# Ch. 16 Chemical Equilibrium

16.1 Characteristics of a System at Chemical Equilibrium

- 1. Not completely on product or reactant side have some of each
  - "product favored" equilibrium- more product
  - "reactant favored" mostly reactant
- 2. "Dynamic Equilibrium"
  - forward rate = reverse rate
  - reactions happen, but cancel each other out, so that no overall change
     "steady state" = "equilibrium"
  - It may seem like nothing is changing or happening, but is molecular action ("dynamic")
- Previous Examples

   Vapor Pressure (closed container)
   Liquid → vapor
   Saturated solution
   solid → dissolved
   Weak acid/weak electrolyte
   HF → H<sup>+</sup> + F<sup>O</sup>
- 3. In achieving an equilibrium it doesn't matter whether you start from left side or right side
  - Either way, you end up with the same balance between reactants and products once equilibrium has been established
  - Figure 14.1 Moore, Fig T-117, 118 Brown

# The Equilibrium "Constant"

A. Intro

A 
$$\frac{k_f}{k_r}$$
 B At equilibrium, rate<sub>forward</sub> = rate reverse  
Rate forward:

Equality:

Kc

Rearrange:

Notes

- 1. K<sub>c</sub> is a constant
- 2. Each reaction has its own unique "K" constant
  - called the "EQUILIBRIUM CONSTANT"
- 3. Ratio of product over reactant
  - <u>concentrations are used</u> in "M" (Molarity) = mole/liter
- 4. For gases, a  $K_p$  constant based on gas pressures can also be used. (16.3)
  - I'll do molarity ones for test problems and home-made problems. But the setup logic is the same for gas problems, in book or online homework or whatever.



#### Amounts of materials before and after equilibrium is Achieved:

#### Forward and Reverse Rates Prior to and After Equilibrium is Achieved:



Chemistry: The Science in Context 3/e Figure 16.2 © 2012 W. W. Norton & Company, Inc.

#### Actual Product/Reactant Ratios "Q" versus Equilbrium Product/Reactant Ratios "K"



- B. Qualitative things the value of K tells us:
- 1. At equilibrium, is the product favored or the reactant?
  - $K >> 1 \rightarrow$  product favored
  - K << 1  $\rightarrow$  reactant favored

**<u>Concept Problem</u>**: A = Ba.  $K_c=10^3$ b.  $K_c = 10^{-3}$ 

- 2. If the <u>actual</u> initial ratio Q does not equal the equilibrium ratio K, in which direction will reaction go to achieve equilibrium? (In other words, if you start out not at equilibrium, how will the system respond to get to equilibrium?) (Section 16.5)
  - If actual ratio "Q" < K, the product/reactant ratio will need to increase in order to reach the target "K"
    - Practical:
  - If actual ratio "Q" > K, the product/reactant ratio will need to decrease in order to reach the target "K"
    - Practical:

Concept Problem: $A \Longrightarrow B$  $K_c=0.20$ How will [A] and [B] change/respond to reach equilibrium (which will go up and which will got down?) if initial conditions are:

a. [A] = 0.20 M and [B] = 0.00 M

b. [A] = 0.10 M and [B] = 0.50 M

- 3. What will specific concentrations be at equilibrium?
  - If you know K and other information, you can solve for all the equilibrium concentrations

<u>Concept Problem</u>: A = B  $K_c=0.20$ 

- a. If the system is at equilibrium and [A] = 0.10 M, what must be [B]?
- b. If the system is at equilibrium and [B] = 0.10 M, what must be [A]?
- c. If the system is <u>not</u> at equilibrium, and the initial scenario has [B] = 0.60 M, what will be the concentrations after equilibrium is achieved?

#### Writing K expressions: General (16.2)

$$aA + bB \longrightarrow cC + dD$$
  $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ 

- 1. Products over reactants
- 2. To the "coefficient" power
- 3. Straight from the balanced equation
  - don't need mechanism, etc.
  - Not like a rate law where equation doesn't really tell you anything

Write K<sub>c</sub> Expressions

a. 
$$N_2(g) + 3 H_2(g) \implies 2 NH_3(g)$$

b. 
$$A(g) + 2 B(g) \implies 3 C(g) + D(g)$$

Heterogeneous Equilibria (16.6): Do not include solids or liquids (solvents) in K expressions

- The concentrations of solids and liquids (solvents) are constant, so just wrap into K
- only gases and "aqueous things" (solutes) appear in K expressions
  - these are things whose concentrations are **not** constant
  - $\circ$  A(g), B(aq) Yes
  - $\circ$  C(l), D(s) No
- When water is involved as either a reactant or a product, it does **not** appear in the K expression (when the reaction takes place in aqueous solvent)

Ex. CuOH(s)  $\longrightarrow$  Cu<sup>+</sup>(aq) + OH<sup>-</sup>(aq)

$$\mathbf{K}_{1} = \frac{[Cu^{+}][OH^{-}]}{[CuOH]} \quad \text{so} \quad \mathbf{K}_{2} = [Cu^{+}][OH^{-}]$$

Write K Expressions

a.  $NaF(aq) + H_2O(l) \implies HF(aq) + NaOH(aq)$ 

b. 
$$CaCO_3(s) \implies CaO(s) + CO_2(g)$$

c. 
$$HF(aq) + H_2O(1) \implies H_3O^+(aq) + F^-(aq)$$

# Manipulating Equilibrium Constant Expressions. K's for Related Reactions. (16.4)

- When a reaction is written in the reverse direction, the K value is inversed
  - $K_{reverse} = 1/K_{forward}$
- When the coefficients for a reaction are doubled or halved, the K value ends up being squared or "square rooted"
- 1. Suppose  $A + B \implies C$   $K_c=10^4$

What is K for  $C \implies A + B$ (Draw both the expression and the actual K value)

2. Suppose A + B - C  $K_c = 10^4$ 

What is K for  $2A + 2B \implies 2C$ (Draw both the expression and the actual K value)

16.3 Calculating K values

• Key: You need all equilibrium concentrations. Then you can plug into K expression and solve.

Two ways to know all the equilibrium concentrations.

- 1. You are simply given all of the equilibrium concentrations. (easy)
- 2. You are given all of the <u>initial</u> concentrations, and <u>at least one final concentration</u>, but then must use the "ICE" (<u>I</u>nitial-<u>C</u>hange-<u>E</u>quilibrium) method to figure out what they would all be at equilibrium (harder)

A. Given all of the Equilibrium concentrations, solve for K (easy)

Solution steps:

- a. Based on the balanced reaction, write out the correct K expression
- b. Enter the known concentrations values and solve for K

1. For A  $\implies$  B + C, find K<sub>c</sub> if [A] = 0.26 M, [B] = 0.26 M, [C] = 0.93 M.

2. For A + 2B  $\implies$  2C + D, find K<sub>c</sub> if [A] = 0.15, [B] = 0.18, [C]=  $2.0 \times 10^{-4}$ , [D] =  $3.0 \times 10^{-6}$ 

# B. Given all of the initial concentrations, and at least one final concentration, solve for K (harder) (16.8).

Solution steps:

- a. Based on the balanced reaction, write out the correct K expression
- <u>b.</u> Use the "ICE" (<u>I</u>nitial-<u>C</u>hange-<u>E</u>quilibrium) method to figure out the equilibrium concentrations
- c. Enter the equilibrium concentration values and solve for K

# Using the "ICE" Method to Calculate K, Given Initial Concentrations and One Final Concentration

- 1. Write balanced equation, and expression for K<sub>c</sub>
- 2. Make an "ICE" table, and enter the knowns
  - a. <u>I</u>nitial
  - b. Change
  - c. <u>Equilibrium</u>
- 3. Find the Change for the chemical whose final concentration is known
- 4. Use stoichiometric relationship to determine the change in concentrations for the others
- 5. From the initial concentrations and the deduced changes, determine all equilibrium concentrations
- 6. With all equilibrium concentrations now known, plug into the K<sub>c</sub> expression and solve for K
- 7. Check: Does Answer Make Any Sense?
  - Note: equilibrium concentrations must be in Molarity, moles/liter. If information is given in grams or moles plus solvent volume, you will need to convert into molarity.

Use the ICE method to find the equilibrium concentrations and the K values for the following:

3. I	2A + 2B 0.20 0.30	$ \longrightarrow C + 0 $	- 2D 0.10	K <sub>c</sub> =
С				
E	0.10			$K_c =$
4. I	A + 0.20	2B 0.20	$\begin{array}{ccc} C & + & D \\ 0 & & 0 \end{array}$	K <sub>c</sub> =
С				
Е	0.15			K <sub>c</sub> =

### **Chemical Meaning of K**

- 1.  $K_c >> 1$  Product Favored
- 2. K<sub>c</sub><< 1 Reactant Favored
- 3.  $K_c \approx 1$  Significant quantities of both products and reactants---calculations required
- There are many cases where  $K_c \ll 1$ , but small amount of product are still very important.

### Some more Uses for K Values

A. Predicting the direction of a reaction, given information about actual situation. (<u>16.5 Equilibrium</u> Constants K and Reaction Quotients O)

K=equilibrium Q=<u>actual</u> ratios (same format)

- If Q=K, you're at equilibrium. The situation won't change
- If Q<K, you're not at equilibrium. You are short on product, so reactions will go to products to achieve equilibrium. Shift from left to right.
- If Q>K, you're not at equilibrium. You have excess product, so products will go to reactants to achieve equilibrium. Shift from right to left.
- 1.  $A + B \stackrel{\longrightarrow}{\longrightarrow} C$   $K_c = 72$ Suppose [A], [B], and [C] all begin at 0.33 M:

a. What is Q?

b. Which direction will the reaction go to achieve equilibrium?

c. What will happen to the concentrations of: (will they go up or down?)

[A] [B] [C]

# **B.** Calculating Equilibrium Concentrations, Given K and Some Other Information (16.8, 2)

1. If all but one equilibrium concentration is given: (easy, plug and chug...)

Solution steps:

- a. Based on the balanced reaction, write out the correct K expression
- b. Enter the known K and the known concentrations values and solve for the unknown concentration

Example.  $HF(aq) = H^+(aq) + F^-(aq)$   $K_c = 6.8 \times 10^{-4}$ 

a. Find  $[H^+]$  if [HF] = 0.10 and  $[F^-] = 0.10$ .

b. Find  $[F^-]$  if [HF] = 0.20 and  $[H^+] = 10^{-3}$ .

2. If K number and initial concentrations are given, but no equilibrium concentrations are given, use ICE to calculate the equilibrium concentrations.

# Using the "ICE" Method to Calculate Equilibrium Concentrations, Given Only Initial Concentrations and K<sub>c</sub>

- 1. Write balanced equation, and expression for K<sub>c</sub>
- 2. Make an "ICE" table, and enter the known initial concentrations
  - a. <u>I</u>nitial
  - b. <u>C</u>hange
  - c. <u>E</u>quilibrium
- 3. Use "x" to define the change of one substance.
- 4. Use stoichiometric relationships to determine the changes in the concentrations for the others, in terms of "x".
- 5. Calculate the equilibrium concentrations of all chemicals in terms of initial concentrations and "x", and enter them in the table.
  - Ex: 0.30 x, or 0.30 2x, or 0.00 + x, or 0.00 + 2x .....
  - <u>If K is small</u> so that "x" is likely to be small, <u>use the simplifying</u> <u>assumption</u> that  $[A]_{initial} - "x" = [A]_{initial}$ 
    - $\circ$   $\,$  This is often justified, and can greatly simplify the math.
    - Ex: 0.20 x = 0.20 if x is smaller than 0.01
- 6. Solve for "x" (This is the hard part!)
- 7. <u>Once "x" is known, use it to solve for the actual equilibrium</u> <u>concentrations</u>
- 8. Check: Does Answer Make Any Sense?
- Check: If you made the "simplifying assumption", was it justified? (Was "x" < 5% of [A]<sub>initial</sub>?)

Note: Some hard math!! Quadratics are tedious!

• If possible, being able to avoid needing to solve quadratics saves a lot of time (and mistakes)

# \*Great simplifying assumption (avoids a lot of quadratics):

- 1. changes "x" are often small
  - For something with nonzero original concentration, the change "x" in concentration is often so small that it doesn't significantly change the original concentration
  - [original concentration] "x" (change in concentration) = [original concentration]
- 2. Useful strategy:
  - a. Make the simplifying assumption
  - b. Check at end whether "x" > 5% of the original concentration
    - If not, the simplifying assumption is pretty good
    - If yes, the simplifying assumption is not valid and leads to some nontrivial error. In which case you need to go back and solve completely (often involving quadratic or perhaps even worse).

<u>If "x" ="</u>	<u>Then <math>0.20-x =</math></u>	After roudoff	<u>Is simplifying</u> assumption valid?
2 x 10 <sup>-7</sup>	0.20 - 0.0000002 =	<u>to 2 sig. 11g.</u>	
2 x 10 <sup>-6</sup>	0.20 - 0.000002 =		
2 x 10 <sup>-5</sup>	0.20 - 0.00002 =		
2 x 10 <sup>-4</sup>	0.20 - 0.0002 =		
2 x 10 <sup>-3</sup>	0.20 - 0.002 =		
2 x 10 <sup>-2</sup>	0.20 - 0.02 =		

### **Concept Example: Why is the Simplifying Assumption Often Justifiable?** 0.20-x = ???

# -Check at end. If x>5% of number, the assumption causes trouble.

### Problems

1. If  $0.10 \text{ mol of } N_2O_4$  is added to 1L flask, what will be the concentrations at equilibrium?

Quadratic Required. K too  $N_2O_4 = 2NO_2$ K = 0.211large to justify simplificationInitialChange

<u>Equilibrium</u>

### **Equilibrium:**

 $[N_2O_4]$ 

 $[NO_2]$ 

2. Find final concentrations:

	HA 🛁	► H+ +	+ A <sup>-</sup>	$K_c = 1.6 \times 10^{-7}$
<b>Initial Concentrations</b>	0.20	0	0	
<u>Change</u>				
<u>Equilibrium</u>				
<u>Equilibrium with</u> Simplifying Assumption				
Equilibrium:				
[HA]				
$[\mathrm{H}^+]$				
[A <sup>-</sup> ]				

3. Find final concentrations give	en: A	#	В	+	С	$K_c = 2.4 \times 10^{-6}$
<u>Initial</u>	0.30	)				
<u>Change</u>						
<u>Equilibrium</u>						
<u>Equilibrium with</u> <u>Simplifying Assumption</u>						
Equilibrium:						
4. Find final concentrations give	en: A	<del>, 1</del>	В	+	С	$K_{c} = 0.018$
Initial	0.30	)	2		2	
Change						
<u>Equilibrium</u>						
Equilibrium:						

5. Find final concentrations	given: <u>A "S</u>	<u>quare Root</u>	" Simplification	
	A +	B 💳	C + D	$K_{c} = 0.060$
<u>Initial</u>	0.30	0.30		
<u>Change</u>				
<u>Equilibrium</u>				

6.	Find final concentrations give	n: So A	lution v	with a 2B	nd Wi +	thout Simplify C	Ving Assumption $K_c = 2.0 \times 10^{-8}$
Ini	tial	0.20					
Ch	ange						
Eq	<u>uilibrium</u>						
<u>Eq</u> Sin	uilibrium with nplifying Assumption				1	a. 110 i	
Wi	th Simplifying Assumption				With	out Simplifying	g Assumption

Solution With and Without Simplifying Assumption	1:
$A \implies 2B + C$	

With and Without Simplifying Assumption: A = 2B + C  $K_c = 2.0 \times 10^{-8}$ 

<u>With</u> I 0.20 0 0	<u>Without</u> (using $.20 - x$ for [A] at eq)
C -x 2x x	
E .20-x 2x x	$(2x)^2 x$
$E^* 0.20 x x$	$K = 2.0 \times 10^{-6} = \frac{1}{0.20 - x}$
So $K = 2.0 \times 10^{-8} = \frac{(2x)^2 x}{10^{-8}} = \frac{4x^3}{10^{-8}}$	So $2.0 \ge 10^{-8} (0.20 - x) = 4 x^3$
0.20 .20	
	So $4.0 \ge 10^{-9} - 2.0 \ge 10^{-8} \ge 4x^3$
$0.4 \ge 10^{-8} = 4x^3$ Easy	
$x^3 = 1.0 x 10^{-9}$ $x = 1.0 x 10^{-3}$	So $4x^3 + 2.0 \times 10^{-8}x - 4.0 \times 10^{-9} = 0$
	Not Easy!!!

# 16.7 How Systems Respond When an Equilibrium is Disturbed. LeChatelier's Principle.

- 1. At Equilibrium, there is a steady state of concentrations.
- 2. How does a system respond when an equilibrium is disturbed?

**Le Chatelier's Principle**: when a system is disturbed from equilibrium, it responds so as to reduce or counteract the effect of the change.

- 1. A revised equilibrium gets reestablished
  - a. Usually the same K value must still apply
    - unless the temperature is changed
  - b. But different actual concentrations result
    - whether you added or subtracted a reactant, a product, some solvent, or the volume
- 2. The reaction can move in the forward direction (more reactants go to product side) or the reverse direction (more products go back to starting materials) as needed to offset a change
- Qual: If something extra is added, react from that side toward the other to remove some of it If something is removed, react from the other side to replace it

LeChateliers's Principle: Summary

A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner as to reduce or counteract the effect of the change.

Factor that Changes	Direction of the Change	Direction to Restore
		Equilibrium
1. Concentration	↑ Reactant	Forward
	↑ Product	Reverse
2. Temperature	$\uparrow$ T, when $\Delta H > 0$	Forward – K increases
	↑ T, when $\Delta H < 0$	Reverse – K decreases
3. Volume	$\uparrow$ V, when $\Delta n_{gas} > 0$	Forward
	$\uparrow$ V, when $\Delta n_{gas} = 0$	No effect
A change in volume	$\wedge$ V, when $\Delta n_{gas} < 0$	Reverse
impacts gas pressure.		
An increase in volume		
reduces pressure.		

If you reverse any of the Changes above, the Direction to reach Equilibrium reverses

3 Factors That can Be Changed	Goals
1) Concentrations	1) restore $Q = K$
2) Temperature	2) offset change
3) Volume (which impacts gas pressure)	

# LeChatelier's Principle: Response to Disrupted Equilibria

 $2 A (g) \implies B (g) + Heat$   $\Delta H < 0$  (exothermic)

TABLE 16.4Responses of an Exothermic Reaction [2A(g) = B(g)] at Equilibrium to Different Kinds of Stress						
Kind of Stress		How Stress Is Relieved	Direction of Shift			
Add A		Remove A	To the right			
Remove A		Add A	To the left			
Remove B		Add B	To the right			
Add B		Remove B	To the left			
Increase tempera by adding heat	ature	Consume some of the heat	To the left			
Decrease temper by removing hea	rature t	Generate heat	To the right			
Increase pressure compressing the mixture	e by reaction	Reduce moles of gas to relieve pressure increase	To the right			
Decrease pressur expanding volum	re by ne	Increase moles of gas to maintain equilibrium pressure	To the left			

Chemistry: The Science in Context 3/e Table 16.4 © 2012 W. W. Norton & Company, Inc.

- A. Concentration Change: Addition or Removal of Either a Reactant or a Product
  - 1. If you add (or remove) a chem, at that moment  $Q \neq K$
  - 2. The system (and concentrations) will shift forward or backward to adjust Q so Q = K
    - NOTE: K value does not change
    - many chemical ways to remove a chem (precipitations, acid-base, etc.)

<u>Example</u>

	<u>Immediate</u>	Direction to	Respon	se (follow	ving dis	ruption) :
<b>Disruption</b>	Impact on Q	Restore Eq	[A]	[B]	[C]	[D]
Add A	Q < K	Forward	$\checkmark$	$\checkmark$	$\uparrow$	$\wedge$
Add B						
Add C						
Add D						
Remove A						
Remove B						
Remove C						
Remove D						

$$A + B = C + D$$

## B. Volume Change: Only Relevant When Gases are Involved

- 1. When the volume changes, it causes a change in concentrations
  - at the instant of change  $Q \neq K$
  - note: the actual K value is unchanged

#### 2. Qualitative sense:

a. When the volume expands, you want to generate <u>more gas molecules</u> to fill it
b. When the volume shrinks, you want to get rid of gas molecules so it isn't too full

- 3. Volume changes will only matter if one side of the equation has more gas on it than the other
  - if moles of gas are equal on both sides, volume changes have no impact

<b>Disruption</b>	<b>Response</b>
Volume Increase	Shift toward side with more gas
Volume Decrease	Shift toward side with less gas

- 4. Volume and Pressure: A different qualitative way to understand why a system will respond
  - When the volume expands, pressure decreases
  - a. When the volume expands and the pressure drops, you want to generate <u>more gas</u> <u>molecules</u> to fill the container and <u>restore pressure</u>
  - b. When the volume shrinks, you want to get rid of gas molecules to unclutter the container and to restore the original pressure

# Volume Example

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

Volume Change	Direction to	Response of moles of:
	<u>Restore Eq</u>	$2H_2(g) + O_2(g) \Longrightarrow 2H_2O$
Increase		
Decrease		

# C. Temperature Change

- 1. View heat as either a reactant or a product
  - $\Delta H > 0$  Endothermic Heat is required, on Reactant Side
  - $\Delta H < 0$  Exothermic Heat is produced, on Product Side
- 2. When the temperature rises, the system responds so as to remove extra heat
- 3. When the temperature drops, the system responds so as to replace missing heat
- 4. When the system shifts to the right or to the left in response to a temperature change, this means that chemical concentrations change, too
- 5. A Temperature Changes Causes a Changes in the K Value
  - Because the Product/Reactant Ratio Changes
    - $\Delta H > 0$  Rise in temp  $\rightarrow$  shift to right  $\rightarrow$  K rises
    - $\Delta H > 0$  Drop in temp  $\rightarrow$  shift to left  $\rightarrow$  K drops
    - $\Delta H < 0$  Rise in temp  $\rightarrow$  shift to left  $\rightarrow$  K drops
    - $\Delta H < 0$  Drop in temp  $\rightarrow$  shift to right  $\rightarrow$  K rises
- 1. Write in "heat" as reactant or product, and predict the responses when temperature changes:

A 💳 B

 $\Delta H < O$ 

Temperature Change	Direction to	Response of moles of:	Response of
	Restore Eq	A 💳 B	K Value
Increase			
Decrease			

2. Write in "heat" as reactant or product, and predict the responses when temperature changes:

A 💳 B

 $\Delta H > O$ 

Temperature Change	<u>Direction to</u> <u>Restore Eq</u>	Response of moles of: A $\stackrel{\longrightarrow}{\longrightarrow}$ B	Response of K Value
Increase			
Decrease			

3. Write in "heat" as reactant or product, and predict the responses to the changes:

$$N_2(g) + 3H_2(g) \implies 2NH_3(g) \qquad \Delta H > O$$

Direction to	Response of moles of:	Response of
Destant Ex	$N(x) + 2H(x) \rightarrow 2NH(x)$	V V las
<u>Restore Eq</u>	$N_2(g) + 3H_2(g) = 2NH_3(g)$	K value
	Direction to Restore Eq	Direction to     Response of moles of:       Restore Eq $N_2(g) + 3H_2(g) = 2NH_3(g)$

D. Addition Catalyst: Equilibrium is reached faster, but the actual K value or equilibrium product/reactant ratios are unchanged.

# Some Math Tips: CHEMICAL EQUILIBRIA Chem 210-Jasperse Ch. 16

1.  $(a + b)^2 = a^2 + 2ab + b^2$ 

example:  $(0.24 - x)^2 = 0.0576 - 0.48x + x^2 = x^2 - 0.48x + 0.0576$ 

example:  $(3.2e-5 - x)^2 = 1.02e-9 - 6.4e-5 x + x^2 = x^2 - 6.4e-5 x + 1.02e-9$ 

2. Quadratic Equation:  $ax^2 + bx + c = 0$   $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ 

example:  $x^2 - 1.48x + 0.0576 = 0$  x = 1.44 or 0.04

example:  $x^2 - .60 x + 0.025 = 0$  x = 0.43 or 0.17

Note 1: Quadratics are a bother to solve. Avoid them if possible. Often the "simplifying assumption" (see #4) can enable you to avoid quadratic solutions.

Note 2: Quadratics can often give 2 answers, but one will frequently be nonsense.

# 3. "SIMPLIFYING ASSUMPTION": If m>>x, then m - x = m (approximately)

examples: 0.14 - 3.6e-5 = 0.14 1.23e-3 - 1.0e-6 = 1.23e-3

Use: for many equations in which K is small, "x" will also be relatively small. In these circumstances, the degree to which the starting materials react ("x") will be relatively insignificant from their concentrations perspective, and we can assume the equilibrium concentration of the reactants will not differ significantly from their initial concentration.

- THE SIMPLIFYING ASSUMPTION WILL OFTEN MAKE THE USE OF THE QUADRATIC EQUATION UNNEEDED
- Guide: If "x" is >5% of "m", then the simplifying assumption is not appropriate.
- 4. The "Square Root" Simplification: If both numerator and denominator have "squares", it is convenient to take the square root of both sides to simplify

examples:  $0.10 = x^2/(0.050 - x)^2$  Take square root of both sides: 0.316 = x/(0.050 - x)Rearrange: 0.0158 - 0.316x = xSolve for "x": x = 0.012

5.  $\mathbf{m} = \mathbf{x}^{\mathbf{n}}$ 

To solve for x, when "m" and "n" are known:

- a. enter "m"
- b. hit  $x^{1/y}$  or button (depending on your calculator)

c. enter "n"

example:

 $25 = x^{3} x = 2.92$ 1.48e-6 = x<sup>3</sup> x = 0.0114 2.14e-13 = x<sup>4</sup> x = 6.80e-4

# Using the "ICE" Method to Calculate K, Given Initial Concentrations and One Final Concentration

- 1. Write balanced equation, and expression for  $K_c$
- 2. Make an "ICE" table, and enter the knowns
  - a. <u>I</u>nitial
  - b. <u>C</u>hange
  - c. <u>E</u>quilibrium
- 3. Find the Change for the chemical whose final concentration is known
- 4. Use stoichiometric relationship to determine the change in concentrations for the others
- 5. From the initial concentrations and the deduced changes, determine all equilibrium concentrations
- 6. With all equilibrium concentrations now known, plug into the K<sub>c</sub> expression and solve for K
- 7. Check: Does Answer Make Any Sense?
- Note: equilibrium concentrations must be in Molarity, moles/liter. If information is given in grams or moles plus solvent volume, you will need to convert into molarity.

# Using the "ICE" Method to Calculate Equilibrium Concentrations, Given Only Initial Concentrations and K<sub>c</sub>

- 1. Write balanced equation, and expression for  $K_{\rm c}$
- 2. Make an "ICE" table, and enter the known initial concentrations
  - a. <u>I</u>nitial
  - b. Change
  - c. <u>E</u>quilibrium
- 3. Use "x" to define the change of one substance.
- 4. Use stoichiometric relationships to determine the changes in the concentrations for the others, in terms of "x".
- 5. Calculate the equilibrium concentrations of all chemicals in terms of initial concentrations and "x", and enter them in the table.
  - Ex: 0.30 x, or 0.30 2x, or 0.00 + x, or 0.00 + 2x .....
  - <u>If K is small</u> so that "x" is likely to be small, <u>use the simplifying</u> <u>assumption</u> that  $[A]_{initial} - "x" = [A]_{initial}$ 
    - $\circ~$  This is often justified, and can greatly simplify the math.
    - Ex: 0.20 x = 0.20 if x is smaller than 0.01
- 6. Solve for "x" (This is the hard part!)
- 7. <u>Once "x" is known, use it to solve for the actual equilibrium</u> <u>concentrations</u>
- 8. Check: Does Answer Make Any Sense?
- Check: If you made the "simplifying assumption", was it justified? (Was "x" < 5% of [A]<sub>initial</sub>?)

# LeChateliers's Principle: Summary

A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner as to reduce or counteract the effect of the change.

Factor that Changes	Direction of the Change	Direction to Restore
		Equilibrium
1. Concentration	↑ Reactant	Forward
	↑ Product	Reverse
2. Temperature	$\uparrow$ T, when $\Delta H > 0$	Forward – K increases
	$\uparrow$ T, when $\Delta H < 0$	Reverse – K decreases
3. Volume	$\uparrow$ V, when $\Delta n_{gas} > 0$	Forward
	$\uparrow$ V, when $\Delta n_{gas} = 0$	No effect
A change in volume	$\uparrow$ V, when $\Delta n_{gas} < 0$	Reverse
impacts gas pressure.		
An increase in volume		
reduces pressure.		

If you reverse any of the Changes above, the Direction to reach Equilibrium reverses

# Ch. 17 Acids and Bases

Acid/base character (pH) of a solution has enormous impact

- a. lake biosystem (acid rain)
- b. farming/gardening (soil pH, alkalinity, etc)
- c. rusting/corrosion
- d. biology
- cells, proteins, blood, enzymes, hormones need very tight pH control
- Most bio reaction mechanisms involve  $H^+$  transfer  $\rightarrow$  [H<sup>+</sup>] has huge impact on rates

17.1 Bronsted-Lowry Concept of Acids/Bases

	Bronsted-Lowry D	efinitio	<u>n</u>	Lewi	<u>s Defin</u>	ition		
Acid	$\mathbf{H}^{(\pm)}$ donor			Lone	-pair ac	ceptor		
<u>Base</u>	H <sup>⊕</sup> acceptor			Lone	-pair do	onor		
Acid and	d water:	HC1	+	H <sub>2</sub> O	÷	H₃O⊕	+	cl $\Theta$
Base and	d water:	NH <sub>3</sub>	+	H <sub>2</sub> O	<del>~~</del>	НО⊖	+	NH4 <sup>⊕</sup>
<u>Notes:</u> 1. An • 2. A <u>b</u> •	<b>acid loses</b> an H $\oplus$ ar A neutral acid becom A cationic acid becom <b>ase gains</b> an H $\oplus$ an A neutral base becom An anionic base becom	nd gets nes an <b>a</b> nes neu id gets i nes a <b>ca</b> omes ne	more ne nion aft utral afte more po tion aft eutral aft	egative ter loss o sitive er gain ter gain	of H <sup>(+)</sup> f H <sup>(+)</sup> of H <sup>(+)</sup> of H <sup>(+)</sup>		HCl $\rightarrow$ H <sub>3</sub> O $\oplus$ H $\oplus$ + H $\oplus$ +	$ \begin{array}{c} C1 \stackrel{\bigcirc}{\rightarrow} \\ \rightarrow H_2O \end{array} $ $ \begin{array}{c} NH_3 \rightarrow NH_4 \stackrel{\oplus}{\rightarrow} \\ \stackrel{\bigcirc}{\rightarrow} OH \rightarrow H_2O \end{array} $

# The change in either charge or number of H's can help identify whether a chemical is functioning as an acid or a base.

- 3. Every base needs a lone pair which gets used to bond to the new hydrogen
  - The two electrons involved in the new bond to hydrogen always come from an electron pair on the base





Water can function as either a base (accepting an H<sup>⊕</sup> when an acid is placed in water) or as an acid (donating an H<sup>⊕</sup> when a base is placed in water)

- 5. In every acid-base reaction, you must have both an acid (a chemical functioning as the H  $^{\oplus}$ 
  - donor) and also a base (a lone-pair donating chemical functioning as the H  $\oplus$  acceptor)
  - An acid can't give unless there is some basic lone-pair to take.....

Terminology: H ⊕ = "proton"

# Conjugate Acid-Base Pairs

Structures that differ by one H and one charge unit are referred to as conjugate acid-base pairs

Conjugate Acid	Conjugate Base	Conjugate Acid	Conjugate Base
HF	$_{\rm F}$ $\ominus$	H₃O ⊕	$H_2O$
HC1	cl $\ominus$	H <sub>2</sub> O	$_{\rm HO}$
$H_2SO_4$	$_{\mathrm{HSO}_{4}} \ominus$	$_{ m NH_4} \oplus$	NH <sub>3</sub>
$_{\mathrm{HSO}_{4}} \odot$	$SO_4^{2-}$		

1. Draw the conjugate bases	2. Draw the conjugate acids
a. HCN	a. SO <sub>4</sub> <sup>2-</sup>
b. HBr	b. NH <sub>3</sub>
c. CH <sub>4</sub>	c. Cl $\ominus$

Relative Strengths of Acids and Bases

	Acid	Base	
Strong acids, 100%	HC1	$Cl^{\Theta}$	Nonbases
Ionized in H <sub>2</sub> O	$H_2SO_4$	$_{\mathrm{HSO}_{4}} \ominus$	
	$H^{\oplus}(aq) = H_3O^+$	$H_2O$	
	HSO <sub>4</sub> -	SO4 <sup>2-</sup>	
	HF	$_{\rm F} \Theta$	
	$H_2CO_3$	$_{\rm HCO_3} \ominus$	
	$_{ m NH_4}$ $\oplus$	NH <sub>3</sub>	
	$HCO_3 \ominus$	$CO_{3}^{2-}$	
	$H_2O$	$_{ m OH}$	
Nonacids	$_{OH} \Theta$	O <sup>2-</sup>	Strong bases, 100%
	H <sub>2</sub>	$_{\rm H} \ominus$	Protonated in H <sub>2</sub> O

- Stronger acids have weaker conjugate bases and weaker acids have stronger conjugate bases
- Stronger bases have weaker conjugate acids and weaker bases have stronger conjugate acids

# **Relative Strength of Acids and Bases**



Chemistry: The Science in Context 3/e Figure 17.4 © 2012 W. W. Norton & Company, Inc.

#### Conjugate Pairs in Acid-Base Reactions and Acid-Base Equilibria

- 1. Note: Some acid-base reactions go entirely to the product side, or stay entirely on left side
- 2. But many acid-base reactions involve equilibria, in which a proton is shuffling back and forth from side to side
- 3. In the example shown, a proton (H  $\oplus$  ) jumps back and forth between F and O.
  - a. Going from left to right, F is the giver (HF = acid) and O the acceptor (H<sub>2</sub>O = base)
  - b. Returning from right back to left, O is the giver (H<sub>3</sub>O  $\oplus$  = acid) and F the acceptor (F  $\oplus$  = base)

$$HF + H_2O \implies H_3O \oplus + F^{\bigcirc}$$

# Notes

- 1. Each <u>side</u> of every acid-base reaction has one thing that functions as an acid and the other as a base. (This is true on the right side as well as on the left side).
- 2. Every acid-base reaction has 2 conjugate pairs
  - a. For the acid on the left, it's conjugate base appears on the right side
  - b. For the <u>base</u> on the left, it's <u>conjugate acid</u> appears on the right side.

<u>Problems</u>: For each of the species in the following equilibria, mark whether it functions as an acid or a base?

- For each of the species in the following equilibrium, draw an arrow to it's conjugate.
- a.  $NH_3$  + HClO  $\implies$   $NH_4$   $\oplus$  + ClO  $\ominus$ Notes/Notice: 1. Notice the change in H-count and the change in charge for each of these 2. The <u>acid</u> on the left always loses a hydrogen and becomes one step b. HCN + H<sub>2</sub>PO<sub>3</sub> $\ominus$   $\Longrightarrow$  H<sub>3</sub>PO<sub>3</sub> + CN $\ominus$ unit more negative 3. The <u>base</u> on the left always gains a hydrogen and becomes more positive 4. <u>Cations usually function as acids</u>
  They are positive, and want to c.  $CH_3NH_2 + CH_3OH_2 \oplus \implies CH_3NH_3 \oplus +$ CH<sub>3</sub>OH get rid of H  $^{\oplus}\,$  to alleviate positive charge 5. <u>An anion usually function as a</u> base • It usually wants to get more d.  $H_2O$  +  $HSO_4 \bigcirc$   $\implies$   $H_3O \oplus$  +  $SO_4^{-2}$ positive, and the negative charge always means it has a lone-pair available Some exceptions, such as • example "d"

# Acid/Base Strength

- <u>Strong acids</u> are better H<sup>⊕</sup> donors than <u>weaker acids</u>
   Strong bases are better H<sup>⊕</sup> acceptors than weaker bases
- 2. Acid/base strength depends on <u>love for H</u>  $\oplus$
- Consider the conjugate pair of  $Z^{\bigcirc}$  and HZ
  - a. High H  $\oplus$  Love: Suppose Z  $\oplus$  really loves H  $\oplus$ 
    - 1. Then  $Z \bigcirc$  is a strong base
      - It aggressively grabs  $H^{\oplus}$  from somebody else
    - 2. Then HZ is a very weak acid or a total non-acid
      - Z tightly holds onto the H  $\oplus$
      - It doesn't let anybody else steal H<sup>⊕</sup> unless it's a base who loves H<sup>⊕</sup> even more
  - b. Low H  $\oplus$  Love: Suppose Z  $\oplus$  doesn't have much love for H  $\oplus$ 
    - 1. Then  $Z^{\bigcirc}$  is a weak base or a totally non-base
      - It's very weak about grabbing  $H^{\oplus}$  from somebody else
    - 2. Then HZ is acidic
      - Z is very weak about holding onto the H  $^{\oplus}$
      - Some base who loves  $H^{\bigoplus}$  more can easily steal the  $H^{\bigoplus}$  away and leave  $Z^{\bigoplus}$  behind
- 3. <u>Love for H</u>  $^{\oplus}$  and the Competition between Competing Bases

HX	+	$Z^{\bigcirc}$	<del>~~</del>	$X^{\ominus}$	+	ΗZ
acid		base		base		acid

NOTICE: There is one hydrogen, but two things (Z  $^{\bigcirc}\,$  and X  $^{\bigcirc}$  ) competing for it.

- a. Whichever base loves H  $\oplus$  <u>more</u> will be the <u>stronger base</u>, and the equilibrium will drive to the opposite direction  $\rightarrow$  to the conjugate acid of the strong base
- b. Whichever base loves  $H^{\oplus}$  <u>less</u> will lose the competition and remain in its basic form
- 1. Strong love for  $H^{\oplus}$  = strong base
- 2. Equilibrium goes from strong base to weak base, favors the side where the weaker base lies.
- 3. In the same way, the equilibrium always goes from the stronger acid to the weaker acid, and always favors the side with the weaker acid
- 4. The weaker acid and weaker base are always on the same side, and the stronger acid and stronger base are always together on the other side

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4.	Acid-Base Stre	ength and the	Direction of A	Acid-Base E	Equilibria
----	----------------	---------------	----------------	-------------	------------

			Z de C Z C annoi			
*Acid/base reaction	*Acid/base reactions always go from stronger acid/base to weaker acid + base					
K	favors weaker					
HCl + Stronger acid	NaOH → stronger base	H <sub>2</sub> O + Na <sup>⊕</sup> weaker wea acid	Cl <sup>⊖</sup> ker base	K large (K >>1)		
$H_2S + weaker acid$	F <sup>⊖</sup> ← weaker base	HF + stronger acid	HS <sup>(_)</sup> stronger base	K small (K <1)		

a. Stronger acid + base always on same side

b. If you know any of relative strengths, can predict sense, K

c. If given K info, can identify weaker/stronger

# Problems

1. HF is stronger than HNO<sub>2</sub>. Predict the "direction" of the reaction, and say whether K will be greater or less than 1. (ID each as acid or base)

$$HF + Na \stackrel{\oplus}{=} NO_2 \stackrel{\bigcirc}{=} Na \stackrel{\oplus}{=} F \stackrel{\bigcirc}{=} + HNO_2 \qquad K \qquad 1$$

2. Predict the "direction" of the reaction, and say whether K will be greater or less than 1.

$$HF + Cl \ominus HCl + F \ominus K$$
 1

3. Classify each as the weaker or stronger acid or base.

$$HA + B \bigcirc A \bigcirc + HB \qquad K = 10^3$$

4. Classify each as the weaker or stronger acid or base.

HCN + SO<sub>4</sub><sup>2-</sup> HSO<sub>4</sub>
$$\bigcirc$$
 + CN  $\bigcirc$  K = 10<sup>-5</sup>

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# 5. <u>Direct Relationship between strengths of conjugate acid/base</u>

Acid Strength	Strength of Conjugate Base
Strong	Nonbasic
Weak	Weak
Nonacid	Strong base

Note: there is a huge range of strengths within the "weak" category

	Acid	Base	
Strong acids, 100%	HC1	Cl⊖	Nonbases
Ionized in H <sub>2</sub> O	$H_2SO_4$	$_{\mathrm{HSO_{4}}} \ominus$	
	$\mathrm{H}^{\oplus}(\mathrm{aq}) = \mathrm{H}_{3}\mathrm{O}^{+}$	$H_2O$	
	HSO <sub>4</sub> -	$SO_4^{2-}$	
	HF	$_{\rm F} \Theta$	
	$H_2CO_3$	$HCO_3 \Theta$	
	$\mathrm{NH_4}^{\oplus}$	NH <sub>3</sub>	
	$HCO_3 \bigcirc$	$CO_{3}^{2-}$	
	$H_2O$	$_{\rm OH}$	
Nonacids	OH⊖	O <sup>2-</sup>	Strong bases, 100%
	$H_2$	$_{\rm H} \ominus$	Protonated in H <sub>2</sub> O

The weaker the acid, the stronger it's conjugate base The stronger the acid, the weaker it's conjugate base

# 6. <u>Strong Acids versus Weak Acids versus Nonacids</u>. How do they Differ in Water?

a. <u>Strong acids</u> ionize completely in water

$$\mathrm{HCl} + \mathrm{H}_{2}\mathrm{O} \xrightarrow{} \mathrm{H}_{3}\mathrm{O} \stackrel{\oplus}{=} + \mathrm{Cl} \stackrel{\bigcirc}{=}$$

- There is <u>NO</u> acid left, no acid where the H and the Cl are bonded.
- Goes completely to the product side.
- b. Weak acids ionize incompletely in water
  - An equilibrium exists
  - Normally only a small amount of product ion is present at equilibrium, and most of the weak acid is in it's undissociated form

$$HF + H_2O \implies H_3O \stackrel{(+)}{=} + F \stackrel{(-)}{=} K = 10^{-5}$$

- There is plenty of HF left. But meaningful amounts of  $H_3O \oplus + F \oplus$  ions present.
- Some "weak" acids are stronger or weaker than others.
- c. <u>Nonacids:</u> Don't ionize at all in water.
  - No equilibrium exists
  - Stays completely on the left side

$$CH_4 + H_2O \leftarrow H_3O \oplus + CH_3 \bigcirc$$

# 17.1 Recognizing Acids

# 1) Memorize Six strong acids

HCl HBr HI HNO<sub>3</sub> H<sub>2</sub>SO<sub>4</sub> HClO<sub>4</sub>

# • Assume all other acids are weak acids

• The conjugate anions of these strong acids are nonbasic

# 2) Weak acids

 a. Usually formula written with H in front HF HCN H<sub>2</sub>S H<sub>2</sub>CO<sub>3</sub> → acids CH<sub>4</sub> NH<sub>3</sub> SiH<sub>4</sub> → nonacids

\* Note: NOT ALL H's are acidic!!

b. Carboxylic acids (RCOOH, where R is generic for almost anything)



- The "R" group can be anything, but is usually hydrocarbon
- The anion is stabilized by resonance
- Carboxylic acids are often written as: CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>5</sub>COOH, etc.
- c. Ammonium Ions are weak acids (see more under bases, amines)
  - Conjugate acids of neutral amine bases
  - Formal positive charge on nitrogen
  - Unlike most acids, these are cationic species

$$NH_4 \oplus$$
,  $CH_3NH_3 \oplus$ ,  $(CH_3)_2NH_2 \oplus$ ,  $C_6H_5NH_3 \oplus$ , etc.

# Recognizing Bases

- 1. Soluble metal hydroxides  $\Rightarrow$  strong bases
  - All Group 1 metal hydroxides, many Group 2...
  - Group 1 metal hydroxides produce 1 mole of hydroxide per mole of formula
  - Soluble Group 2 metal hydroxides produce 2 moles of hydroxide per formula

Group 1	Group 2
LiOH, NaOH, KOH	Ca(OH) <sub>2</sub> , Ba(OH) <sub>2</sub>

NaOH (aq)  $\rightarrow$  Na  $\stackrel{\bigcirc}{\oplus}$  (aq) +  $\stackrel{\bigcirc}{\odot}$  OH(aq) (<u>Complete</u>) 1 mole 1 mole

$Ca(OH)_2 (aq) \rightarrow Na^{(+)}$	$(aq) + 2 \stackrel{\bigcirc}{\odot} OH(aq) (\underline{Complete})$
1mole	2 mole

• most Transition-metal hydroxides have limited solubility and aren't effectively strong

 $\begin{array}{ccc} CuOH(S) & & \hline & Cu^+(aq) + & OH^-(aq) \\ 1mole & & less than 1mole & (Incomplete) \end{array}$ 

2. Amines: Neutral N Compounds  $\Rightarrow$  weak bases

Parent:  $H_3N: + H_2O \longrightarrow OH + NH_4^{(+)}$ weak base weak acid

• Other amines have N: in common, but replace one or more of the hydrogens with other thing, usually carbon groups

Conjugate acids = "Ammonium" Ions
$NH_4 \oplus$
CH₃NH₃ ⊕
$(CH_3)_2NH_2^{\oplus}$
C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> ⊕

- N lone pairs accept H  $\oplus$
- Amines are the only "neutral bases". All other bases have anionic charge.
  - The conjugate acids are called "ammonium ions" (see earlier)
    - "Amines" = neutral, weakly basic
    - "Ammoniums" = cationic, weakly acidic
- The ammonium ions have formal  $\oplus$  charge on N

# 3. Any conjugate base of a weak acid is weak base

# 4. Any conjugate base of a non-acid is a strong base

# 5. Any conjugate base of a strong acid is a <u>non base</u>

Note: Most Anions are Basic. Whenever you see an anion, consider whether it will be basic!

# 6. Evaluating the Basicity of Anions

- a. Draw the conjugate acid of the anion
- b. Evaluate the acidity of the conjugate "acid" as strongly acidic, weakly acidic, or nonacidic
- c. Based on the acidity of the acid, decide what the strength of the anion base would be.

Conjugate Acid Strength	<b>Strength of Conjugate Base</b>
Strong acid	Nonbasic
Weak acid	Weak Base
Non-acid	Strong base

Base Strength	Anion	Conjugate Acid	Acid Strength
	$_{\rm F} \ominus$	HF	
	$\odot_{ m CN}$	HCN	
	$_{\text{H}_2\text{PO}_4}$	H <sub>3</sub> PO <sub>4</sub>	
	Cl $\ominus$	HCl	
	$^{\rm H}\odot$	H <sub>2</sub>	
	$\odot_{ m CH_3}$	CH <sub>4</sub>	

### Note: Most anions are basic

- Memorize the six anions derived from strong acids that are not basic
- Assume any other anion is basic

Six strong Acids	HCl	HBr	HI	HNO <sub>3</sub>	$H_2SO_4$	HClO <sub>4</sub>
Six Non-Basic Anions	cl⊖	$_{\mathrm{Br}} \ominus$	$_{\rm I} \ominus$	$NO_3 \Theta$	$_{\mathrm{HSO}_{4}} \odot$	$ClO_4 \Theta$

### **Recognizing and Classifying Acid/Base Character of Ionic Formulas**

1. Distinguish molecular from ionic formulas

### 2. For ionics, check each ion separately

- a. Is the cation acidic?
  - 1. No if it's a group 1 or group 2 metal cation
  - 2. Yes if it's a transition metal cation
  - 3. Yes if it's an ammonium cation

### b. Is the anion basic?

- 1. No if it's one of the six non-basic anions derived from strong acids
- 2. Yes if it's any other anion

- 1. Classify as Strong Acid, Weak Acid, Strong Base, Weak Base, or Non-acid/base
  - a. HBr
  - b. HF
  - c. CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>
  - d. CH<sub>3</sub>CH<sub>2</sub>COOH
  - e. H<sub>2</sub>SO<sub>4</sub>
  - f. H<sub>3</sub>PO<sub>4</sub>
  - g. HClO
  - h. ClO  $\Theta$
  - i.  $Cl^{\Theta}$
  - j. NO3⊖
  - k. O<sup>2-</sup>
  - 1. CH4
  - m. NaOH
  - n. NaF
  - o. KCl
  - p. NH4NO3
  - q. FeBr<sub>3</sub>

Autoionization of water (17.2). pH and pOH

 $H_2O(1) + H_2O(1) \longrightarrow H_3O^{\textcircled{}}(aq)^+ OH^{\textcircled{}}(aq) \quad K_w = 1.00 \text{ x } 10^{-14} =$ 

- 1. Water is both weakly acidic and basic
- 2. Amount of ions is teensy but very important
- 3.  $K_w = 1.00 \text{ x} 10^{-14}$  always true
- 4. If either  $[H_3O^{\oplus}]$  or  $[HO^{\odot}]$  known, can calculate other

 $[H_{3}O^{\oplus}][OH^{\odot}] = 1.00 \text{ x } 10^{-14}$  Memorize!

Neutral:	$[H_{3}O^{\oplus}] = 1 \times 10^{-7} = [OH^{\odot}] pH = 7$	Note: $H^{\oplus}$ vs. $H_{3}O^{\oplus}$
Acidic:	$[H_3O^{\bigoplus}] > 1 \ge 1 \ge 10^{-7} > [OH^{\bigoplus}] pH < 7$	• $H^{\oplus}$ (proton) in water exists as $H_3O^{\oplus}$
Basic:	$[H_{3}O^{\oplus}] < 1 \times 10^{-7} < [OH^{\odot}] pH > 7$	(hydronium).
		• But H <sup>(+)</sup> is easier to write!
		• They are really the same thing.

# The pH Scale (17.2)

$pH = -1og[H_3O \oplus ]$	$[H_3O^+] = 10^{-pH}$	Much nicer numbers		
<b>On calculator</b> : enter [H <sup>+</sup> ], hit "log", and correct the sign from negative to positive	On calculator: enter pH, switc sign from positive to negative, an 10 <sup>x</sup> button (depending on calculator)	h the nd hit		
1. Higher numberer pH $\rightarrow$ less H	$1^{\oplus}$ , less acidic, more basic			
Lower numbered pH $\rightarrow$ more	H $^{\oplus}$ , more acidic, more less <sup>+</sup>			
pH 3.0 4.6	10.2			
more acidi	c			
less acid	ic			
2. $pH = 7$ neutral	pH < 7 acidic p	H > 7 basic		
<ul> <li>pH change of 1 = tenfold change in [H<sup>⊕</sup>] Change of 2 = 100-fold change pH change of 8 → 4 isn't double the acid or half the acid, it's 10 thousand times more!</li> </ul>				
4. Number of significant figures	in [H <sup>+</sup> ] = number of digits <u>after</u> de	cimal in pH		
$[H^+] = 3.6 \times 10^{-6} \rightarrow pH = 5.44$ 2 sig fig $\rightarrow 2$ after decimal				

- 5. Small pH changes  $\rightarrow$  death
  - 7.35 < blood < 7.45
  - bio rates are often strongly H<sup>+</sup> catalyzed, with 2<sup>nd</sup> or 3<sup>rd</sup> order rate dependence on [H<sup>+</sup>]

6. pOH = - log[OH <sup>-</sup> ]	$[OH^{-}] = 10^{-pOH}$
just like pH = -log [H <sup>+</sup> ]	just like $[H^+] = 10^{-pH}$

7. Since  $10^{-14} = [H^+] [OH^-] \rightarrow$  take negative log of both sides  $\rightarrow 14.00 = pH + pOH$ 

To know any one allows you to find any of the others!

Problems

1. Find pH for following

a.  $[H_3O^+] = 1.0 \times 10^{-4}$ b.  $[H^+] = 1.0 \times 10^{-11}$ c.  $[H^+] = 3.2 \times 10^{-4}$ d.  $[OH^-] = 1.0 \times 10^{-8}$ e.  $[OH^-] = 5.8 \times 10^{-4}$ f. pOH = 8.30

# 2. Find pOH:

c. pH = 3.95

3. Find both

 $[H^+]$ 

[OH<sup>-</sup>]

- a. pH = 3.72
- b. pH = 9.81
- c.  $[H^+] = 3.5 \times 10^{-8}$

d.  $[OH^{-}] = 4.1 \times 10^{-3}$ 

Equilibrium Expressions and Ionization Constants for Acids, Bases. (17.3) A. Acids

HA (aq) + H<sub>2</sub>0 (l)  $\longrightarrow$  H<sub>3</sub>0  $\oplus$  (aq) + A  $\ominus$  (aq) K<sub>a</sub> =  $\frac{[H_3O^+][A^-]}{[HA]}$  $\mathbf{K}_{\mathbf{a}} = \frac{[H_3 O^+][A^-]}{[HA]}$ Shorthand: HA  $\longrightarrow$  H  $\oplus$  + A  $\ominus$ 

- 1. Strong acids: ionize completely ( $K_a = infinity$ )
- 2. Weak acids:  $K_a < 1$
- 3. Larger  $K_a \Rightarrow$  stronger acid Smaller  $K_a \Rightarrow$  weaker acid
- 4. For weak acids, ionizations may be minimal but is still significant

• for math calculations, the "simplifying assumption" is usually useful

- 5. Since  $A^{\bigcirc}$  and HA are conjugates:
  - larger  $K_a \Rightarrow$  less basic A  $\bigcirc$ 
    - (stronger acid  $\rightarrow$  weaker base)
  - smaller  $K_a \Rightarrow$  more basic A  $\bigcirc$ (weaker acid  $\rightarrow$  stronger base)

#### **B.** Bases

Generic	$Base(aq) + H_20(l) \longrightarrow OH^{\bigcirc}(aq) + Base-H^{\textcircled{+}}(aq)$ Conjugate acid	$\mathbf{K}_{\mathbf{b}} = \frac{[OH^{-}][BH^{+}]}{[B]}$
Anionic Base	$A \bigcirc + H_20 \longrightarrow OH \bigcirc + HA$ Conjugate acid	$\mathbf{K}_{\mathbf{b}} = \frac{[OH^{-}][HA]}{[A^{-}]}$
Neutral Amine Base	$\begin{array}{c} NH_3 + H_20 \longrightarrow OH \begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\mathbf{K}_{\mathbf{b}} = \frac{[OH^{-}][NH_{4}^{+}]}{[NH_{3}]}$

### 16.7 Calculations involving K<sub>a</sub>, K<sub>b</sub>, pH, pOH

A. <u>Strong Acids</u>:  $[HA] = [H^{\oplus}] \Rightarrow pH$ 

- $\mathrm{HCl} \rightarrow \mathrm{H}^{\oplus} + \mathrm{Cl}^{\ominus}$ • Complete ionization
- To know the concentration of the strong acid is to know the concentration of H  $\oplus$

# B. Strong Bases: complete formation of $OH \ominus$

- $[NaOH] = [OH^{\bigcirc}] \Rightarrow pOH, pH$ 
  - o for a group one metal hydroxide (NaOH, etc.), you get exactly as many moles of hydroxide as you put in of NaOH, and [NaOH] = [OH  $\bigcirc$  ]

○ NaOH → Na 
$$\oplus$$
 + OH  $\in$ 

- For a group two metal hydroxide, you get two moles of hydroxide for every one mole of ٠ formula that you put in.
  - $1 \operatorname{Ba(OH)}_2 \rightarrow 1 \operatorname{Ba}^{2+} + 2 \operatorname{OH}^{\bigcirc}$ 0
  - $\circ$  [OH  $\bigcirc$ ] = 2 ([Ba(OH)<sub>2</sub>]
- Since  $[OH \ominus]$  is knowable, you can then plug in, and find pOH, pH, and/or  $[H \ominus]$

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- 1. What is the pH of  $1.36 \times 10^{-3}$  M H<sub>2</sub>SO<sub>4</sub>?
- 2. An HCl solution has pH = 2.16. what is [HCl]?
- 3. What is pH for 0.013 M KOH solution?
- 4. What is pH for a solution that is 0.013 M in Ca(OH)<sub>2</sub>?
- 5. What is the pH if 22 g of Ba(OH)<sub>2</sub> (90 g/mol) is dissolved in 760 mL of water?

# C. <u>Weak Acids Calculation: Equilibrium, Ka, and pH</u> ICE-able (Section 17.3)

1. <u>Major Application 1</u>: Given a known K<sub>a</sub>, Solve for pH When a Known Amount of Weak Acid is Placed in a Known Amount of Water

Logic: Use  $K_a \rightarrow$  solve for [H  $\oplus$  ]  $\rightarrow$  solve for pH

<u>Steps</u>

- 1. Whether it's given in molarity or not, convert the sample/solvent ratio into Molarity
- 2. Set up an ICE table
- 3. Solve for equilibrium [H  $\oplus$  ]
  - Use simplifying assumption if K<sub>a</sub> is reasonably small
  - Use another simplifying assumption that the original population of  $H^{\oplus}$  is also reasonably small relative to the final, equilibrium amount of  $H^{\oplus}$
- 4. Use  $[H^{\oplus}]$  to solve for pH
- 5. Or: If  $K_a$  is small enough so that the simplifying assumption is reasonable, you can directly plug into the equation shown above

	HA	<del>~~</del>	H⊕	+	$A^{\ominus}$
Initial	[HA] <sub>init</sub>		1.0 x 10 <sup>-7</sup>		0
Change					
Equilibrium					
Equilibrium After Simplifying Assumptions					
K <sub>a</sub> =					

When is simplifying assumption safe? Use the >100K rule:		If $\frac{[\text{HA}]_{\text{init}}}{K_{a}} > 100 \rightarrow \text{simplifying assumption is safe}$		
When the simplifying assumptions are used:	K <sub>a</sub> =	$\frac{[\mathrm{H}^{+}]^{2}}{[\mathrm{HA}]_{\mathrm{init}}}$	$[\mathbf{H}^{\oplus}] = \sqrt{K_a \times [\mathbf{HA}]_{\text{init}}}$	
When the first simplifying assumption is not used (but the second one is)	K <sub>a</sub> =	$\frac{\left[H^{+}\right]^{2}}{\left[HA\right]_{init} - \left[H^{+}\right]}$	[H <sup>①</sup> ] requires a quadratic solution	

2. <u>Major Application 2</u>: Given a measured pH, Solve for  $K_a$  When a Known Amount of Weak Acid is Placed in a Known Amount of Water

Logic: Use pH 
$$\rightarrow$$
 solve for [H  $\oplus$ ]  $\rightarrow$  solve for K

$$K_{a} = \frac{\left[H^{+}\right]^{2}}{\left[HA\right]_{init}}$$

# Weak Acid pH/K<sub>a</sub> Problems

1. pH  $\rightarrow$  K<sub>a</sub> What is K<sub>a</sub> for an acid if an 0.15 M solution is prepared and found to have pH = 4.86?

Logic:

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2.  $K_a \rightarrow pH$  What is pH for a 0.15 M solution of an acid with  $Ka = 2.2 \times 10^{-6}$ ? Logic:

3. If an 0.23 M solution of an acid gives pH = 3.82, what is  $K_a$  for acid?

4. If a 0.11 M solution has a  $Ka = 1.3 \times 10^{-8}$  acid, what is pH?

# D. Weak Base Calculations involving K<sub>b</sub> and pH (Section 17.3)

	$A^{\bigcirc}$	$+ H_2O$	HA	+	$_{\rm HO} \odot$
Initial	$[A^{\bigcirc}]_{init}$		0		1.0 x 10 <sup>-7</sup>
Change					
Equilibrium					
Equilibrium After Simplifying Assumptions					
K <sub>b</sub> =					

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When the simplifying assumptions are used:	$\mathbf{K}_{\mathbf{b}} = \frac{[\mathrm{HO}^{-}]^{2}}{[\mathrm{A}^{-}]_{\mathrm{init}}}$	$[\mathbf{HO}^{\bigcirc}] = \sqrt{\mathbf{K}_{b} \times [\mathbf{A}^{-}]_{init}}$
When the first simplifying assumption is not used but the second one is	$K_b = \frac{[HO^-]^2}{[A^-]_{init}} - [HO^-]$	[HO <sup>()</sup> ] requires a quadratic solution

<b>Applications</b>		
1. pH → K <sub>b</sub>	Strategy:	$\mathrm{pH}  \mathrm{pOH}  [\mathrm{HO}^{\ominus}]  \mathrm{K}_{\mathrm{b}}$
2. K <sub>b</sub> → pH	Strategy:	$K_b \rightarrow [HO^{\odot}] \rightarrow pOH \rightarrow pH$

**<u>Problems: pH and Kb</u>** 1. pH  $\rightarrow$  Kb What is Kb if a 0.123 M solution of a weak base gives pH=10.62?

2.  $K_b \rightarrow pH$  If  $K_b$  for a weak base is  $1.6 \times 10^{-5}$ , what is the pH of a 0.222 M solution of the base?

- E. Relationship Between Ka and Kb for Conjugate acids/bases (Section 16.7, p 794)
- Review: stronger the acid, weaker the conjugate base (and vice versa)

$$K_{a} \times K_{b} = 1.0 \times 10^{-14}$$

Review Table 16.2

- 1. Given one, can solve for other.
- 2. Tables routinely provide only one; expect you to solve for other
- 3. Can rank relative strengths of acids(or bases) given info about conjugates
- 4. Toughest problem: given  $K_a$  for conjugate acid, calculate pH for a solution of weak base
  - Logic:  $K_a \rightarrow K_b \rightarrow [HO^{\odot}] \rightarrow pOH \rightarrow pH$

$$\frac{\text{Derivation of } \mathbf{K}_{a}\mathbf{K}_{b}=10^{-14} \text{ (not responsible for derivation, just for interest)}}{\mathbf{K}_{a}=\frac{[H_{3}0^{+}][A^{-}]}{[HA]} \mathbf{K}_{b}=\frac{[OH^{-}][HA]}{[A^{-}]}$$
So  $\mathbf{K}_{a}\mathbf{K}_{b}=\left(\frac{[H_{3}O^{+}][A^{-}]}{[HA]}\right)\frac{[OH^{-}][HA]}{[A^{-}]} = [H_{3}O^{+}][OH^{-}]=1.0 \times 10^{-14}$ 
Thus  $\mathbf{K}_{a}\mathbf{K}_{b}=\mathbf{K}_{w}=10^{-14}$ 

Acid Strength	Ka	<u>K</u> <sub>b</sub>	<u>Strength of</u> Conjugate Base
Strong	$K_a > 1$	$K_b < 1 \ge 10^{-14}$	Nonbasic
Weak	$1 \ge 10^{-14} < K_a < 1$	$1 \ge 10^{-14} \le K_b \le 1$	Weak
Nonacid	$K_a < 1 \ge 10^{-14}$	$K_{b} > 1$	Strong base

# Problems Involving Relationship between Ka and Kb for Conjugated Acid/Base

Substance	HF	HN <sub>3</sub>	HCN
Ka	6.8 x 10 <sup>-4</sup>	1.9 x 10 <sup>-3</sup>	4.9 x 10 <sup>-10</sup>
Relative Acidity			
Conjugate Base			
Relative Basicity			
K <sub>b</sub>			

1. Rank the acidity for the three weak acids, 1 being strongest.

2. Rank the basicity, 1 being the stongest, for: NaCN NaF NaN<sub>3</sub>

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Substance	HF	HN <sub>3</sub>	HCN
Ka	6.8 x 10 <sup>-4</sup>	1.9 x 10 <sup>-3</sup>	4.9 x 10 <sup>-10</sup>
Conjugate Base			
K <sub>b</sub>			

3. What is  $K_b$  for  $N_3$ ?

4. What is pH for a solution that is 0.12 M in NaF-?

Logic:

5. What is pH for a solution that is 0.20 M in NaCN?

Logic:

## **Polyprotic Acids: More than One H<sup>+</sup> Available (Section 17.4)** H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>CO<sub>3</sub>,...

1. Each  $H^+$  gets successively less acidic (by > 1000)

Relative			Conjugate	Relative
Acidity	Acid		Base	Basicity
	H <sub>3</sub> PO <sub>4</sub>	$K_{a1} = 10^{-3}$	$H_2PO_4^-$	
	$H_2PO_4^-$	$K_{a2} = 10^{-8}$	HPO4 <sup>2-</sup>	
	HPO <sub>4</sub> -2	$K_{a3} = 10^{-13}$	PO4 <sup>3-</sup>	

- 2. As acids in water, only consider the first ionization.
- When <u>base</u> is added, however, all H<sup>+</sup>'s come off (stoichiometry permitting) H<sub>3</sub>PO<sub>4</sub> + H<sub>2</sub>O = H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>PO<sub>4</sub><sup>-</sup> But H<sub>3</sub>PO<sub>4</sub> + 3 OH<sup>-</sup> → 3 H<sub>2</sub>O + PO<sub>4</sub><sup>3-</sup>
- 4.  $H_2SO_4$ : 1<sup>st</sup> strong, 2<sup>nd</sup> weak

water

water

5. Some anions are complex: both acidic and basic!!

$$HCO_{3}^{-} \stackrel{-}{\longrightarrow} H^{+} + CO_{3}^{2-}$$

$$H_{2}0$$

$$OH^{-} + H_{2}CO_{3}$$

### **Polyprotic Acid/Base Problems**

1. Which is the stronger acid?

H <sub>3</sub> PO <sub>4</sub>	$H_2PO_4^-$
$H_2SO_4$	HSO4 <sup>-</sup>

2. Which is the stronger base?

HCO <sub>3</sub> -	CO3 <sup>2-</sup>
HSO4-	$SO_4^{2-}$

TABLE 17.6 Ionization Equilibria for Two Triprotic Acids		
	Phosphoric A	Acid
(1) HO—	$ \begin{array}{c} 0 \\ \parallel \\ P \\ -OH \end{array} \xrightarrow{O} HO \\ \parallel \\ HO \\ -P \\ -OH \end{array} \begin{array}{c} 0 \\ -P \\ -O^{-} + H \\ -P \\ -OH \end{array} $	H <sup>+</sup> $K_{a_1} = 7.11 \times 10^{-3}$
(2) HO-	$ \begin{array}{c} O \\ \square \\ -P \\ -O \\ \square \\ OH \end{array} \begin{array}{c} O \\ -O \\ -O \\ -O \\ -P \\ OH \end{array} \begin{array}{c} O \\ \square \\ OH \end{array} \begin{array}{c} O \\ \square \\ O \\ OH \end{array} \begin{array}{c} O \\ \square \\ OH \end{array} $	• H <sup>+</sup> $K_{a_2} = 6.32 \times 10^{-8}$
(3) <sup>-</sup> O–	$ \begin{array}{c} O \\ -P \\ -P \\ OH \end{array} \begin{array}{c} O \\ -O \\ O \\ O \end{array} \begin{array}{c} O \\ -P \\ O \end{array} \begin{array}{c} O \\ O \end{array} \end{array}{c} O \\ O \end{array} \begin{array}{c} O \\ O \\ O \end{array} \end{array}{c} O \end{array} \begin{array}{c} O \\ O \\ O \end{array} \end{array}{c} O \end{array}{c} O \\ O \end{array} \end{array}{c} O \end{array}{c} O \end{array}{c} O \\ O \end{array}{c} O \end{array}{c} O \end{array}{c} O \\ O \\ O \end{array}{c} O \\ O \end{array}{c} O \end{array}{c} O \\ O \end{array}{c} O \\ O \end{array}{c} O \\ O \end{array}{c} O \\ O \\ O \\ O \end{array}{c} O \\ O \\ O \\ O \\ O \\ O \end{array} $ {c} O \\ O	H <sup>+</sup> $K_{a_3} = 4.5 \times 10^{-13}$
Citric Acid		
(1) HO—	$\begin{array}{c} CH_2COOH & CH_2COO \\ -C-COOH \rightleftharpoons HO-C-CO \\ -C-COOH & -C-CO \\ -CH_2COOH & CH_2CO \end{array}$	DO <sup>-</sup> DOH + H <sup>+</sup> $K_{a_1} = 7.44 \times 10^{-4}$ DOH
(2) HO—	$\begin{array}{ccc} CH_2COO^- & CH_2CO\\ -C-COOH \rightleftharpoons HO-C-CC\\ -C+2COOH & HO-C-CC\\ -C+2COOH & CH_2CO\end{array}$	$OO^-$ $OO^- + H^+   K_{a_2} = 1.73 \times 10^{-5}$ OOH
(3) HO-	$\begin{array}{ccc} CH_2COO^- & CH_2CO\\ -C-COO^- \rightleftharpoons HO-C-CO\\ -CH_2COOH & CH_2CO\\ -CH_2CO\\ -CH_2C$	$OO^-$ $OO^- + H^+   K_{a_3} = 4.02 \times 10^{-7}$ $OO^-$

# Polyprotic Acids: Each H becomes less acidic

Chemistry: The Science in Context 3/e Table 17.6 © 2012 W. W. Norton & Company, Inc.

### **Acid-Base Properties of Common Salts**

TABLE 17.7         Acid-Base Properties of Some Common Salts					
Anion Is Derived from a	Cation Is Derived from a	pH of Aqueous Solutions	Example		
Strong acid	Strong base	7	NaCl		
Strong acid	Weak base	<7	NH <sub>4</sub> Cl		
Weak acid	Strong base	>7	NaF		
Weak acid	Weak base	Depends on relative values of $pK_a$ and $pK_b$	$pK_a < pK_b$ , acidic; $NH_4F$ $pK_b > pK_a$ , basic; $NH_4HCO_3$ $pK_a = pK_b$ , neutral; $CH_3COONH_4$		

Chemistry: The Science in Context 3/e Table 17.7 © 2012 W. W. Norton & Company, Inc.

#### Acid-Base Properties of Salts (Ionic Compounds) (Section 17.6)

NH <sub>4</sub> Cl	MgBr <sub>2</sub>	NaCN
pH<7	pH=7	pH>7
acidic	neutral	basic

Recall: "salts" formed by acid/base reactions "salt"=<u>ionic</u>

Example:	SA/SB	$HCl + NaOH \rightarrow H_20 + NaCl$	neutral
	WA/SB	$HF + NaOH \rightarrow H_2O + NaF$	basic
	SA/WB	$HCl + NH_3 \rightarrow NH_4^+Cl^-$	acidic
	WA/WB	$HF + NH_3 \rightarrow NH_4^+F^-$	can't tell

Observations:

- 1. Salts can be acidic, basic, or neutral.
- 2. Depends on strengths of acids/bases from which they form.
- 3. The "ions" in the salts are conjugates; may be acidic or basic!!
- A. General Logic to Predict: Identify Ions individually. Check Cation, then Anion.
  - 1. Cations: acidic or neutral
    - a. Group I or II metal cations are <u>neutral</u> Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, ... No impact on pH
    - b. Ammoniums are acidic
      - $NH_4^+$ ,  $CH_3NH_3^+$  etc.
    - c. Al<sup>3+</sup>, T-metal cations are <u>acidic in water</u>. (Not for test)
      - $Al^{3+} \rightarrow [Al(H_2O)_6]^{3+} \xrightarrow{\longrightarrow} H^+ + [Al(OH)(H_2O)_5]^{2+}$ Weak acid

For test purpose, assume metal cations are neutral, ammonium cations acidic

2. Anions: basic or neutral

- a. Neutral: conjugates of strong acids Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>
- b. basic: conjugates of weak acids (or non acids) F<sup>-</sup>, ClO<sup>-</sup>, ...
- 3. "Amphoteric" anions derived from polyprotic acids: can be acidic or basic -not test responsible

HCO3<sup>-</sup>, H2PO4<sup>-</sup>, HSO3<sup>-</sup>

B. Predicting acidic/neutral/basic (qualitatively)

Cation	anion	salt solution	example
Neutral	neutral	neutral	NaCl, KNO <sub>3</sub>
Acidic	neutral	acidic	NH <sub>4</sub> Cl, Fe(NO <sub>3</sub> ) <sub>3</sub>
Neutral	basic	basic	NaF, K(ClO)
Acidic	basic	can't predict	$NH_4F$ , $Fe(N_3)_3$
		(without $\mathbf{K}$ s)	

# **Predicting Acid/Base Character for Ionic Formulas**

- 1. Predict as acidic, basic, neutral, or can't tell.
  - a. Na<sub>2</sub>SO<sub>3</sub> e. NaNO<sub>3</sub>

b.  $MgCl_2$  f.  $KN_3$ 

c.  $NH_4CN$  g.  $Li_2CO_3$ 

- d. Ba(NO<sub>3</sub>)<sub>2</sub> h. CH<sub>3</sub>NH<sub>3</sub>Br
- 2. Rank the following in terms of increasing pH, 1 being the lowest. (ID as strong/weak acid, strong/weak base, or neutral first!)

NaCl NH4Cl ZnF2 HNO3 KOH

## Molecular Structure and Acid/Base Strength (17.5)

- Why is something strong or weak? Acidic or Basic? Can we predict from structure, without K's?
- A. Key Factors on Acid Strength
  - **1.** Stability of conjugate  $A^{\bigcirc}$  and Electronegativity\*\*\*\*\*\*
    - Think Anion!
    - Think electronegativity and -electron love

 $CH_4 \rightarrow H^+ + \bigcirc CH_3$  Horrible. Carbon not electronegative, can't handle  $\bigcirc$ HF → H<sup>+</sup> + F  $\bigcirc$  Way stronger. Fluorine electronegative, can handle  $\bigcirc$ 

- 2. H-A bond strength: stronger  $\rightarrow$  <u>less</u> acidic
  - Why H-F (strong bond) is weak acid, but H-Cl, H-Br, H-I are strong acids
  - Row 2 bonds (H-F, O-H, N-H, C-H) usually stronger than row 3,4 analogs
- 3. Resonance
  - For two oxyanions, one with resonance is more stable than one without
- B. Practical Pattern

1. Horizontal Periodic Pattern: Acidity increase left  $\rightarrow$  right CH<sub>4</sub> NH<sub>3</sub> H<sub>2</sub>O HF K<sub>a</sub> 10<sup>-50</sup> 10<sup>-32</sup> 10<sup>-14</sup> 10<sup>-4</sup>

Note: e<sup>-</sup> love, electronegativity/bond-polarity, anion stability all agree

Rank: Acidity of: SiH<sub>4</sub> SH<sub>2</sub> HCl PH<sub>3</sub>

Vertical Periodic Pattern: Acidity Increases Top → Bottom
 -due to decreasing H-A bond strength (even though contrary to e<sup>-</sup> love)

HF <	HCl	H <sub>2</sub> O <	< H <sub>2</sub> S $<$	H <sub>2</sub> Se
Weak	strong	$K_a = 10^{-14}$	10-9	10-6

Note: Basicity of conjugates linked!!

Horizontal:  $\bigcirc$  NH<sub>2</sub> > F  $\bigcirc$  Vertical: F  $\bigcirc$  > Cl  $\bigcirc$ 

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C. "Oxoacids" : "Extra" Oxygens's increase acidity (17.5)

HClO<sub>4</sub> > HClO<sub>3</sub>> HClO<sub>2</sub> > HClO Strong weak  $\begin{array}{ll} H_2SO_4 > H_2SO_3 \\ strong & weak \end{array}$ 

Why? Extra electron-loving oxygen

- 1. Stabilizes resulting anion
- 2. Polarizes O-H
- 3. Weakens O-H

# • Any <u>Neutral</u> Oxoacid with $\geq 2$ extra O's is a <u>strong</u> Acid

• Compare how many oxygens there are versus hydrogens

Strong: H<sub>2</sub>SO<sub>4</sub>, HClO<sub>3</sub> weak: H<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>3</sub>

Carboxylic Acids: Famous class of oxoacids: RCOOH or RCO<sub>2</sub>H (R is usually an H or a carbon chain.)

• Resonance stabilization of conjugate anion makes the anion more stable

$$\begin{array}{c} O \\ H \\ H \end{array} \xrightarrow{H} \begin{array}{c} H \\ H \end{array} \xrightarrow{H} \begin{array}{c} O \\ H \end{array} \xrightarrow{O} \begin{array}{O} \end{array} \xrightarrow{O} \begin{array}{O} O \\ H \end{array} \xrightarrow{O} \begin{array}{O} O \\ \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \\ \end{array} \xrightarrow{O} \begin{array}{O} O \\ \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \\ \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \\ \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \\ \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \\ \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} O \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \begin{array}{O} \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \end{array} \xrightarrow{O} \end{array}$$

	Gen Chem II Jasperse	Ch. 17a Chemical Equilibrium: Acid-Base Eq	uilibria in Water 27
<u>Pr</u>	edicting Acid/Base Prop	erties and Trends	Why?
1.	Which are acidic vs. bas	c vs. neutral in water?	
	HClO <sub>3</sub>	CH <sub>3</sub> COOH CH <sub>3</sub> NH <sub>2</sub> Ca(OH) <sub>2</sub>	
2.	Rank Acidity (1 stronges	it)	
	HF H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> CH <sub>4</sub>	
3.	Rank Acidity (1 stronges	.t)	
	HClO <sub>4</sub>	$HClO_3 \qquad H_2SO_4 \qquad H_2SO_3$	
4.	Rank Acidity (1 stronges	t)	
	$H_2O$ $H_2S$	$H_2Se$	
5.	Rank Acidity (1 stronges	t)	
	HBr H <sub>2</sub> Se	H <sub>3</sub> As H <sub>4</sub> Ge	
6.	Which would be stronge	r?	
	HBrO <sub>3</sub>	vs HBrO	
7.	Rank Basicity (1 stronge	st)	
		$ \ominus_{CH_3} \ \ominus_{NH_2} \ \ominus_{OH} \ F \ominus $	
8.	Rank Basicity (1 stronge	st)	
	HPO4 <sup>2-</sup>	$_{\text{H}_2\text{PO}_4} \odot _{\text{HSO}_4} \odot$	

# Lewis Acids and Bases: focus on electron pairs, not H<sup>+</sup> movement. (18.1)

Lewis acid: e- pair acceptor	Covers	"acid-base"	chemistry	that	doesn't
Lewis base: e- pair donor	involve	$\mathrm{H}^{+}$			





Other Examples



Notes: 1. A "base" must have a lone pair (F<sup>-</sup>, OH<sub>2</sub>, NH<sub>3</sub>, ....)
2. All <u>anions</u> have lone pairs → Lewis Base potential
3. An "acid" must be able to accept a lone pair -all <u>cations</u> can!! -some neutrals: BF<sub>3</sub>, SO<sub>2</sub>, ...

### Lewis Acid/Base Problems

1. Which would <u>not</u> be a Lewis acid?

AlCl<sub>3</sub> Ti<sup>4+</sup>

ZnSO<sub>4</sub>

- 2. Identify the Lewis acid and Lewis Base
- a.  $Fe^{3+} + 6 H_2O \rightarrow [Fe(H_2O)_6]^{3+}$  b.  $H^+ + CH_3NH_2 \rightarrow CH_3NH_3$

 $NO_3 \Theta$ 

c.  $\operatorname{Br-CH}_3 + I \stackrel{\bigcirc}{\rightarrow} \operatorname{Br}^{\bigcirc} + I-\operatorname{CH}_3$ d.  $\operatorname{Ni}^{2+} + 4\operatorname{N}_3 \stackrel{\bigcirc}{\rightarrow} [\operatorname{Ni}(\operatorname{N}_3)_4]^{2-}$  CH. 16 Acid-Base Chemistry Math Review Key Equations, Numerical Relationships 1. [H<sup>+</sup>][HO<sup>-</sup>] = 1.00 x 10<sup>-14</sup>

- 2.  $pH = -log[H^+]$   $pOH = -log[OH^-]$   $[OH^-] = 10^{-pH}$  (on calculator, enter -pH, then punch the  $10^x$  button)  $[OH^-] = 10^{-pOH}$  (on calculator, enter -pOH, then punch the 10x button)
- 3. pH + pOH = 14 pH = 14 pOH

#### Weak acid problems

$$K_a = [H^+][A^-]/[HA]$$

but when HA is placed in water,  $[H^+] = [A^-]$  so:

4.  $K_a = \frac{[H^+]^2}{[HA]_{init}}$  5.  $[H^{(+)}] = \sqrt{K_a \times [HA]_{init}}$ 

 $\mathbf{x} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ 

When the simplifying assumptions are used:

When the first simplifying assumption is not used (but the second one is)  $6. \quad K_a = \frac{[H^+]^2}{[HA]_{init} - [H^+]} \qquad [H^{\textcircled{+}}] \text{ requires}$  a quadratic solution

7. Quadratic Equation: for 
$$ax^2 + bx = c = 0$$

**base problems**  $K_b = [Base-H^+][OH^-]/[Base]$  but when Base is place in water,  $[Base-H^+] = [OH^-]$  so:

When the simplifying assumptions are used:	8. $K_b = \frac{[HO^-]^2}{[Base]_{init}}$	9. $[HO^{\bigcirc}] = \sqrt{K_b \times [Base]_{init}}$
When the first simplifying assumption is not used but the second one is	10. $K_b = \frac{[HO^-]^2}{[Base]_{init}} - [HO^-]$	[HO <sup>(C)</sup> ] requires a quadratic solution

11.  $K_aK_b = 10^{-14}$  for a conjugate acid/base pair. Note: This relationship is routinely used when a K value for your acid or base is not provided, but the K value for it's conjugate is. So get it indirectly.

# Some Calculation Logic Scenarios

- 1. Strong acid  $\rightarrow$  pH[Strong acid]  $\rightarrow$  [H  $\oplus$ ]  $\rightarrow$  pH2. Strong base  $\rightarrow$  pH[Strong base]  $\rightarrow$  [HO  $\bigcirc$ ]  $\rightarrow$  pOH  $\rightarrow$  pH
- 3. Weak acid +  $K_a \rightarrow pH$  [Weak acid] +  $K_a \rightarrow [H^{(+)}] \rightarrow pH$
- 4. pH of weak acid  $\rightarrow K_a$  pH  $\rightarrow$  solve for [H  $\oplus$ ]  $\rightarrow K_a$
- 5. Weak base +  $K_b \rightarrow pH$  [Weak base] +  $K_b \rightarrow [HO \bigcirc ] \rightarrow pOH \rightarrow pH$
- 6. pH of weak base  $\rightarrow K_b$  pH  $\rightarrow$  solve for [HO  $\bigcirc$ ]  $\rightarrow$  pOH  $\rightarrow$  pH
- 7. Weak base + K<sub>a</sub> of conjugate acid  $\rightarrow$  pH  $K_a \rightarrow K_b \rightarrow [HO^{\bigcirc}] \rightarrow pOH \rightarrow pH$

Simple Acid-Base Concept Map

