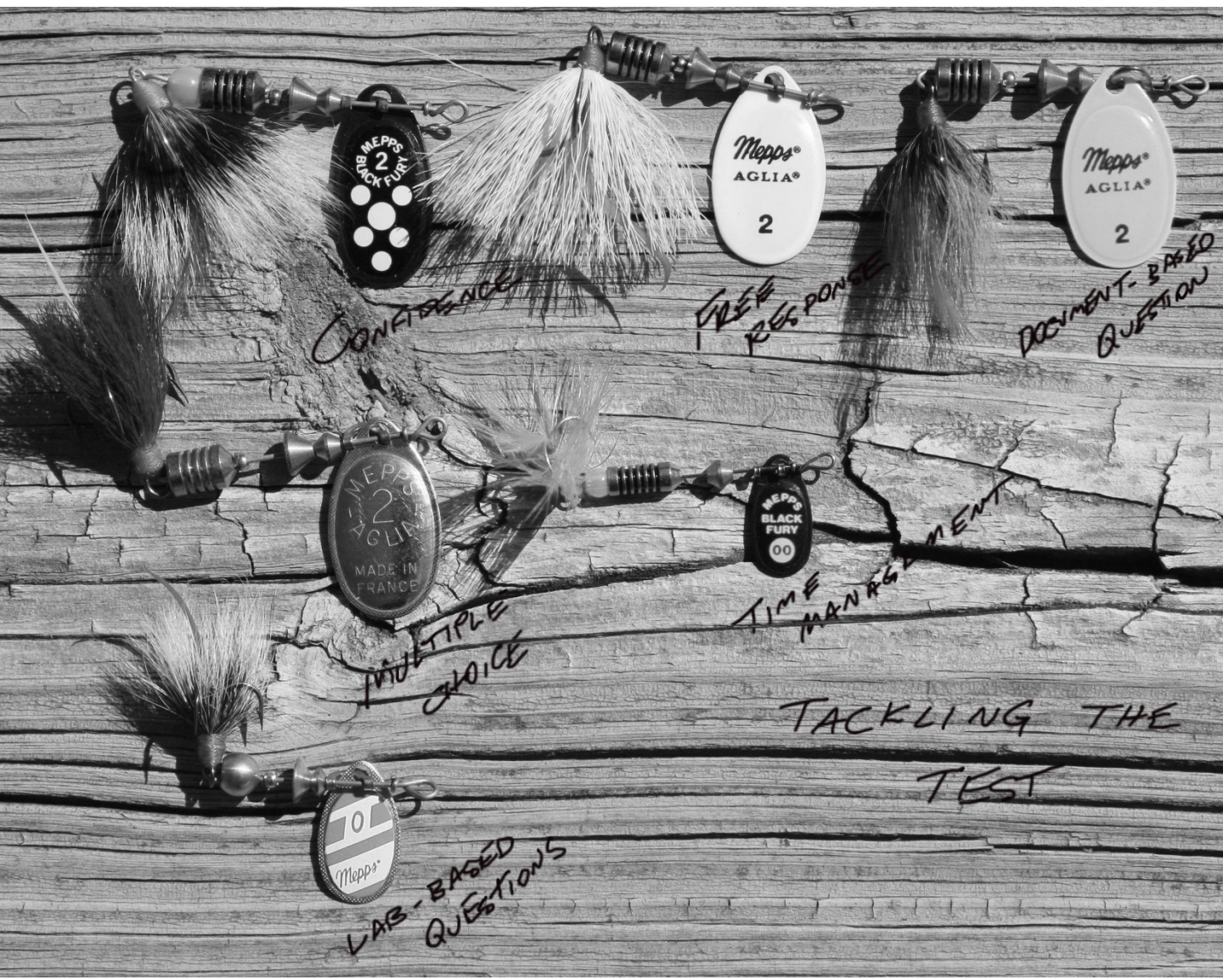


Chemistry

Acid Base Equilibrium



Periodic Table of the Elements

1 H 1.0079																	2 He 4.0026	
3 Li 6.941	4 Be 9.012																9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30																17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29	
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)	§Not yet named						

*Lanthanide Series:		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†Actinide Series:		90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

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

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$
$$= K_a \times K_b$$

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

$$14 = \text{pH} + \text{pOH}$$

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

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

1 atm = 760 mm Hg

$$= 760 \text{ torr}$$

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, $F = 96,485$ coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



What I Absolutely Have to Know to Survive the AP Exam

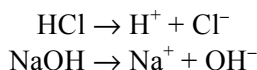
The following might indicate the question deals with acid – base equilibrium:

pH, pOH, $[H_3O^+]$, $[OH^-]$, strong and weak, salt hydrolysis, solubility product, K_a , K_b , acid or base dissociation constant, percent ionized, Bronsted-Lowry, Arrhenius, hydronium ion, etc...

Acids and Bases: *By Definition!*

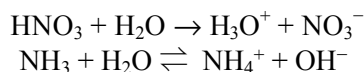
Arrhenius

- Acids: Hydrogen ion, H^+ , donors
- Bases: Hydroxide ion, OH^- donors



Bronsted-Lowry

- Acids: proton donors (lose H^+)
- Bases: proton acceptors (gain H^+)



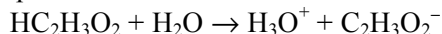
Hydrogen Ion, Hydronium Ion, Which is it!!!?

Hydronium – H^+ riding piggy-back on a water molecule; water is polar and the + charge of the naked proton is greatly attracted to “Mickey's chin” (i.e. the oxygen atom)

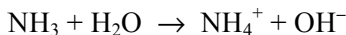
- H_3O^+ “Anthony”
- H^+ “Tony”
- Often used interchangeably in problems; if H_3O^+ is used be sure water is in the equation!

Bronsted–Lowry and Conjugate Acids and Bases: *What a Pair!*

Acid and conjugate base pairs differ by the presence of one H^+ ion.



- $HC_2H_3O_2$ is the acid; thus $C_2H_3O_2^-$ is its conjugate base (what remains after the H^+ has been donated to the H_2O molecule)
- H_2O behaves as a base in this reaction. The hydronium ion is its conjugate acid (what is formed after the H_2O accepts the H^+ ion)



- NH_3 is the base; thus NH_4^+ is its conjugate acid (what is formed after the NH_3 accepts the H^+ ion)
- H_2O behaves as an acid in this reaction. The hydroxide ion is its conjugate base (what remains after the H^+ has been donated to NH_3)

Understanding conjugate acid/base pairs is very important in understanding acid-base chemistry; this concepts allows for the understanding of many complex situations (buffers, titrations, etc...)

Important Notes...

Amphiprotic/amphoteric--molecules or ions that can behave as EITHER acids or bases; water, some anions of weak acids, etc... fit this bill.

Monoprotic – acids donating one H^+

Diprotic – acids donating two H^+

Polyprotic – acids donating 3+ H^+

Regardless, always remember: **ACIDS ONLY DONATE ONE PROTON AT A TIME!!!**

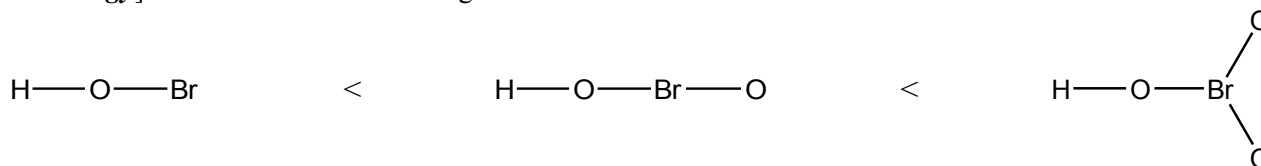


Ionization: *That's What it's All About!*

Relative Strengths

A strong acid or base ionizes completely in aqueous solution (100% ionized [or very darn close to it!])

- The equilibrium position lies far, far to the right (favors products)...
- Since a strong acid/base dissociates into the ions, the concentration of the $\text{H}_3\text{O}^+/\text{OH}^-$ ion is equal to the original concentration of the acid/base respectively.
- They are strong electrolytes.
- **Do Not** confuse concentration (M or mol/L) with strength!
- Strong Acids
 - Hydrohalic acids: HCl, HBr, HI; Nitric: HNO_3 ; Sulfuric: H_2SO_4 ; Perchloric: HClO_4
- Oxyacids! More oxygen atoms present, the stronger the acid WITHIN that group. The H^+ that is “donated” is bonded to an oxygen atom. The oxygen atoms are highly electronegative and are pulling the bonded pair of electrons AWAY from the site where the H^+ is bonded, “polarizing it”, which makes it easier [i.e. requires *less energy*] to remove – thus the stronger the acid!



- Strong Bases
 - Group IA and IIA (1 and 2) metal hydroxides; be cautious as the poor solubility of $\text{Be}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ limits the effectiveness of these 2 strong bases.
 - IT'S A 2 for 1 SALE with the Group 2 (IIA) ions), i.e. $0.10M \text{Ca}(\text{OH})_2$ is $0.20M \text{OH}^-$

Where the fun begins...

A weak acid or base does not completely ionize (usually $< 10\%$)

- They are weak electrolytes.
- The equilibrium position lies far to the left (favors reactants)...
- $[\text{H}^+]$ is much *less than* the acid concentration – thus to calculate this amount and the resulting pH you must return to the world of EQUILIBRIUM Chemistry!
- The vast majority of acid/bases are weak. Remember, **ionization not concentration!!!!**
- Acids and Bases ionize one proton (or H^+) at a time!
- For weak acid reactions: $\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \text{ where } K_a \text{ is typically much less than } 1$$

- For weak base reactions: $\text{B} + \text{H}_2\text{O} \rightarrow \text{HB}^+ + \text{OH}^-$

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \text{ where } K_b \text{ is typically much less than } 1$$



Ionization: *That's What it's All About! con't.*

Working it Out!

Calculating the pH of weak acids simply requires some quick problem solving...

- MONUMENTAL CONCEPT...
 - On the AP Exam the weak acid will be significantly weak so that the initial $[HA]_0$ is mathematically the same as the equilibrium concentration – i.e. there is no need to subtracting the amount of weak acid ionized as it is mathematically insignificant.
- If given the concentration of the weak acid, HA and the ionization constant for the acid, K_a , plug both into the equilibrium expression and solve. Both H_3O^+ and A^- are equal (remember it's 1:1 always) so call them x and solve.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Thus all you need to know is...

$$K_a = \frac{[x][x]}{[M_0]} \text{ where } x = [H_3O^+] \quad \text{or} \quad K_b = \frac{[x][x]}{[M_0]} \text{ where } x = [OH^-]$$

- Never forget $K_a \times K_b = 1 \times 10^{-14}$
- Very important when you are given the ionization constant for the acid but need the conjugate base and vice-versa.
- Percent Ionization
 - Often will be asked to determine how ionized the weak acid or base is...

$$\% = \frac{[x]}{[M_0]} \times 100 \quad \text{where } x = [H_3O^+] \text{ or } [OH^-]$$

Salts and pH: *It's all about Hydrolysis*

A salt is the PRODUCT of an acid base reaction; SOME salts affect the pH of the solution.

So... an easy way to tell, you ask...?

- Ask yourself, which acid and which base are needed to make that salt?...were they strong or weak?
 1. A salt such as $NaNO_3$ does not affect the pH of the solution; if it could hydrolyze water the following would happen:

$$Na^+ + 2 H_2O \rightarrow NaOH + H_3O^+$$

$$NO_3^- + H_2O \rightarrow HNO_3 + OH^-$$
 – Neither of the salt's ions can hydrolyze water because it would result in the formation of a strong acid (HNO_3) or a strong base ($NaOH$), which would ionize 100% back into the ions.
 2. K_2S would make the solution more basic—SB (KOH) & WA (H_2S)
 - NOTE: Only the ion that forms a weak acid or base through water hydrolysis can actually hydrolyze water.
 - In this case:

$$S^{2-} + H_2O \rightarrow H_2S + OH^-$$
 The increase in OH^- ions means the anion of this salt makes the solution more basic...
 3. NH_4Cl would make the solution more acidic—since WB (NH_4OH – or NH_3) & SA (HCl)
 - In this case:

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$
 The increase in H_3O^+ ion means the solution is more acidic...



Salts and pH: *It's all about Hydrolysis con't*

Working it Out!

Calculating the pH of a salt solution

- A salt in solution is either behaving as a weak acid or a weak base.
- Remember, this means they do not ionize much. So treat them just like any other weak acid or base.
- The MAJOR DIFFERENCE; no K_a or K_b value will be provided. The salt is the conjugate acid or base to some weak acid or base that is provided - that K will be given you need to convert it.
 - Example, the salt $\text{NaC}_2\text{H}_3\text{O}_2$; the K_a for $\text{HC}_2\text{H}_3\text{O}_2$ is typically provided. The K_b needs to be calculated.
 - $K_a \times K_b = 1 \times 10^{-14}$ Very important!
 - Then solve as shown below to find the pH...

$$K_b = \frac{[x][x]}{[M_o]} \text{ where } x = [\text{OH}^-]$$



Acid – Base Equilibrium Cheat Sheet

Relationships

Equilibrium Expression

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

$$K_a = \frac{[x][x]}{[M_o]} \text{ where } x = [\text{H}_3\text{O}^+]$$

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

$$K_b = \frac{[x][x]}{[M_o]} \text{ where } x = [\text{OH}^-]$$

$$\% = \frac{[x]}{[M_o]} \times 100 \text{ where } x = [\text{H}_3\text{O}^+] \text{ or } [\text{OH}^-]$$

$$K_a \times K_b = 1 \times 10^{-14}$$

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

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} @ 25^\circ\text{C}$$

Acidic $\text{pH} < 7$ $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

Neutral $\text{pH} = 7$ $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

Basic $\text{pH} > 7$ $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

Conjugate acids and bases

$$K_{sp} = [\text{M}^+]^x[\text{A}^-]^y \quad \text{MA}(s) \rightleftharpoons x\text{M}^+(aq) + y\text{A}^-(aq)$$

Connections

Equilibrium

Buffers and Titrations

Precipitation and Qualitative Analysis

Bonding and Lewis Structures – justify oxyacid strengths

Potential Pitfalls

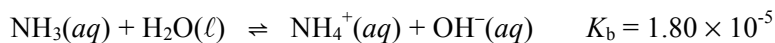
K_a or K_b with salt pH

Weak acids and bases – be sure you know what you are using, acid or base – K_a or K_b ; solving a K_b problem gives $[\text{OH}^-]$ thus you are finding the pOH!

Weak is about IONIZATION not CONCENTRATION

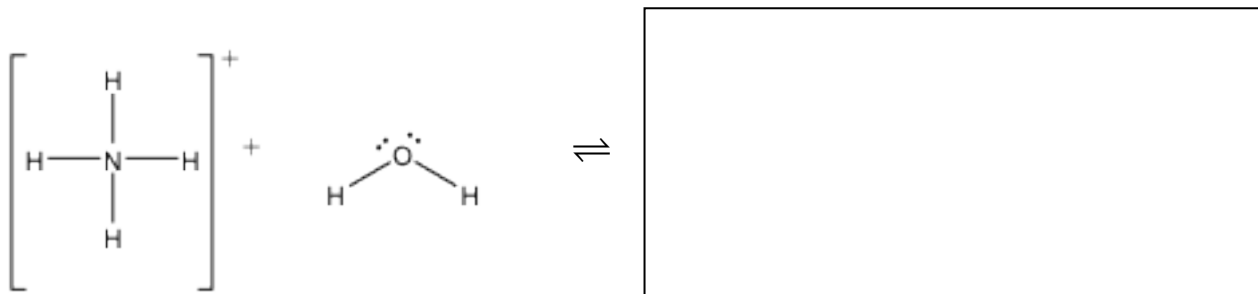


NMSI SUPER PROBLEM



1. Ammonia reacts with water as indicated in the reaction above.
 - (a) Write the equilibrium constant expression for the reaction represented above.
 - (b) Calculate the pH of a 0.150 M solution of NH_3 .
 - (c) Determine the percent ionization of the weak base NH_3 .
 - (d) Calculate the hydronium ion, H_3O^+ , concentration in the above solution. Be sure to include units with your answer.

When a specified amount of ammonium nitrate (NH_4NO_3) is dissolved in water, the ammonium ions hydrolyze the water according to the partial reaction shown below. The resulting solution has a pH of 4.827.



- (e) Complete the reaction above by drawing the *complete* Lewis structures for *both* products of the hydrolysis reaction.
- (f) Determine the
 - (i) molarity (M) of the ammonium ions in this solution
 - (ii) number of moles ammonium ions in 250 mL of the above solution.