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
        - o "steady state" = "equilibrium"
    - It may seem like nothing is changing or happening, but is molecular action ("dynamic")

3. Previous Examples
    1. Vapor Pressure (closed container) Liquid $\rightleftharpoons$ vapor

    2. Saturated solution solid $\rightleftharpoons$ dissolved

    3. Weak acid/weak electrolyte $HF \rightleftharpoons H^+ + F^{\ominus}$

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

<u>The Equilibrium "Constant"</u>

A. Intro

Rate forward:

$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$ $\boxed{\text{At equilibrium, rate}_{\text{forward}} = \text{rate}_{\text{reverse}}}$

Rate reverse:

Equality:

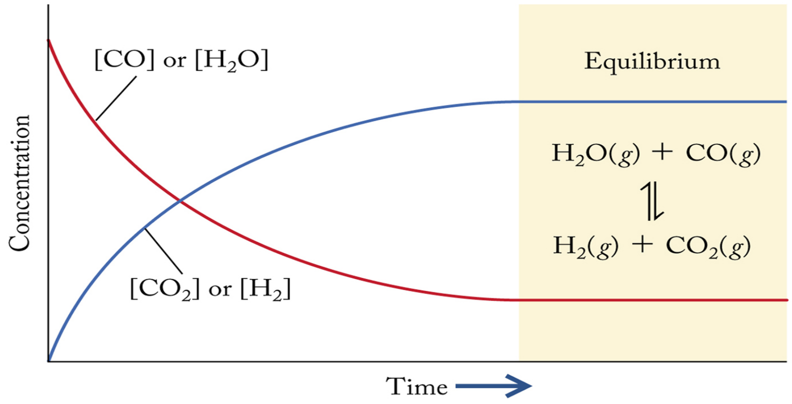
K_c

Rearrange:

<u>Notes</u>

1. K_c is a constant
2. Each reaction has its own unique "K" constant
    - called the "EQUILIBRIUM CONSTANT"
3. Ratio of **<u>product</u>** **<u>over reactant</u>**
    - **<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:



Chemistry: The Science in Context 3/e Figure 16.1
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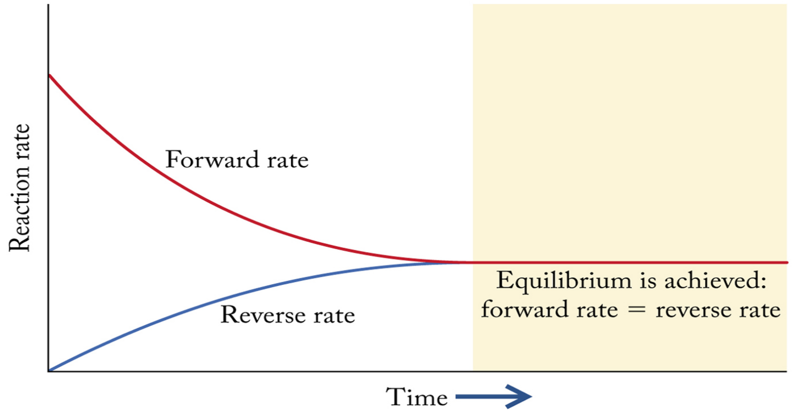
1. At equilibrium, amounts stay constant.
2. Prior to equilibrium amounts were changing.

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



Chemistry: The Science in Context 3/e Figure 16.2
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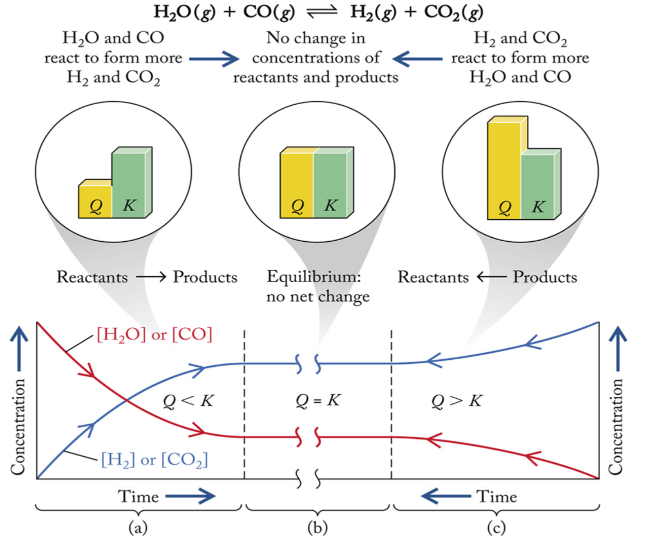
1. At equilibrium, rates are equal
2. Prior to equilibrium, rates were not equal.

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



Chemistry: The Science in Context 3/e Figure 16.5
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1. "K" is the product/reactant ratio, if at equilibrium.
2. "Q" is the actual product/reactant ratio, whether at equilibrium or not
3. If "Q" = "K", you're at equilibrium
4. If "Q"≠ "K", you're NOT at equilibrium.
5. If "Q" < "K", need to make more product.
6. If "Q" > "K", need to make more reactants.

B. Qualitative things the value of K tells us:

1. At equilibrium, is the product favored or the reactant?
    - K >> 1 → product favored
    - K << 1 → reactant favored

Concept Problem: $A \rightleftharpoons B$ Find [B]/[A] ratios if:

a. $K_c = 10^3$ b. $K_c = 10^{-3}$

2. If the **actual** 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: $A \rightleftharpoons B$ $K_c = 0.20$

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

Concept Problem: $A \rightleftharpoons B$ $K_c = 0.20$

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 **not** 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)

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

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_c Expressions

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

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

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
  - A(g), B(aq) Yes
  - 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. $CuOH(s) \rightleftharpoons Cu^+(aq) + OH^-(aq)$

$$K_1 = \frac{[Cu^+][OH^-]}{\underbrace{[CuOH]}_{\text{Constant}}} \quad \text{so} \quad \mathbf{K_2=[Cu^+][OH^-]}$$

Write K Expressions

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

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

c. $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

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 $A + B \rightleftharpoons C$ $K_c=10^4$

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

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

   What is K for $2A + 2B \rightleftharpoons 2C$
   (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 **initial** concentrations, and **at least one final concentration**, but then must use the "ICE" (**I**nitial-**C**hange-**E**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 $A \rightleftharpoons B + C$, find K_c if [A] = 0.26 M, [B] = 0.26 M, [C] = 0.93 M.

2. For $A + 2B \rightleftharpoons 2C + D$, find K_c if [A] = 0.15, [B] = 0.18, [C]= 2.0×10^{-4}, [D] = 3.0×10^{-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
- b. Use the "ICE" (**I**nitial-**C**hange-**E**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_c
2. Make an "ICE" table, and enter the knowns
   - a. Initial
   - b. Change
   - c. Equilibrium
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_c 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.	2A +	2B $\rightleftharpoons$	C +	2D	K_c=
I	0.20	0.30	0	0.10	
C					
E	0.10				K_c=

4.	A +	2B $\rightleftharpoons$	C +	D	K_c=
I	0.20	0.20	0	0	
C					
E	0.15				K_c=

Chemical Meaning of K

1. $K_c >> 1$ Product Favored
2. $K_{c<<}$ 1 Reactant Favored
3. $K_c \approx 1$ Significant quantities of both products and reactants---calculations required

- There are many cases where K_c « 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. (**16.5 Equilibrium Constants K and Reaction Quotients Q)**

K=equilibrium Q=actual 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. $A + B \rightleftharpoons C$ $K_c = 72$

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

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_c

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the known initial concentrations
   a. Initial
   b. Change
   c. Equilibrium
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 …..
   - **If K is small** so that "x" is likely to be small, **use the simplifying assumption** that $[A]_{initial}$ – "x" = $[A]_{initial}$
     - 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. **Once "x" is known, use it to solve for the actual equilibrium concentrations**
8. Check: Does Answer Make Any Sense?
9. Check: If you made the "simplifying assumption", was it justified? (Was "x" < 5% of $[A]_{initial}$?)

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).

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

If "x" ="	Then 0.20-x =	After roudoff to 2 sig. fig.	Is simplifying assumption valid?
2×10^{-7}	$0.20 - 0.0000002 =$		
2×10^{-6}	$0.20 - 0.000002 =$		
2×10^{-5}	$0.20 - 0.00002 =$		
2×10^{-4}	$0.20 - 0.0002 =$		
2×10^{-3}	$0.20 - 0.002 =$		
2×10^{-2}	**$0.20 - 0.02 =$**		

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

Problems

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

Quadratic Required. K too large to justify simplification $N_2O_4 \rightleftharpoons 2NO_2$ $K = 0.211$

Initial

Change

Equilibrium

Equilibrium:

$[N_2O_4]$

$[NO_2]$

2. Find final concentrations:

$HA \rightleftharpoons H^+ + A^-$ $K_c = 1.6 \times 10^{-7}$

Initial Concentrations 0.20 0 0

Change

Equilibrium

Equilibrium with Simplifying Assumption

Equilibrium:

$[HA]$

$[H^+]$

$[A^-]$

3. Find final concentrations given:

	A	$\rightleftharpoons$	B	$+$	C	$K_c = 2.4 \times 10^{-6}$
Initial	0.30					
Change						
Equilibrium						
Equilibrium with Simplifying Assumption						

Equilibrium:

4. Find final concentrations given:

	A	$\rightleftharpoons$	B	$+$	C	$K_c = 0.018$
Initial	0.30					
Change						
Equilibrium						

Equilibrium:

5. Find final concentrations given: **A "Square Root" Simplification**

	A	$+$	B	$\rightleftharpoons$	C	$+$	D	$K_c = 0.060$
Initial	0.30		0.30					
Change								
Equilibrium								

6. Find final concentrations given: Solution with and Without Simplifying Assumption

$A \rightleftharpoons 2B + C \qquad K_c = 2.0 \times 10^{-8}$

Initial 0.20

Change

Equilibrium

Equilibrium with Simplifying Assumption

With Simplifying Assumption | Without Simplifying Assumption

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

$A \rightleftharpoons 2B + C$

With

I	0.20	0	0
C	-x	2x	x
E	.20-x	2x	x
E*	0.20	x	x

So $K = 2.0 \times 10^{-8} = \dfrac{(2x)^2 x}{0.20} = \dfrac{4x^3}{.20}$

$0.4 \times 10^{-8} = 4x^3$ **Easy**

$x^3 = 1.0 \times 10^{-9}$ **$x = 1.0 \times 10^{-3}$**

Without (using .20 – x for [A] at eq)

$K = 2.0 \times 10^{-8} = \dfrac{(2x)^2 x}{0.20 - x}$

So $2.0 \times 10^{-8} (0.20 - x) = 4x^3$

So $4.0 \times 10^{-9} - 2.0 \times 10^{-8} x = 4x^3$

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	↑ T, when $\Delta H > 0$	Forward – K increases
	↑ T, when $\Delta H < 0$	Reverse – K decreases
3. Volume	↑ V, when $\Delta n_{gas} > 0$	Forward
	↑ V, when $\Delta n_{gas} = 0$	No effect
A change in volume impacts gas pressure. An increase in volume reduces pressure.	↑ V, when $\Delta n_{gas} < 0$	Reverse

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

$2\ A\ (g) \rightleftharpoons B\ (g) + \text{Heat}$ **$\Delta H < 0$ (exothermic)**

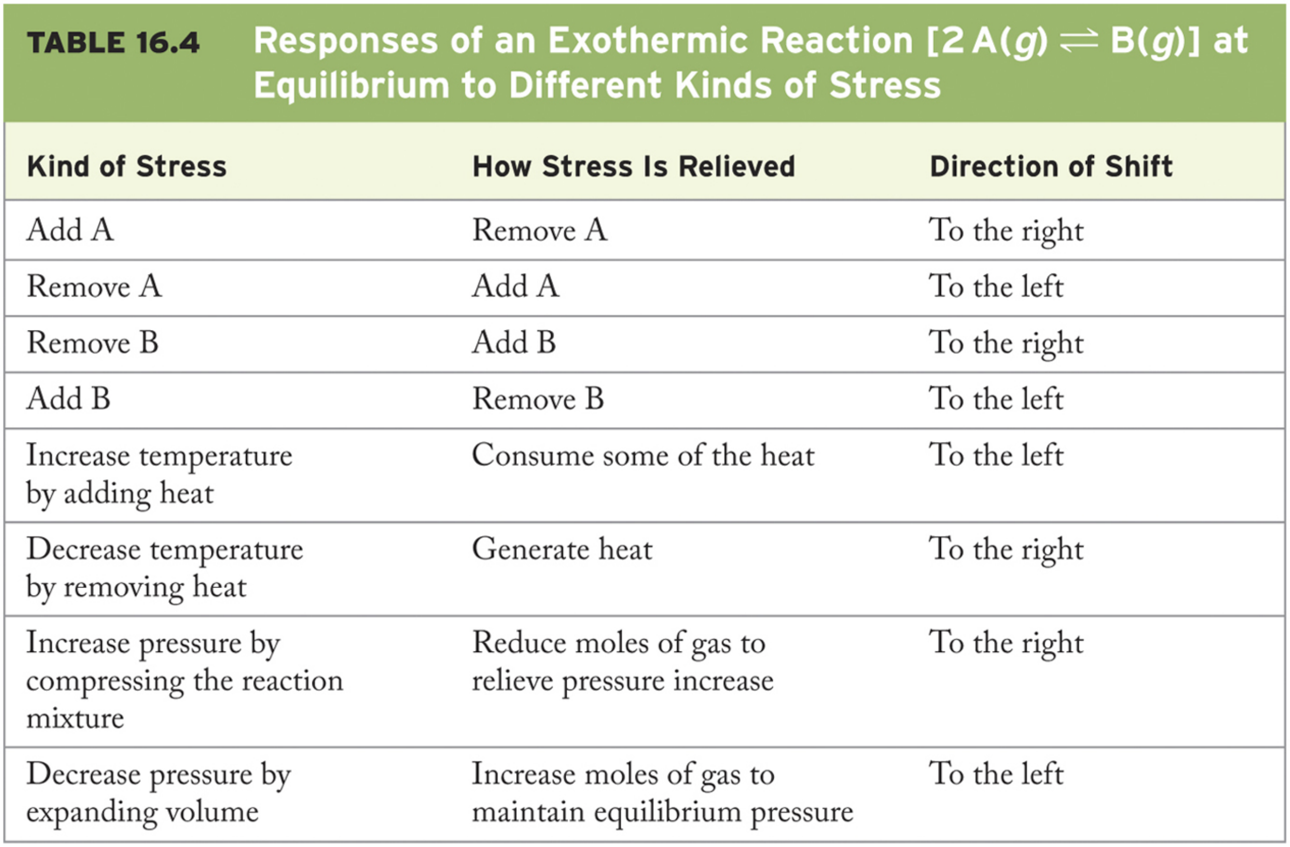


TABLE 16.4 **Responses of an Exothermic Reaction [$2\,A(g) \rightleftharpoons B(g)$] at Equilibrium to Different Kinds of Stress**

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 temperature by adding heat	Consume some of the heat	To the left
Decrease temperature by removing heat	Generate heat	To the right
Increase pressure by compressing the reaction mixture	Reduce moles of gas to relieve pressure increase	To the right
Decrease pressure by expanding volume	Increase moles of gas to maintain equilibrium pressure	To the left

Chemistry: The Science in Context **3/e Table 16.4**

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 $Q = K$
   - **<u>NOTE: K value does not change</u>**
   - many chemical ways to remove a chem (precipitations, acid-base, etc.)

<u>Example</u>

$$A + B \rightleftharpoons C + D$$

<u>Disruption</u>	<u>Immediate Impact on Q</u>	<u>Direction to Restore Eq</u>	Response (following disruption) :			
			[A]	[B]	[C]	[D]
Add A	$Q < K$	Forward	↓	↓	↑	↑
Add B						
Add C						
Add D						
Remove A						
Remove B						
Remove C						
Remove 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 <u>get rid of gas molecules</u> 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

<u>Disruption</u>	**<u>Response</u>**
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 molecules</u> to fill the container and <u>restore pressure</u>
   b. When the volume shrinks, you want to <u>get rid of gas molecules</u> to unclutter the container and to restore the original pressure

Volume Example

$$2H_2\,(g) + O_2\,(g) \rightleftharpoons 2H_2O\,(g)$$

Volume Change	Direction to Restore Eq	Response of moles of: $2H_2\,(g) + O_2\,(g) \rightleftharpoons 2H_2O$
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 → shift to right → K rises
        - $\Delta H > 0$ Drop in temp → shift to left → K drops
        - $\Delta H < 0$ Rise in temp → shift to left → K drops
        - $\Delta H < 0$ Drop in temp → shift to right → K rises

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

$A \rightleftharpoons B$ $\Delta H < O$

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

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

$A \rightleftharpoons B$ $\Delta H > O$

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

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

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

Disruption	Direction to Restore Eq	Response of moles of: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Response of K Value
1. Temperature Increase			
2. Volume Increase			
3. Added N_2			
4. Removal of NH_3			
5. Reduced temperature			
6. Added NH_3			
7. Removal of N_2			
8. Volume reduction			

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: $(3.2e\text{-}5 - x)^2 = 1.02e\text{-}9 – 6.4e\text{-}5\ x + x^2 = x^2 – 6.4e\text{-}5\ x + 1.02e\text{-}9$

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: $0.14 – 3.6e\text{-}5 = 0.14$ $1.23e\text{-}3 – 1.0e\text{-}6 = 1.23e\text{-}3$

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: $0.0158 – 0.316x = x$
Solve for "x": $x = 0.012$

5. $m = x^n$

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:

$25 = x^3$ $x = 2.92$
$1.48e\text{-}6 = x^3$ $x = 0.0114$
$2.14e\text{-}13 = x^4$ $x = 6.80e\text{-}4$

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. Initial
    b. Change
    c. Equilibrium
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_c 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_c

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the known initial concentrations
    a. Initial
    b. Change
    c. Equilibrium
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 …..
    - **If K is small** so that "x" is likely to be small, **use the simplifying assumption** that $[A]_{initial} - \text{"x"} = [A]_{initial}$
        - 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. **Once "x" is known, use it to solve for the actual equilibrium concentrations**
8. Check: Does Answer Make Any Sense?
9. Check: If you made the "simplifying assumption", was it justified? (Was "x" < 5% of $[A]_{initial}$?)

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	↑ T, when $\Delta H > 0$	Forward – K increases
	↑ T, when $\Delta H < 0$	Reverse – K decreases
3. Volume	↑ V, when $\Delta n_{gas} > 0$	Forward
	↑ V, when $\Delta n_{gas} = 0$	No effect
A change in volume impacts gas pressure. An increase in volume reduces pressure.	↑ V, when $\Delta n_{gas} < 0$	Reverse

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 → $[H^+]$ has huge impact on rates

17.1 Bronsted-Lowry Concept of Acids/Bases

	Bronsted-Lowry Definition	Lewis Definition
Acid	**$H^{\oplus}$ donor**	Lone-pair acceptor
Base	**$H^{\oplus}$ acceptor**	Lone-pair donor

Acid and water: $HCl + H_2O \rightarrow H_3O^{\oplus} + Cl^{\ominus}$

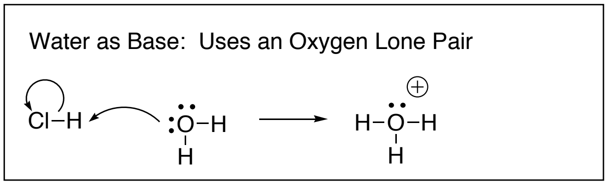
Base and water: $NH_3 + H_2O \rightleftharpoons HO^{\ominus} + NH_4^{\oplus}$

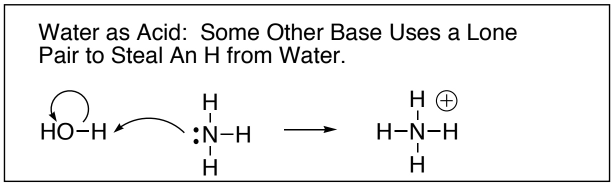
Notes:

1. An **acid** **loses** an $H^{\oplus}$ and gets more negative
   - A neutral acid becomes an **anion** after loss of $H^{\oplus}$ $HCl \rightarrow Cl^{\ominus}$
   - A cationic acid becomes neutral after loss of $H^{\oplus}$ $H_3O^{\oplus} \rightarrow H_2O$
2. A **base** **gains** an $H^{\oplus}$ and gets more positive
   - A neutral base becomes a **cation** after gain of $H^{\oplus}$ $H^{\oplus} + NH_3 \rightarrow NH_4^{\oplus}$
   - An anionic base becomes neutral after gain of $H^{\oplus}$ $H^{\oplus} + {}^{\ominus}OH \rightarrow H_2O$

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 as Base: Uses an Oxygen Lone Pair


Water as Acid: Some Other Base Uses a Lone Pair to Steal An H from Water.

4. Water can function as either a base (accepting an $H^{\oplus}$ when an acid is placed in water) or as an acid (donating an $H^{\oplus}$ 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: $H^{\oplus}$ = "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
HF	$F^{\ominus}$
HCl	$Cl^{\ominus}$
H_2SO_4	$HSO_4^{\ominus}$
$HSO_4^{\ominus}$	SO_4^{2-}

Conjugate Acid	Conjugate Base
$H_3O^{\oplus}$	H_2O
H_2O	$HO^{\ominus}$
$NH_4^{\oplus}$	NH_3

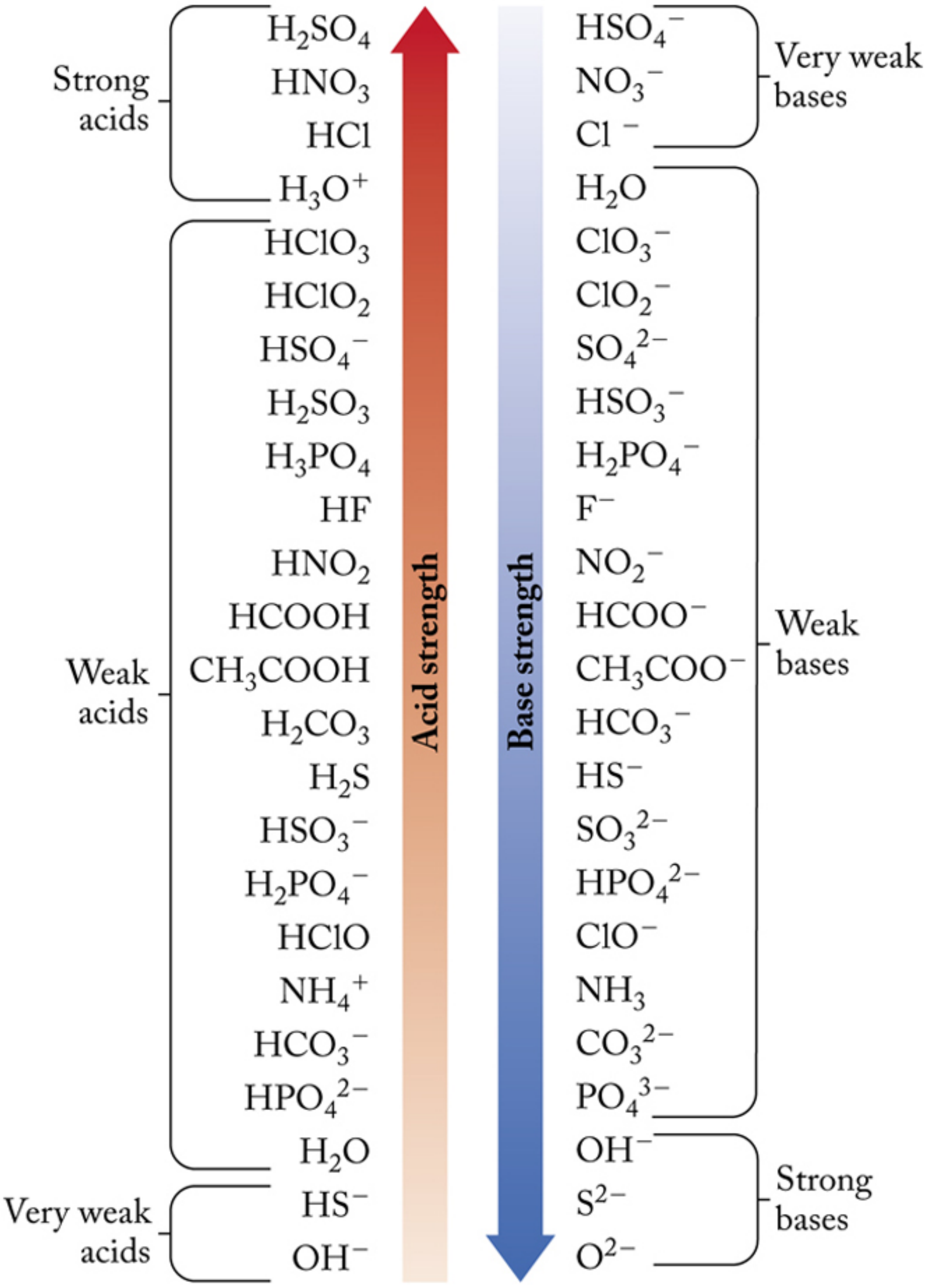
1. Draw the conjugate bases	2. Draw the conjugate acids
a. HCN	a. SO_4^{2-}
b. HBr	b. NH_3
c. CH_4	c. $Cl^{\ominus}$

Relative Strengths of Acids and Bases

	Acid		Base	
Strong acids, 100% Ionized in H_2O	HCl		$Cl^{\ominus}$	Nonbases
	H_2SO_4		$HSO_4^{\ominus}$	
	$H^{\oplus}$ (aq) = H_3O^+		H_2O	
	HSO_4^-		SO_4^{2-}	
	HF		$F^{\ominus}$	
	H_2CO_3		$HCO_3^{\ominus}$	
	$NH_4^{\oplus}$		NH_3	
	$HCO_3^{\ominus}$		CO_3^{2-}	
	H_2O		$OH^{\ominus}$	
Nonacids	$OH^{\ominus}$		O^{2-}	Strong bases, 100% Protonated in H_2O
	H_2		$H^{\ominus}$	

- 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**

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_2O = base)
    b. Returning from right back to left, O is the giver ($H_3O^{\oplus}$ = acid) and F the acceptor ($F^{\ominus}$ = base)

$$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus}$$

Notes

1. Each side 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 base on the left, it's conjugate acid appears on the right side.

Problems: 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. $NH_3 + HClO \rightleftharpoons NH_4^{\oplus} + ClO^{\ominus}$

b. $HCN + H_2PO_3^{\ominus} \rightleftharpoons H_3PO_3 + CN^{\ominus}$

c. $CH_3NH_2 + CH_3OH_2^{\oplus} \rightleftharpoons CH_3NH_3^{\oplus} + CH_3OH$

d. $H_2O + HSO_4^{\ominus} \rightleftharpoons H_3O^{\oplus} + SO_4^{-2}$

Notes/Notice:

1. Notice the change in H-count and the change in charge for each of these
2. The acid on the left always loses a hydrogen and becomes one step unit more negative
3. The base on the left always gains a hydrogen and becomes more positive
4. **Cations usually function as acids**
    - They are positive, and want to get rid of $H^{\oplus}$ to alleviate positive charge
5. **An anion usually function as a base**
    - It usually wants to get more positive, and the negative charge always means it has a lone-pair available
    - Some exceptions, such as example "d"

Acid/Base Strength

1. **Strong acids** are better $H^{\oplus}$ donors than **weaker acids**
   Strong bases are better $H^{\oplus}$ acceptors than weaker bases

2. Acid/base strength depends on love for $H^{\oplus}$

- Consider the conjugate pair of $Z^{\ominus}$ and HZ
  a. High $H^{\oplus}$ Love: Suppose $Z^{\ominus}$ really loves $H^{\oplus}$
     1. Then $Z^{\ominus}$ 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 $H^{\oplus}$ unless it's a base who loves $H^{\oplus}$ even more
  b. Low $H^{\oplus}$ Love: Suppose $Z^{\ominus}$ doesn't have much love for $H^{\oplus}$
     1. Then $Z^{\ominus}$ 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 $H^{\oplus}$ more can easily steal the $H^{\oplus}$ away and leave $Z^{\ominus}$ behind

3. Love for $H^{\oplus}$ and the Competition between Competing Bases

$$\underset{\text{acid}}{HX} \quad + \quad \underset{\text{base}}{Z^{\ominus}} \quad \rightleftharpoons \quad \underset{\text{base}}{X^{\ominus}} \quad + \quad \underset{\text{acid}}{HZ}$$

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

a. Whichever base loves $H^{\oplus}$ **more** will be the **stronger base**, and the equilibrium will drive to the opposite direction → to the conjugate acid of the strong base
b. Whichever base loves $H^{\oplus}$ **less** 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

4. Acid-Base Strength and the Direction of Acid-Base Equilibria

*Acid/base reactions **always** go from stronger acid/base to weaker acid + base

K favors weaker

HCl +	NaOH →	H_2O +	$Na^{\oplus}$ $Cl^{\ominus}$	K large (K >>1)
Stronger acid	stronger base	weaker acid	weaker base	

H_2S +	$F^{\ominus}$ ←	HF +	$HS^{\ominus}$	K small (K <1)
weaker acid	weaker base	stronger acid	stronger base	

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_2. Predict the "direction" of the reaction, and say whether K will be greater or less than 1. (ID each as acid or base)

$HF + Na^{\oplus} NO_2^{\ominus}$ $Na^{\oplus} F^{\ominus} + HNO_2$ K 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.

$HA + B^{\ominus}$ $A^{\ominus} + HB$ $K = 10^3$

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

$HCN + SO_4^{2-}$ $HSO_4^{\ominus} + CN^{\ominus}$ $K = 10^{-5}$

5. **Direct Relationship between strengths of conjugate acid/base**

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% Ionized in H_2O	HCl	$Cl^{\ominus}$	Nonbases
	H_2SO_4	$HSO_4^{\ominus}$	
	$H^{\oplus}$ (aq) = H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	HF	$F^{\ominus}$	
	H_2CO_3	$HCO_3^{\ominus}$	
	$NH_4^{\oplus}$	NH_3	
	$HCO_3^{\ominus}$	CO_3^{2-}	
	H_2O	$OH^{\ominus}$	
Nonacids	$OH^{\ominus}$	O^{2-}	Strong bases, 100% Protonated in H_2O
	H_2	$H^{\ominus}$	

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

6. **Strong Acids versus Weak Acids versus Nonacids. How do they Differ in Water?**

a. **Strong acids** ionize completely in water

$$HCl + H_2O \rightarrow H_3O^{\oplus} + Cl^{\ominus}$$

- There is **NO** 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

$$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus} \qquad K = 10^{-5}$$

- There is plenty of HF left. But meaningful amounts of $H_3O^{\oplus}$ + $F^{\ominus}$ ions present.
- Some "weak" acids are stronger or weaker than others.

c. **Nonacids:** Don't ionize at all in water.

- No equilibrium exists
- Stays completely on the left side

$$CH_4 + H_2O \leftarrow H_3O^{\oplus} + CH_3^{\ominus}$$

17.1 Recognizing Acids

1) **Memorize** Six **strong acids**

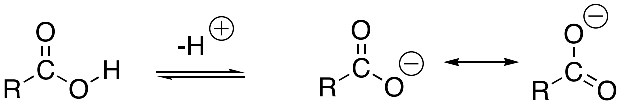
HCl HBr HI HNO_3 H_2SO_4 $HClO_4$

- **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_2S H_2CO_3 → acids
      CH_4
      NH_3 SiH_4 → 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_3COOH, C_2H_5COOH, 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 …	$Ca(OH)_2$, $Ba(OH)_2$ …

$NaOH\,(aq) \rightarrow Na^{\oplus}\,(aq) + {}^{\ominus}OH(aq)$ (Complete)
1mole 1 mole

$Ca(OH)_2\,(aq) \rightarrow Na^{\oplus}\,(aq) + 2\,{}^{\ominus}OH(aq)$ (Complete)
1mole 2 mole

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

$CuOH(S) \rightleftharpoons Cu^{+}(aq) + OH^{-}(aq)$
1mole less than 1mole (Incomplete)

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

Parent: $H_3N: + H_2O \rightleftharpoons {}^{\ominus}OH + NH_4^{\oplus}$
weak base weak acid

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

Amines Bases (examples)	Conjugate acids = "Ammonium" Ions
NH_3	$NH_4^{\oplus}$
CH_3NH_2	$CH_3NH_3^{\oplus}$
$(CH_3)_2NH$	$(CH_3)_2NH_2^{\oplus}$
$C_6H_5NH_2$	$C_6H_5NH_3^{\oplus}$

- 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 non base**

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	**Strength of Conjugate Base**
Strong acid	Nonbasic
Weak acid	Weak Base
Non-acid	Strong base

Base Strength	Anion	Conjugate Acid	Acid Strength
	$F^{\ominus}$	HF	
	${}^{\ominus}CN$	HCN	
	$H_2PO_4^{\ominus}$	H_3PO_4	
	$Cl^{\ominus}$	HCl	
	$H^{\ominus}$	H_2	
	${}^{\ominus}CH_3$	CH_4	

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_3	H_2SO_4	$HClO_4$
Six Non-Basic Anions	$Cl^{\ominus}$	$Br^{\ominus}$	$I^{\ominus}$	$NO_3^{\ominus}$	$HSO_4^{\ominus}$	$ClO_4^{\ominus}$

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. $CH_3CH_2NH_2$

d. CH_3CH_2COOH

e. H_2SO_4

f. H_3PO_4

g. HClO

h. $ClO^{\ominus}$

i. $Cl^{\ominus}$

j. $NO_3^{\ominus}$

k. O^{2-}

l. CH_4

m. NaOH

n. NaF

o. KCl

p. NH_4NO_3

q. $FeBr_3$

<u>Autoionization of water (</u>17.2). pH and pOH

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq)^{+} \; OH^{\ominus}(aq) \qquad \mathbf{K_w = 1.00 \times 10^{-14}} =$$

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

$[H_3O^{\oplus}][OH^{\ominus}] = \mathbf{1.00 \times 10^{-14}}$ **Memorize!**

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

The pH Scale (17.2)

$pH = -\log[H_3O^{\oplus}]$	$[H_3O^+] = 10^{-pH}$
On calculator: enter $[H^+]$, hit "log", and correct the sign from negative to positive	**On calculator**: enter pH, switch the sign from positive to negative, and hit 10^x button (depending on calculator)

Much nicer numbers

1. Higher numberer pH → less $H^{\oplus}$, less acidic, more basic
   Lower numbered pH → more $H^{\oplus}$, more acidic, more less$^+$

   pH 3.0 4.6 10.2

   $\longleftarrow$

   more acidic

   $\longrightarrow$

   less acidic

2. pH = 7 neutral pH < 7 acidic pH > 7 basic

3. pH change of 1 = tenfold change in $[H^{\oplus}]$
   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!

4. Number of significant figures in $[H^+]$ = number of digits after decimal in pH

   $[H^+] = 3.6 \times 10^{-6}$ → pH = 5.44
   2 sig fig → 2 after decimal

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

6. $pOH = -\log[OH^-]$ just like $pH = -\log[H^+]$	**$[OH^-] = 10^{-pOH}$** just like $[H^+] = 10^{-pH}$

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

Skills: interconvert among

$[\mathbf{H^+}] \Leftrightarrow [\mathbf{OH^-}]$

$\Updownarrow \qquad \Updownarrow$

pH $\Leftrightarrow$ **pOH**

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

Problems

1. Find pH for following

a. $[H_3O^+] = 1.0\times10^{-4}$

b. $[H^+] = 1.0\times10^{-11}$

c. $[H^+] = 3.2\times10^{-4}$

d. $[OH^-] = 1.0\times10^{-8}$

e. $[OH^-] = 5.8\times10^{-4}$

f. pOH = 8.30

2. Find pOH:

a. $[H^+] = 3.9\times10^{-5}$

b. $[OH^-] = 3.9\times10^{-5}$

c. pH = 3.95

3. Find both	$[H^+]$	$[OH^-]$
a. pH = 3.72		
b. pH = 9.81		
c. $[H^+] = 3.5\times10^{-8}$		
d. $[OH^-] = 4.1\times10^{-3}$		

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

A. Acids

$HA\ (aq) + H_20\ (l) \rightleftharpoons H_30^{\oplus}\ (aq) + A^{\ominus}\ (aq)$ $\qquad K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

Shorthand: $HA \rightleftharpoons H^{\oplus} + A^{\ominus}$ $\qquad \mathbf{K_a} = \dfrac{[H_3O^+][A^-]}{[HA]}$

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 $A^{\ominus}$ and HA are conjugates:
    - larger $K_a \Rightarrow$ less basic $A^{\ominus}$ (stronger acid → weaker base)
    - smaller $K_a \Rightarrow$ more basic $A^{\ominus}$ (weaker acid → stronger base)

B. Bases

Generic	$Base(aq) + H_20(l) \rightleftharpoons OH^{\ominus}\ (aq) + Base\text{-}H^{\oplus}\ (aq)$ Conjugate acid	$\mathbf{K_b} = \dfrac{[OH^-][BH^+]}{[B]}$
Anionic Base	$A^{\ominus} + H_20 \rightleftharpoons OH^{\ominus} + HA$ Conjugate acid	$\mathbf{K_b} = \dfrac{[OH^-][HA]}{[A^-]}$
Neutral Amine Base	$NH_3 + H_20 \rightleftharpoons OH^{\ominus} + NH_4^{\oplus}$ Amine Ammonium	$\mathbf{K_b} = \dfrac{[OH^-][NH_4^+]}{[NH_3]}$

16.7 Calculations involving K_a, K_b, pH, pOH

A. **Strong Acids**: $[HA] = [H^{\oplus}] \Rightarrow$ pH

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

B. **Strong Bases**: complete formation of $OH^{\ominus}$

- $[NaOH] = [OH^{\ominus}] \Rightarrow$ pOH, pH
    - for a group one metal hydroxide (NaOH, etc.), you get exactly as many moles of hydroxide as you put in of NaOH, and $[NaOH] = [OH^{\ominus}]$
    - $NaOH \rightarrow Na^{\oplus} + OH^{\ominus}$
- For a group two metal hydroxide, you get two moles of hydroxide for every one mole of formula that you put in.
    - $1\ Ba(OH)_2 \rightarrow 1\ Ba^{2+} + 2\ OH^{\ominus}$
    - $[OH^{\ominus}] = 2\ ([Ba(OH)_2])$
- Since $[OH^{\ominus}]$ is knowable, you can then plug in, and find pOH, pH, and/or $[H^{\oplus}]$

Some pH Calculations Involving Strong Acids or Bases

1. What is the pH of 1.36×10^{-3} M H_2SO_4?

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 $Ca(OH)_2$?

5. What is the pH if 22 g of $Ba(OH)_2$ (90 g/mol) is dissolved in 760 mL of water?

C. Weak Acids Calculation: Equilibrium, K_a, and pH ICE-able (Section 17.3)

Two Key Equations	$K_a=\dfrac{[H^+]^2}{[HA]_{init}}$	$[H^+]=\sqrt{K_a\cdot[HA]}$;

1. **Major Application 1**: $\boxed{\text{Given a known } K_a\text{, Solve for pH}}$ When a Known Amount of Weak Acid is Placed in a Known Amount of Water

$\boxed{\text{Logic: Use } K_a \rightarrow \text{solve for } [H^{\oplus}] \rightarrow \text{solve for pH}}$

Steps

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_a 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	$\rightleftharpoons$	$H^{\oplus}$	+	$A^{\ominus}$
Initial	$[HA]_{init}$		1.0×10^{-7}		0
Change					
Equilibrium					
Equilibrium After Simplifying Assumptions					

$K_a =$

When is simplifying assumption safe? Use the >100K rule:	If $\frac{[HA]_{init}}{K_a} > 100$ → simplifying assumption is safe

When the simplifying assumptions are used:	$\mathbf{K_a}$**=** $\frac{[H^+]^2}{[HA]_{init}}$	$[\mathbf{H}^{\oplus}]\mathbf{=}\sqrt{K_a \times [HA]_{init}}$
When the first simplifying assumption is not used (but the second one is)	$K_a = \frac{[H^+]^2}{[HA]_{init} - [H^+]}$	$[H^{\oplus}]$ requires a quadratic solution

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

$\boxed{\text{Logic: Use pH} \rightarrow \text{solve for } [H^{\oplus}] \rightarrow \text{solve for } K_a}$

$$K_a = \frac{[H^+]^2}{[HA]_{init}}$$

<u>Weak Acid pH/K_a Problems</u>

1. pH → K_a What is K_a for an acid if an 0.15 M solution is prepared and found to have pH = 4.86?

Logic:

2. K_a → pH What is pH for a 0.15 M solution of an acid with $Ka = 2.2\times10^{-6}$?
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 $Ka = 1.3\times10^{-8}$ acid, what is pH?

D. Weak Base Calculations involving K_b and pH (Section 17.3)

	$A^{\ominus}$	$+ H_2O$	$\rightleftharpoons$	HA	+	$HO^{\ominus}$
Initial	$[A^{\ominus}]_{init}$			0		1.0×10^{-7}
Change						
Equilibrium						
Equilibrium After Simplifying Assumptions						

$K_b =$

When is simplifying assumption safe? Use the >100K rule:	If $\frac{[\text{base}]_{init}}{K_b} > 100$ → simplifying assumption is safe

When the simplifying assumptions are used:	**K_b=** $\frac{[HO^-]^2}{[A^-]_{init}}$	**$[HO^{\ominus}]=\sqrt{K_b \times [A^-]_{init}}$**
When the first simplifying assumption is not used but the second one is	K_b= $\frac{[HO^-]^2}{[A^-]_{init} - [HO^-]}$	$[HO^{\ominus}]$ requires a quadratic solution

Applications

1. pH → K_b Strategy: pH → pOH → $[HO^{\ominus}]$ → K_b
2. K_b → pH Strategy: K_b → $[HO^{\ominus}]$ → pOH → pH

Problems: pH and K_b

1. pH → K_b What is K_b if a 0.123 M solution of a weak base gives pH=10.62?

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

E. Relationship Between K_a and K_b for Conjugate acids/bases (Section 16.7, p 794)

- Review: stronger the acid, weaker the conjugate base (and vice versa)

$$\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$$

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: $K_a \rightarrow K_b \rightarrow [HO^{\ominus}] \rightarrow pOH \rightarrow pH$

Derivation of $K_aK_b=10^{-14}$ (not responsible for derivation, just for interest)

$$K_a=\frac{[H_30^+][A^-]}{[HA]} \qquad K_b=\frac{[OH^-][HA]}{[A^-]}$$

$$\text{So } K_aK_b=\left(\frac{[H_3O^+][A^-]}{[HA]}\right)\frac{[OH^-][HA]}{[A^-]}=[H_3O^+][OH^-]=1.0\times10^{-14}$$

Thus $\mathbf{K_aK_b=K_w=10^{-14}}$

Acid Strength	**K_a**	**K_b**	**Strength of Conjugate Base**
Strong	$K_a > 1$	$K_b < 1 \times 10^{-14}$	Nonbasic
Weak	$1 \times 10^{-14} < K_a < 1$	$1 \times 10^{-14} < K_b < 1$	Weak
Nonacid	$K_a < 1 \times 10^{-14}$	$K_b > 1$	Strong base

Problems Involving Relationship between K_a and K_b for Conjugated Acid/Base

Substance	HF	HN_3	HCN
K_a	6.8×10^{-4}	1.9×10^{-3}	4.9×10^{-10}
Relative Acidity			
Conjugate Base			
Relative Basicity			
K_b			

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

2. Rank the basicity, 1 being the stongest, for: NaCN NaF NaN_3

Substance	HF	HN_3	HCN
K_a	6.8×10^{-4}	1.9×10^{-3}	4.9×10^{-10}
Conjugate Base			
K_b			

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^+ Available (Section 17.4)

H_2SO_4, H_3PO_4, H_2CO_3,…

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

Relative Acidity	Acid		Conjugate Base	Relative Basicity
	H_3PO_4	$K_{a1} = 10^{-3}$	$H_2PO_4^-$	
	$H_2PO_4^-$	$K_{a2} = 10^{-8}$	HPO_4^{2-}	
	HPO_4^{-2}	$K_{a3} = 10^{-13}$	PO_4^{3-}	

2. As acids in water, only consider the first ionization.
3. When <u>base</u> is added, however, all H^+'s come off (stoichiometry permitting)
   $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$
   But $H_3PO_4 + 3\ OH^- \rightarrow 3\ H_20 + PO_4^{3-}$

4. H_2SO_4: 1st strong, 2nd weak

$$\begin{array}{ccccccccc} H_2SO_4 & \xrightarrow{\text{water}} & H^+ & + & HSO_4^- & \xrightleftharpoons{\text{water}} & 2H^+ & + & SO_4^{2-} \\ \text{none} & \boxed{\text{Complete}} & & \text{lot} & & \boxed{\text{weak}} & & \text{little} & \end{array}$$

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

$$\begin{tikzcd} HCO_3^- \arrow[r, shift left, harpoon] \arrow[dr, "H_20"] & H^+ + CO_3^{2-} \arrow[l, shift left, harpoon] \\ & OH^- + H_2CO_3 \arrow[ul] \end{tikzcd}$$

Polyprotic Acid/Base Problems

1. Which is the stronger acid?

   H_3PO_4 $H_2PO_4^-$

   H_2SO_4 HSO_4^-

2. Which is the stronger base?

   HCO_3^- CO_3^{2-}

   HSO_4^- SO_4^{2-}

Polyprotic Acids: Each H becomes less acidic

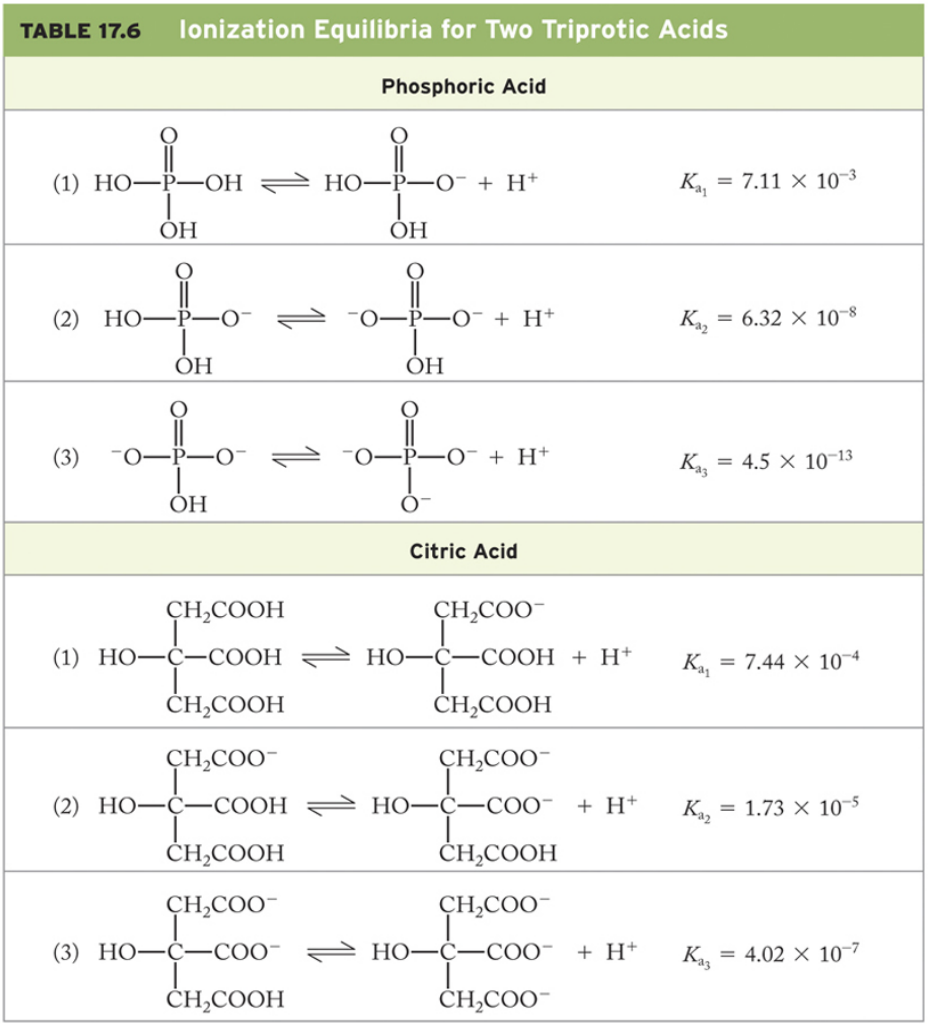


TABLE 17.6 Ionization Equilibria for Two Triprotic Acids

Phosphoric Acid		
(1)	$\mathrm{HO{-}\underset{\underset{\displaystyle OH}{\mid}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}OH \rightleftharpoons HO{-}\underset{\underset{\displaystyle OH}{\mid}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O^- + H^+}$	$K_{a_1} = 7.11 \times 10^{-3}$
(2)	$\mathrm{HO{-}\underset{\underset{\displaystyle OH}{\mid}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O^- \rightleftharpoons {}^-O{-}\underset{\underset{\displaystyle OH}{\mid}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O^- + H^+}$	$K_{a_2} = 6.32 \times 10^{-8}$
(3)	$\mathrm{{}^-O{-}\underset{\underset{\displaystyle OH}{\mid}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O^- \rightleftharpoons {}^-O{-}\underset{\underset{\displaystyle O^-}{\mid}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O^- + H^+}$	$K_{a_3} = 4.5 \times 10^{-13}$
Citric Acid		
(1)	$\mathrm{HO{-}\underset{\underset{\displaystyle CH_2COOH}{\mid}}{\overset{\overset{\displaystyle CH_2COOH}{\mid}}{C}}{-}COOH \rightleftharpoons HO{-}\underset{\underset{\displaystyle CH_2COOH}{\mid}}{\overset{\overset{\displaystyle CH_2COO^-}{\mid}}{C}}{-}COOH + H^+}$	$K_{a_1} = 7.44 \times 10^{-4}$
(2)	$\mathrm{HO{-}\underset{\underset{\displaystyle CH_2COOH}{\mid}}{\overset{\overset{\displaystyle CH_2COO^-}{\mid}}{C}}{-}COOH \rightleftharpoons HO{-}\underset{\underset{\displaystyle CH_2COOH}{\mid}}{\overset{\overset{\displaystyle CH_2COO^-}{\mid}}{C}}{-}COO^- + H^+}$	$K_{a_2} = 1.73 \times 10^{-5}$
(3)	$\mathrm{HO{-}\underset{\underset{\displaystyle CH_2COOH}{\mid}}{\overset{\overset{\displaystyle CH_2COO^-}{\mid}}{C}}{-}COO^- \rightleftharpoons HO{-}\underset{\underset{\displaystyle CH_2COO^-}{\mid}}{\overset{\overset{\displaystyle CH_2COO^-}{\mid}}{C}}{-}COO^- + H^+}$	$K_{a_3} = 4.02 \times 10^{-7}$

***Chemistry: The Science in Context* 3/e Table 17.6**

Acid-Base Properties of Common Salts

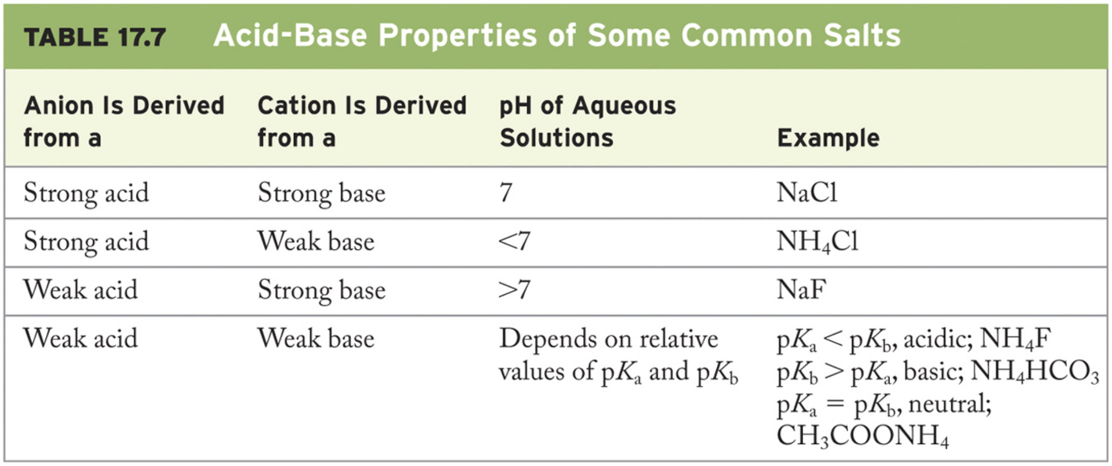


TABLE 17.7 Acid-Base Properties of Some Common Salts

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_4Cl
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**

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

NH_4Cl	$MgBr_2$	NaCN
$pH<7$	$pH=7$	$pH>7$
acidic	neutral	basic

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

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 neutral
        Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, …
        No impact on pH
    b. Ammoniums are acidic
        NH_4^+, $CH_3NH_3^+$ etc.
    c. Al^{3+}, T-metal cations are acidic in water. (Not for test)
        $Al^{3+} \rightarrow [Al(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Al(OH)(H_20)_5]^{2+}$
        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^-, Br^-, I^-, NO_3^-, ClO_4^-
    b. basic: conjugates of weak acids (or non acids)
        F^-, ClO^-, …
3. "Amphoteric" anions derived from polyprotic acids: can be acidic or basic
    -not test responsible
        HCO_3^-, $H_2PO_4^-$, HSO_3^-

B. Predicting acidic/neutral/basic (qualitatively)

Cation	anion	salt solution	example
Neutral	neutral	neutral	NaCl, KNO_3
Acidic	neutral	acidic	NH_4Cl, $Fe(NO_3)_3$
Neutral	basic	basic	NaF, K(ClO)
Acidic	basic	can't predict (without K's)	NH_4F, $Fe(N_3)_3$

Predicting Acid/Base Character for Ionic Formulas

1. Predict as acidic, basic, neutral, or can't tell.

a. Na_2SO_3

e. $NaNO_3$

b. $MgCl_2$

f. KN_3

c. NH_4CN

g. Li_2CO_3

d. $Ba(NO_3)_2$

h. CH_3NH_3Br

2. Rank the following in terms of increasing pH, 1 being the lowest. (ID as strong/weak acid, strong/weak base, or neutral first!)

$NaCl$ NH_4Cl ZnF_2 HNO_3 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 $^{\ominus}$ and Electronegativity*******
   - Think Anion!
   - Think electronegativity and -electron love

   $CH_4 \rightarrow H^+ + {}^{\ominus}CH_3$ Horrible. Carbon not electronegative, can't handle $\ominus$

   $HF \rightarrow H^+ + F^{\ominus}$ Way stronger. Fluorine electronegative, can handle $\ominus$

2. H-A bond strength: stronger → <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 → right

	CH_4	NH_3	H_2O	HF
K_a	10^{-50}	10^{-32}	10^{-14}	10^{-4}

Note: e^- love, electronegativity/bond-polarity, anion stability all agree

Rank: Acidity of: SiH_4 SH_2 HCl PH_3

2. Vertical Periodic Pattern: Acidity Increases Top → Bottom
   -due to decreasing H-A bond strength (even though contrary to e^- love)

   HF < HCl
   Weak strong

   $H_2O < H_2S < H_2Se$
   $K_a=10^{-14}$ 10^{-9} 10^{-6}

<u>Note: Basicity of conjugates linked!!</u>

Horizontal: ${}^{\ominus}NH_2 > F^{\ominus}$ Vertical: $F^{\ominus} > Cl^{\ominus}$

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

$HClO_4 > HClO_3 > HClO_2 > HClO$	$H_2SO_4 > H_2SO_3$
Strong weak	strong weak

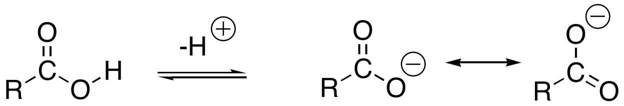
Why? Extra electron-loving oxygen
1. Stabilizes resulting anion
2. Polarizes O-H
3. Weakens O-H

- **Any Neutral Oxoacid with ≥ 2 extra O's is a strong Acid**
  - Compare how many oxygens there are versus hydrogens

Strong: H_2SO_4, $HClO_3$ weak: H_2CO_3, H_3PO_4, H_2SO_3

Carboxylic Acids: Famous class of oxoacids: RCOOH or RCO_2H (R is usually an H or a carbon chain.)

- Resonance stabilization of conjugate anion makes the anion more stable



Predicting Acid/Base Properties and Trends Why?

1. Which are acidic vs. basic vs. neutral in water?

   $HClO_3$ CH_3COOH CH_3NH_2 $Ca(OH)_2$

2. Rank Acidity (1 strongest)

   HF H_2O H_2SO_4 CH_4

3. Rank Acidity (1 strongest)

   $HClO_4$ $HClO_3$ H_2SO_4 H_2SO_3

4. Rank Acidity (1 strongest)

   H_2O H_2S H_2Se

5. Rank Acidity (1 strongest)

   HBr H_2Se H_3As H_4Ge

6. Which would be stronger?

   $HBrO_3$ vs $HBrO$

7. Rank Basicity (1 strongest)

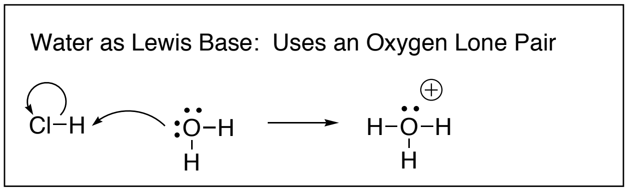
   ${}^{\ominus}CH_3$ ${}^{\ominus}NH_2$ ${}^{\ominus}OH$ $F^{\ominus}$

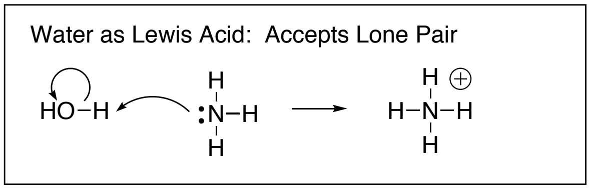
8. Rank Basicity (1 strongest)

   HPO_4^{2-} $H_2PO_4^{\ominus}$ $HSO_4^{\ominus}$

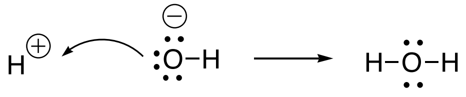
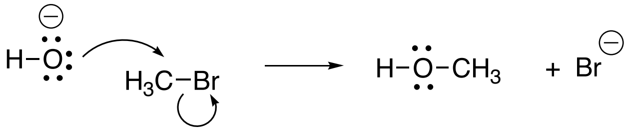
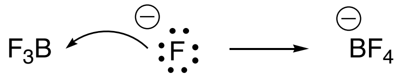
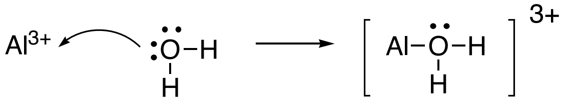
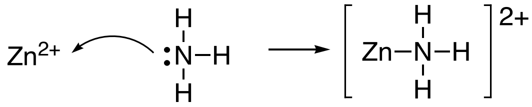
Lewis Acids and Bases: focus on electron pairs, not H^+ movement. (18.1)

Lewis acid: e- pair acceptor **Lewis base: e- pair donor**	Covers "acid-base" chemistry that doesn't involve H^+


Water as Lewis Base: Uses an Oxygen Lone Pair


Water as Lewis Acid: Accepts Lone Pair

Other Examples

a. 	b. 
c. 	d.  How metal hydrates form
e. 	

Notes: 1. A "base" must have a lone pair

(F^-, OH_2, NH_3, ….)

2. All anions have lone pairs → Lewis Base potential
3. An "acid" must be able to accept a lone pair

-all cations can!!

-some neutrals: BF_3, SO_2, …

Lewis Acid/Base Problems

1. Which would not be a Lewis acid?

$AlCl_3$ Ti^{4+} NO_3^{-} $ZnSO_4$

2. Identify the Lewis acid and Lewis Base

a. $Fe^{3+} + 6\ H_2O \rightarrow [Fe(H_2O)_6]^{3+}$

b. $H^+ + CH_3NH_2 \rightarrow CH_3NH_3$

c. $Br\text{-}CH_3 + I^{-} \rightarrow Br^{-} + I\text{-}CH_3$

d. $Ni^{2+} + 4\ N_3^{-} \rightarrow [Ni(N_3)_4]^{2-}$

CH. 16 Acid-Base Chemistry Math Review

Key Equations, Numerical Relationships

1. $[H^+][HO^-] = 1.00 \times 10^{-14}$

2. $pH = -\log[H^+]$

   $[H^+] = 10^{-pH}$ (on calculator, enter –pH, then punch the **10^x** button)

   $pOH = -\log[OH^-]$

   $[OH^-] = 10^{-pOH}$ (on calculator, enter –pOH, then punch the **10x** button)

3. $pH + pOH = 14$ $\qquad pH = 14 - pOH$

Weak acid problems

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

When the simplifying assumptions are used:	**4.** $\mathbf{K_a} = \dfrac{[H^+]^2}{[HA]_{init}}$	**5.** $[\mathbf{H}^{\oplus}] = \sqrt{K_a \times [HA]_{init}}$
When the first simplifying assumption is not used (but the second one is)	6. $K_a = \dfrac{[H^+]^2}{[HA]_{init} - [H^+]}$	$[H^{\oplus}]$ requires a quadratic solution

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

Weak base problems

$K_b = [Base\text{-}H^+][OH^-]/[Base]$ but when Base is place in water, $[Base\text{-}H^+] = [OH^-]$ so:

When the simplifying assumptions are used:	**8.** $\mathbf{K_b} = \dfrac{[HO^-]^2}{[Base]_{init}}$	**9.** $[\mathbf{HO}^{\ominus}] = \sqrt{K_b \times [Base]_{init}}$
When the first simplifying assumption is not used but the second one is	10. $K_b = \dfrac{[HO^-]^2}{[Base]_{init} - [HO^-]}$	$[HO^{\ominus}]$ 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 → pH $\qquad$ [Strong acid] → $[H^{\oplus}]$ → pH
2. Strong base → pH $\qquad$ [Strong base] → $[HO^{\ominus}]$ → pOH → pH
3. Weak acid + K_a → pH $\qquad$ [Weak acid] + K_a → $[H^{\oplus}]$ → pH
4. pH of weak acid → K_a $\qquad$ pH → solve for $[H^{\oplus}]$ → K_a
5. Weak base + K_b → pH $\qquad$ [Weak base] + K_b → $[HO^{\ominus}]$ → pOH → pH
6. pH of weak base → K_b $\qquad$ pH → solve for $[HO^{\ominus}]$ → pOH → pH
7. Weak base + K_a of conjugate acid → pH $\qquad$ K_a → K_b → $[HO^{\ominus}]$ → pOH → pH

Simple Acid-Base Concept Map