entropy "S°" under standard conditions
2. **Standard conditions: 25°C, 1atm, per mole**
   - Factors in size, motion
     - more motion, more disorder
     - translational, rotational, vibrational motion
3. Higher S → higher entropy (which will normally mean more atom movement)
4. Even elements have S ≠ O (unlike $\Delta H_f°$)

Qualitative Guidelines for Entropy (Memorize)

- use these to rank things in terms of entropy
- Use these to compare which side of a reaction (left/reactant side or right/product side) has more entropy
- This will enable you to decide whether entropy is increasing or decreasing
- You can do this without having charts or entropy numbers given to you; you just look at the chemicals and anticipate which will have more entropy
-

1. **Phase**: Gases >>> Liquids > Solids
   a. Huge difference for gases
   b. Related to movement disorder

For any equation, if one side has more gas, always has more entropy

   c. Phase charges ⇒ predictable ΔS

2. **Molecular Size:** larger molecule > smaller molecule (Assuming phase is equal)

   $C_5H_{12} > C_4H_6 > C_3H_8 > C_2H_6$

3. **Number of Molecules**: more molecules > fewer molecules (Assuming phase is equal)

   $2NO + O_2 >> 2NO_2$ (3 molecules versus 2 molecules)

   - For any combination reaction, ΔS negative (entropy decreases)
     Ex: $Ti + O_2 \rightarrow TiO_2$ $(\Delta S < 0)$

   - For any fragmentation reaction, ΔS positive (entropy increases)
     Ex: $CaCO_3 \rightarrow CaO + CO_2$ $(\Delta S > 0)$

4. **Dissolving:** Entropy increases when a solid is dissolved in a solvent
   - Matter get more disorganized
   - Resulting ions/molecules have more motion (translational, rotational)
   - Entropy increases specially for ionics, which dissociate
     - Ionic dissolving is really a special class of fragmentation reaction

$$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

5. **Temperature:** Higher temperature = higher entropy for a given substance
   - At higher temperature, the motion is greater and the atoms are less organized

Skill: Predict Entropy Changes $\Delta S = S\text{ products} - S\text{ reactants}$

a. if products have more entropy, ΔS positive
b. if products have less entropy, ΔS negative

Class Problems

1. From each pair, which has more entropy? Why?

a. $H_2O(l)$ vs. $H_2O(g)$

b. $H_2O(l)$ at 80° vs. $H_2O(l)$ at 20°C

c. $Ca_3(PO_4)_2$ (s) vs. FeO(s)

d. $CaBr_2$ (s) vs. $CaBr_2$ (aq)

e. C_3H_8O (l) vs. C_3H_6 (l) + H_2O (l)

2. Will ΔS be Positive or Negative?   ΔS   Why?

a. $2Mg\ (s) + O_2\ (g) \rightarrow 2MgO\ (s)$

b. $NaNO_3\ (s) \rightarrow NaNO_3\ (aq)$

c. $2C_2H_6\ (l) + 7O_2\ (g) \rightarrow 4CO_2\ (g) + 6H_2\ (g)$

d. $C_4H_8Br_2\ (l) \rightarrow C_4H_8\ (l) + Br_2\ (l)$

e. $AgNO_3\ (aq) + NaCl\ (aq) \rightarrow AgCl\ (s) + NaNO_3\ (aq)$

f. $C_7H_{14}\ (s) \rightarrow C_7H_{14}\ (l)$

g. $CO_2\ (g) \rightarrow CO_2\ (s)$

h. $CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$

Calculating ΔS (14.3,4)

ΔS° = S° (products) - S° (reactants) Units: $\frac{J}{mole \times K}$ (note: J, not kJ)

- Same as for ΔH° but:
  1) units (J not kJ)
  2) elements $\Delta H^\circ_f = O$ $S^\circ \neq O$

- **Remember to factor in the number of moles**

1. Find ΔS° for:

	$CaCO_3(s)$	→	$CaO(s)$	+	$CO_2(g)$
S° =	93		38		213

Note: ΔS° assumes molar amounts of everything.

2. Calculate overall ΔS when 2.3 moles of $CaCO_3$ decomposes.

	$CaCO_3(s)$	→	$CaO(s)$	+	$CO_2(g)$
S° =	93		38		213

Note: ΔS° versus actual ΔS.
When non-molar amounts are used,
multiply ΔS° accordingly.

3. Find ΔS° for:

	C_2H_6 (l)	+	$3O_2$ (g)	→	$2CO_2$ (g)	+	$3H_2O$ (l)
S° =	161		205		214		70

Note: Factor coefficients when calculation ΔS°.

Note: this "combustion" reaction is actually very favorable.
- But it is NOT ΔS favorable.
- It is favorable due to enthalpy, not entropy.

Second Law of Thermodynamics: The Total Entropy of Universe is Increasing

- First Law: Energy is neither created nor destroyed
- Third Law: Entropy at Abolute Zero is Zero

Notes

1. Unlike energy, entropy is not conserved
   a. The universe is constantly getting more messy!
   b. Increasing disorder a fundamental law of nature

2. Total Entropy Changes for the Universe: Whether a Reaction is Product or Reactant Favored

Product-favored Processes:	$\Delta S_{univ} > O$
Reactant-favored Processes:	$\Delta S_{univ} < O$
Equilibrium Situation:	$\Delta S_{univ} = O$

3. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$
   1. The "system" would the reacting chemicals, or the solution in your beaker
      - Measuring changes on the "system" is relatively easy
      - For example, it's easy to tell whether a reaction is exothermic or endothermic by seeing whether a solution gets hotter or colder
   2. But the surroundings count too!!
      - Measuring what happens to the entire surrounding universe is less convenient…

4. A Convenient Way to Find $\Delta S_{surroundings}$: Use the ΔH_{system} (which is easy to measure)
   - Easily measurable enthalpy changes for the "system" essentially measure entropy changes for the surroundings

$$\boxed{\Delta S_{surroundings} = \frac{-\Delta H_{system}}{T}}$$

5. A Convenient Way to Find ΔSuniverse Using Only System Measurements

Given: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$ and $\Delta S_{surroundings} = \frac{-\Delta H_{system}}{T}$

Then: $$\boxed{\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T}}$$

   1. ΔS_{system} and ΔH_{system} can be found relatively easily, but can tell us what happens to the universe
   2. By knowing changes in both the **enthalpy** (ΔH_{system}) and **entropy** (ΔS_{system}) for the **system** alone, you can figures out whether $\Delta S_{universe}$ is favorable or unfavorable
   3. **The more exothermic the reaction, the more positive and favorable is the $\Delta S_{surroundings}$**
      - The energy released heats up the surroundings and makes the surroundings become more disordered

6. A process can have an unfavorable negative ΔS for the system, but the overall process can still be favorable if the surroundings have a favorable positive ΔS as a result of an exothermic reaction

7. Product favored processes associated with:
   a. dispersal of matter (ΔS_{system} positive)
   b. dispersal of energy $\Rightarrow \Delta S$ surroundings positive!!
      1. **Exothermic usually favorable because results in positive $\Delta S_{surroundings}$**
      2. energy release causes heat, faster motion, etc.

8. Nothing is ever spontaneously "ordered "
   1. Only at the expense of something else
   2. Outside work/energy/effort (all of which disorder surroundings) is needed

9. Qualitative Predictions for ΔSuniv, Favorability

- consider ΔS, ΔH for systems
- If there is **agreement** between enthalpy and entropy factors, then it's easy to predict the overall favorability

4 Scenarios:

	Enthalpy ΔH_{system}	ΔH Sign	Entropy ΔS_{system}	ΔS Sign	Enthalpy Entropy	$\Delta S_{universe}$	ΔS_{univ} Sign
1	Good	$\Delta H < 0$	Good	$\Delta S > 0$	Good-Good	Good	$\Delta S_{univ} > 0$
2	Bad	$\Delta H > 0$	Bad	$\Delta S < 0$	Bad-Bad	Bad	$\Delta S_{univ} < 0$
3	Good	$\Delta H < 0$	Bad	$\Delta S < 0$	Good-Bad	Depends	???
4	Bad	$\Delta H > 0$	Good	$\Delta S > 0$	Bad-Good	Depends	???

a. When enthalpy and entropy both agree (cases 1 and 2), it's easy.

b. When enthalpy and entropy **disagree**, the overall favorability depends on the relative magnitudes for the enthalpy and entropy factors, and on the temperature

c. The relative importance of system enthalpy versus entropy decreases at higher temperatures

d. When there is a disagreement, there is normally some cutoff temperature at which the enthalpy and entropy factors cancel each other out and the resulting $\Delta S_{universe} = 0$. This results in a perfect equilibrium situation

e. If product favored, may be entropy driven, enthalpy driven, or driven by both.

Problems: Classify Each of the Following Processes as Product-Favored, Reactant-Favored or impossible to tell without further temperature information (see later). Also note whether $\Delta S_{universe}$ would be positive or negative.

	Product or Reactant Favored?	$\Delta S_{universe}$ Sign
1. A → B $\Delta S° = +52$ J/K $\Delta H° = -32$ KJ/mol		
2. A → B $\Delta S° = -116$ J/K $\Delta H° = +12$ KJ/mol		
3. A → B $\Delta S° = +76$ J/K $\Delta H° = +4$ KJ/mol		

The following Reactions are all **Product-Favored.** Which are enthalpy driven, entropy driven, or favored by both?

4. C → D $\Delta S° = -28$ J/K $\Delta H° = -112$ KJ/mol

5. E → F $\Delta S° = +563$ J/K $\Delta H° = +7.3$ KJ/mol

6. G → H $\Delta S° = +89$ J/K $\Delta H° = -42$ KJ/mol

Free Energy and Free-Energy Changes. Gibbs “Free Energy” = G and (14.5)

G^o = free energy per exactly one mole under standard conditions
ΔG = change in free energy (for a reaction)
ΔG^o = change in free energy for a reaction on a per mole basis
ΔG_f^o = standard free energy of formation for a substance from elements in their standard states

A. $\boxed{\Delta G = \Delta H - T\Delta S}$ Definition: $\Delta G = -T\Delta S_{universe}$

B. Derivation (not test responsible)

---

1. Given: $\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$
2. Recall: $\Delta S_{surroundings} = \dfrac{-\Delta H_{system}}{T}$
3. After substituting: $\Delta S_{universe} = \dfrac{-\Delta H}{T} + \Delta S$
4. Multiply by –T: $-T\,\Delta S_{universe} = \Delta H - T\Delta S$
5. By definition: $\Delta G = -T\Delta S_{universe}$
6. After substituting: $\Delta G = \Delta H - T\Delta S$

Notes

1. ΔG reflects $\Delta S_{universe}$. Since ΔG reflects $\Delta S_{universe}$ it tells whether any process is product favored or not.

2. Value 1: by measuring ΔH, ΔS for system, can find ΔG ($\Delta S_{universe}$) for universe
   - needn’t measure surroundings!! Local system information can tell you everything.

3. Value 2: Each chemical has a standard “free energy” G, so can easily calculate $\Delta G_{reaction}$ (see later)

4. Sign Meaning:
   $\Delta G < O$ product-favored
   $\Delta G > O$ reactant-favored
   **$\Delta G = O$ equilibrium
   - Sign sense is Opposite to that for $\Delta S_{universe}$
   - Given $\Delta G \Rightarrow$ predict whether a reaction is product- or reactant-favored (or equilibrium)
   - Given whether a reaction is product-favored $\Rightarrow$ predict ΔG

5. Sign Review

	Negative	Positive
ΔG	Good	Bad
ΔH	Good	Bad
ΔS	Bad	Good

C. Calculations Involving $\Delta G = \Delta H - T\Delta S$

- given any 3, solve for 4th
- Sometimes you'll need to determine one of these from

Units

ΔG kJ/mol	T Kelvin (not °C)
ΔH kJ/mol	ΔS normally given in J/mol·K (not kJ), so need to be converted from J → kJ

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -394$ kJ/mol
$\Delta S° = 42.9$ J/mol·K

a. What is $\Delta G°$ (in kJ/mol) at 25°C?

b. what is ΔG (in kJ) when 0.32 mol of C reacts? (Note: No º by the ΔG, so you need to adjust for the actual supply of moles.)

2. $C + 2H_2 \rightarrow CH_4$ $\Delta G° = -50.8$ kJ/mol $\Delta H° = -74.5$ kJ/mol
What is $\Delta S°$ (by definition, at 25°C)

D. Calculating ΔG^o_{rxn} based on ΔG_f^o

- ΔG_f^o = standard free energy of formation from elements in standard state
- For elements in standard state: $\Delta G_f^o = 0$, $\Delta H_f^o = 0$, $S^o \neq 0$

$$\boxed{\mathbf{\Delta G^o_{rxn} = \Delta G_f^o\ (products) - \Delta G_f^o\ (reactants)}}$$

- Same format as ΔH, ΔS

3. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
$\Delta G_f^o = -51$ -394 -237

Calculate $\Delta G°_{rxn}$ in kJ/mol:

Qualitative: Predict the signs for:

ΔS^o

ΔG^o

ΔH^o Note: **ΔH dominates over $-T\Delta S$**

E. Temperature and ΔG

$\Delta G = \Delta H - T\Delta S$ High temp ⇒ entropy more important
Low temp ⇒ entropy less important

ΔH	ΔS	$-T\Delta S$	ΔG	Temp	Product-Favored	
-	+	-	-	Any	Yes	Enthalpy/entropy agree
-	-	+	-	Low	Yes	enthalpy wins
			0	Crossover	Equilibrium	Enthalpy/entropy cancel
			+	High	No	entropy
+	-	+	+	Any	No	Enthalpy/entropy agree
+	+	-	+	Low	No	enthalpy
			0	Crossover	Equilibrium	Enthalpy/entropy cancel
			-	High	Yes	entropy

1. If enthalpy, entropy agree, sense of ΔG is same regardless of temp.
2. If enthalpy, entropy disagree, the sense of ΔG changes between low temp (enthalpy control) and high temp (entropy control)
    a. Enthalpy dominates at low temp, entropy takes over at higher temps ($T\Delta S$)
    b. There will be a crossover temperature at which enthalpy and entropy cancel, and the system is at equilibrium

F. Equilibrium and the Crossover Temperature

1. At equilibrium, $\Delta G = 0$
2. $\Delta G = \Delta H - T\Delta S$
3. Therefore, at equilibrium $\boxed{\Delta H = T\Delta S}$
4. Therefore the equilibrium temperature: $\boxed{T_{equil} = -\Delta H / \Delta S}$
5. Remember that T must be in Kelvin, not ºC, and that both ΔH and ΔS must be converted to common units (kJ or J)

G. Phase change: The melting or boiling temperature always involves equilibrium between two phases, and thus always occurs at a crossover temperature with $\Delta G = 0$

- So the temperature at which something will melt or boil can be determined from the ΔH and ΔS for the phase change
    - given ΔH, ΔS calculate mp or bp!!

1. a) What is the melting temp for A? b) Under what temp conditions is process favorable?

$A(s) \rightarrow A(l)$ $\Delta H° = +13.2$ KJ/mol $\Delta S° = +34.3$ J/mol·K

Provide sense of ΔG, ΔH, ΔS (Given Reaction Knowledge!)

Favorable? ΔG ΔH ΔS

1. H_2O (l) → H_2O (g) at 50°C

2. H_2O (l) → H_2O (g) at 200°C

3. C_6H_{12} (l) + $9O_2$ (g) → $6CO_2$ (g) + $6H_2O$ (l)

4. Qualitatively, under what temperature conditions will the following be Product-Favored?
    a. ΔH neg ΔS neg
    b. ΔH neg ΔS pos
    c. ΔH pos ΔS neg
    d. ΔH pos ΔS pos

5. A → B ΔH = -14.9 kJ/mol ΔS = -48 J/mol•K

At what temperatures is the process product-favored?

At what temperature is the process at equilibrium?

At what temperatures is the process reactant-favored?

Key Ch. 14 Equations:

1. $\Delta S^\circ = S^\circ$ (products) – S° (reactants)
2. $\Delta G^\circ = \Delta G_f^\circ$ (products) – ΔG_f° (reactants)
3. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (T in Kelvin)
4. at equilibrium $\Delta H = T\Delta S$