CHEM 206 section 01

LECTURE #22 Fri. March 28, 2008

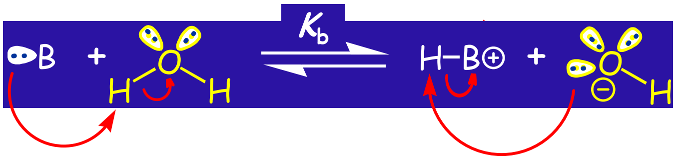
LECTURE TOPICS:

TODAY'S CLASS: **continue Ch.17**

NEXT CLASS: **finish Ch.17**

Describing BASES (17.4): same approach as for acids

For eqm involving reaction of a BASE with H_2O: "K_b"



$$K = \frac{[BH^+][OH^-]}{[:B]\cancel{[H_2O]}}$$

constant ∴ not included

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

$$pK_b = -\log(K_b)$$

...although pK_b not used as much as pK_a

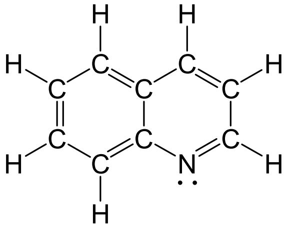
Strong base	Weak base
⬇	⬇
Large K_b	Small K_b
⬇	⬇
Low pK_b	High pK_b

Strongest BASE ever actually present in water is OH^-...

(any strong base dissolved in water immediately & quantitatively deprotonates water to yield OH^-)

Back to problem solving (17.7): using solubility of a base…

Quinoline, C_9H_7N, is a weak base used as a preservative for anatomical specimens and to make dyes. A handbook lists a value of 4.5 for the pK_a of protonated quinoline. Another handbook lists the solubility of quinoline in water at 25°C as 0.6g/100mL. **Use this information to find the pH of a saturated solution of quinoline.**



Are we at a dead end here?

How can you describe a substance's basicity (*i.e.,* its K_b) if you can only find the K_a of its conjugate acid?

An important trick to know: K_a's & K_b's are related

For any acid: K_a is the eqm constant for its rxn with H_2O…

$$C_9H_7NH^+ + H_2O \overset{K_a}{\rightleftharpoons} C_9H_7N + H_3O^+ \qquad K_a = \frac{[C_9H_7N][H_3O^+]}{[C_9H_7NH^+]}$$

K_b is eqm constant for rxn of its conjugate base with H_2O…

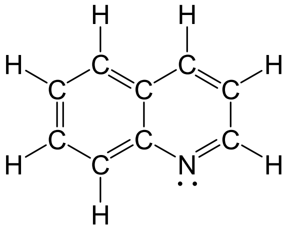
$$C_9H_7N + H_2O \overset{K_b}{\rightleftharpoons} C_9H_7NH^+ + OH^- \qquad K_b = \frac{[C_9H_7NH^+][OH^-]}{[C_9H_7N]}$$

For any conjugate acid-base pair: $K_a \times K_b = K_w$

$$K_a \times K_b = \frac{\cancel{[C_9H_7N]}[H_3O^+]}{\cancel{[C_9H_7NH^+]}} \times \frac{\cancel{[C_9H_7NH^+]}[OH^-]}{\cancel{[C_9H_7N]}} = K_w = 10^{-14}$$

Calculate the pH of a saturated solution of quinoline…

Quinoline, C_9H_7N, is a weak base used as a preservative for anatomical specimens and to make dyes. A handbook lists a value of 4.5 for the pK_a of protonated quinoline. Another handbook lists the solubility of quinoline in water at 25°C as 0.6g/100mL.



$pK_b = 14 - 4.5 = 9.5$ ⇨ $K_b = 10^{-9.5} = 3.16\text{x}10^{-10}$

eqm constant for rxn of BASE with WATER:

$$C_9H_7N + H_2O \overset{K_b}{\rightleftharpoons} C_9H_7NH^+ + OH^-$$

PLAN:

1.) find concentration (M) of sat'd quinoline solution = $[\text{quinoline}]_o$
2.) use eqm calculation to find $[OH^-]_{eqm}$ starting with $[\text{quinoline}]_o$
3.) relate $[OH^-]$ to $[H_3O^+]$ to find pH…

Calculate the pH of a saturated solution of quinoline….

$[C_9H_7N]_o$ = 0.6g / 100mL *for a saturated solution at 25°C*
= (0.6g / 129.16g/mol) / (0.100L)
= 0.0465 M

$$C_9H_7N + H_2O \overset{K_b}{\rightleftharpoons} C_9H_7NH^+ + OH^-$$

	C_9H_7N	H_2O	$C_9H_7NH^+$	OH^-
Initial	0.0465 M	built into K_b	0	0
Change	- x	---	+ x	+ x
Eqm	0.0465 - x	---	+ x	+ x

$$K_b = \frac{[C_9H_7NH^+][OH^-]}{[C_9H_7N]}$$

$$3.16\text{x}10^{-10} = \frac{x^2}{0.0465-x}$$

K < 1000x smaller than initial [ ]
…therefore CAN use approximation

$$3.16\text{x}10^{-10} \approx \frac{x^2}{0.0465}$$

$x = \sqrt{(0.0465*3.16\text{x}10^{-10})}$
$x = 3.83\text{x}10^{-6}$ M = $[OH^-]$

pOH = - log[OH^-]
= 5.42

pH = 14 – pOH
= 8.6 *(…1 SF due to sol'y data)*

makes sense: soln of a weak base should be weakly alkaline (basic: pH >7)

17.4's final bits: **Acid-base properties of salts**

How are the ions related to acids & bases that you know?

(Zumdahl)

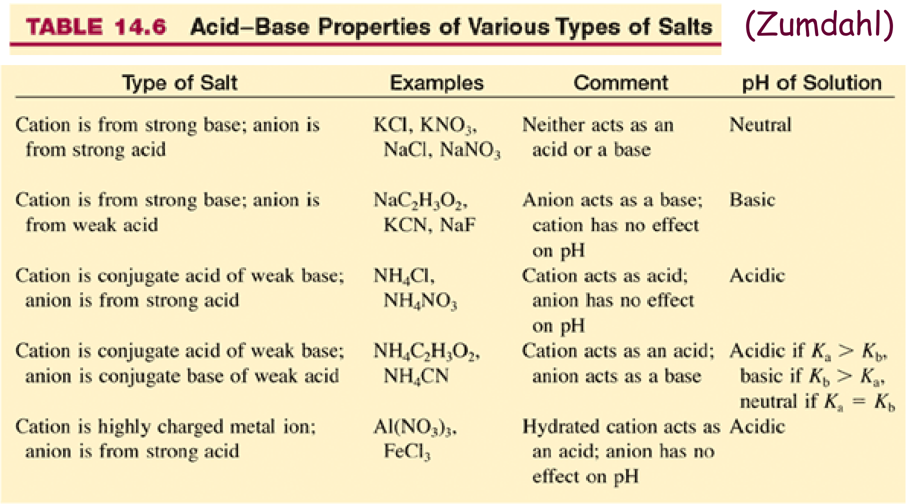


TABLE 14.6 Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO_3, NaCl, $NaNO_3$	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$NaC_2H_3O_2$, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH_4Cl, NH_4NO_3	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$, NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$, $FeCl_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

Finding the pH of a salt solution

Sorbic acid, $HC_6H_7O_2$ (pK_a = 4.77) is widely used in the food industry as a preservative. For example, its potassium salt (potassium sorbate) is added to cheese to inhibit the formation of mould.

Q: What is the pH of a 0.37 M solution of this salt?

ANS:
$K_b = 5.89\times10^{-10}$
→ $x = [OH^-] = 1.48\times10^{-5}$ M
→ pH = 9.17 (2 S.F.)

When a salt's cation & anion will BOTH influence the solution's pH…

APPROACH: (especially at first…)

1.) write an equation for rxn (an eqm!) of each ion with H_2O

⇨ *can it act as an acid or as a base or both?*

2.) find an eqm constant for each rxn (a K_a or K_b)

3.) which rxn is more product favoured? (compare Ks!)

⇨ *i.e., rxn with larger K will dominate!*

ACIDIC OR BASIC WHEN WE DISSOLVE THESE SALTS?

use data to predict…

(a) Ammonium carbonate

(b) Ammonium fluoride

DATA:	K_a
NH_4^+	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}
HCO_3^-	5.6×10^{-11}
HF	7.2×10^{-4}

Recall: for a conjugate acid-base pair: $K_a \times K_b = K_w$

17.7 Calculations with equilibrium constants

Some typical scenarios:

1.) Use solution pH to find K_a (or K_b).

Q: When a solution of weak acid HA (or base B) of known initial concentration is prepared, the pH of the solution is _____. Find K_a (or K_b).

2.) Determine the pH of a solution of a weak acid (or base).

Q: When a solution of known initial concentration of a certain weak base (known K_b) is prepared, what is the pH?

3.) Determine the pH of a solution after an acid/base rxn.

Q: When a known volume of solution of acid HA is mixed with a known volume of strong base, what is the pH of the resulting solution?

(11)

A comprehensive problem: osmotic P of a sol'n of base

From an exam: An aqueous solution of cocaine, a weak base ($C_{17}H_{21}NO_4$), was found to have a pH of 8.53 and an osmotic pressure of 52.7 torr at 15°C. Calculate the K_b of cocaine.

It is the nitrogen atom that makes the molecule basic. (LONE PAIR on N is much more reactive than on O)

$$R_3N: + H_2O \rightleftharpoons R_3N\text{-}H^+ + OH^- \qquad K_b = ?$$

APPROACH?

- use pH to find $[OH^-]$ ...
- notice that $[OH^-] = [R_3N\text{-}H^+]$ due to 1:1 rxn stoichiometry
- Remember: osmotic pressure is caused by total solute conc.
- use $\pi V = nRT$ to find total [solute particles] $= [R_3N:] + [OH^-] + [R_3N\text{-}H^+]$ (...water is solvent!)
- sub into K_b expression

(12)

A comprehensive problem: osmotic P of a sol'n of base

Soln pH = 8.53, but we're interested in cocaine acting as a BASE

⇨ pOH = 14.00 – 8.53 = 5.47

⇨ $[OH^-] = 10^{-5.47} = 3.388\times10^{-6}$ M *(one extra SF…)* = eqm concentration!

As a base: $R_3N: + H_2O \rightleftharpoons R_3N\text{-}H^+ + OH^-$

Initial	unknown	constant…	unknown	unknown
Change	-x		+x	+x
Eqm	calculate via π		same as OH^-	3.388×10^{-6} M

$$K_b = \frac{[R_3NH^+]_{eqm}[OH^-]_{eqm}}{[R_3N]_{eqm}}$$

$$[\text{solutes}]_{eqm} = \pi / RT$$

$$= \frac{(52.7\text{ mmHg})}{(760\text{ mmHg}/1\text{atm})} \times \frac{1}{RT}$$

Remember: osmotic pressure

$\pi V = nRT$ is due to total solute particles!

$$= \frac{6.934\times10^{-2}\text{ atm}}{0.08206\text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\text{K}^{-1} \times 288\text{K}}$$

$= 2.934\times10^{-3}$ M *total solutes*

continued… *now remember where solutes came from*

As a base: $R_3N: + H_2O \rightleftharpoons R_3N\text{-}H^+ + OH^-$

Initial	unknown	constant…	unknown	unknown
Change	-x		+x	+x
Eqm	calculate via π		same as OH^-	3.388×10^{-6} M

Total [solutes]: cocaine reacts with water, so products count too

$[R_3N]_{eqm} + [R_3NH^+]_{eqm} + [OH^-]_{eqm} = 2.934\times10^{-3}$ M total

$[R_3N]_{eqm} = 2.934\times10^{-3} - (3.388\times10^{-6} + 3.388\times10^{-6})$

$= 2.927\times10^{-3}$ M

$$K_b = \frac{[R_3NH^+][OH^-]}{[R_3N]}$$

$$K_b = \frac{[3.388\times10^{-6}][3.388\times10^{-6}]}{[2.927\times10^{-3}]}$$

⇨ $K_b = 3.9\times10^{-9}$ *2SF due to pH…*

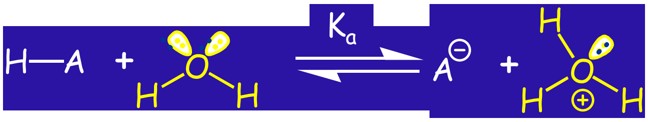
THUS: cocaine is a fairly weak base, $pK_b = 8.41$

SO: conj. acid R_3NH^+ $pK_a = (14 - 8.41) = 5.59$

⇨ to have most molecules protonated, soln needs pH < 5.59

The "protonation state" (H⁺ on *OR* H⁺ off?) **of acids & bases changes with pH…**

Convention: use pK_a to summarize strength & pH-dependence



If half of acid dissociates:

$[A^-] = [HA]$

$$K_a = \frac{\cancelto{1}{[A^-]}\,[H_3O^+]}{\cancel{[HA]}}$$

$K_a = [H_3O^+]$

$\therefore\ pK_a = pH$

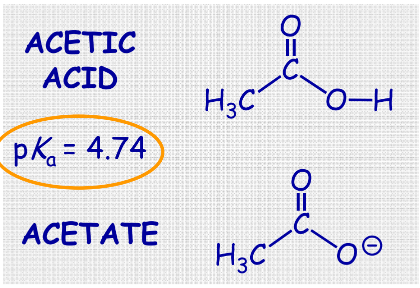
An acid's pK_a is the pH where have <u>equal</u> <u>parts</u> ACID & conjugate BASE!

If pH of solution is:

- Below HA's pK_a ⇨ protonated form (conj. acid) dominates
- Above pK_a ⇨ deprotonated form (conj. base) dominates

⇨**very important for biomolecules!**

p*K*a lets us PICTURE acidity of molecules…
→ a clue to how molecules look at different pHs !



ACETIC ACID

pK_a = 4.74

ACETATE

<u>"Acetic acid" at various pHs</u>

- Below pK_a **acid** form dominates
- At pH = pK_a **50/50** acid/acetate
- Above pK_a **acetate** dominates

What is the speciation in diluted vinegar of pH = 4.50 ?

$[H_3O^+] = (10^{-4.50})$

$= 3.2\times10^{-5}$ M

$K_a = (10^{-4.74})$

$= 1.82\times10^{-5}$

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

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

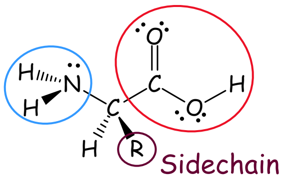
$$= \frac{3.2\times10^{-5}\text{ M}}{1.82\times10^{-5}\text{ M}}$$

$$\boxed{\frac{[HA]}{[A^-]} = \frac{1.8}{1}}$$

Slightly below pK_a, acid form dominates…

Chemistry in context: pK_a & biology…

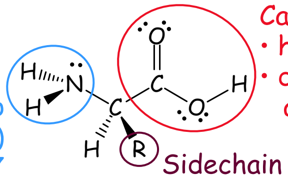
What does an amino acid "look like" at physiological pH?



Carboxylic acid group
- pK_a ~ 4-5

Link to biology: amino acids & pK_a

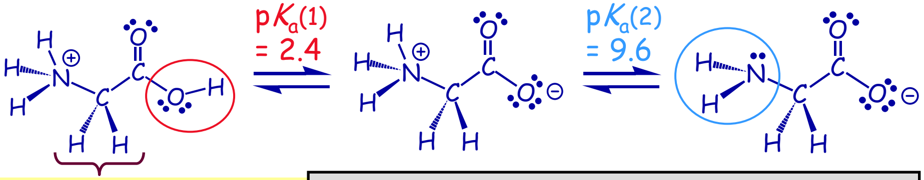
Amino group
- lone pair on N (basic)
- protonated at pH 7



Carboxylic acid group
- has a δ^+ H (acidic)
- deprotonated at pH 7

The simplest amino acid is glycine (R = H):

Below pH 2.4 fully protonated (cationic form)	pH 2.4 – 9.6 zwitterionic (neutral form)	Above pH 9.6 fully basic (anionic form)



In all other amino acids, one H is replaced by a **"sidechain" group**
- R = $-CH_3$, $-CH_2COOH$…
- **many are acidic/basic**
- **crucial…**

THUS: pH affects the charges on proteins
- proteins = chains of amino acids
- ends of chains: ionizable $-NH_2$ & $-COOH$s
- sidechains: many of them also ionizable

⇨ pH affects protein's ability to catalyze rxns & perform other functions

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: Ch.17 (the rest of it)

+ WORK ON Problems from Ch.17