

Spontaneity, Entropy and Free Energy

Dependence of Free Energy on pressure:

→ Free energy of rxn changes as rxn proceeds
bc free energy depends on pressure of gas or on concentration of species (sol'n).

Recall: $G = H - TS$

consider a system of ideal gas, with constant n and T .

$$S_{\text{large vol}} > S_{\text{small vol}}$$

more disorder

$$\therefore S_{\text{low pressure}} > S_{\text{high pressure}}$$

$$\therefore G_{\text{low pressure}} < G_{\text{high pressure}}$$

more pressure
more = free energy.

Relationship between free energy and pressure:

$$G = G^\circ + RT \ln(P)$$

(non-standard) (standard)

G : free energy of gas at P atm

G° : free energy of gas at 1 atm

R : 8.314 J/K.mol

T : K

Note: G at 1 atm : $G = G^\circ + RT \ln(1)$
 $G = G^\circ$

change in Free Energy:



$$\left\{ \begin{array}{l} G_A = G_A^\circ + RT \ln(P_A) \\ G_B = G_B^\circ + RT \ln(P_B) \end{array} \right.$$

$$\begin{aligned} \Delta G &= G_B - G_A \\ &= [G_B^\circ + RT \ln(P_B)] - [G_A^\circ + RT \ln(P_A)] \\ &= \Delta G^\circ + RT(\ln P_B - \ln P_A) \\ &= \Delta G^\circ + RT \ln\left(\frac{P_B}{P_A}\right) \xrightarrow{\textcolor{red}{P_B}} \frac{P_B}{P_A} = Q \end{aligned}$$

∴ Free energy change (ΔG) for non-standard :

$$\boxed{\Delta G = \Delta G^\circ + RT \ln(Q)}$$

$$Q = Q_c \text{ or } Q_p$$

- Rxn mixture = mostly reactants

$$Q \ll 1 \quad \therefore RT \ln(Q) \ll 0 \quad \therefore \Delta G < 0$$

Spontaneous forward : total free energy decrease
as rxn \rightarrow forward

- Rxn mixture = mostly product

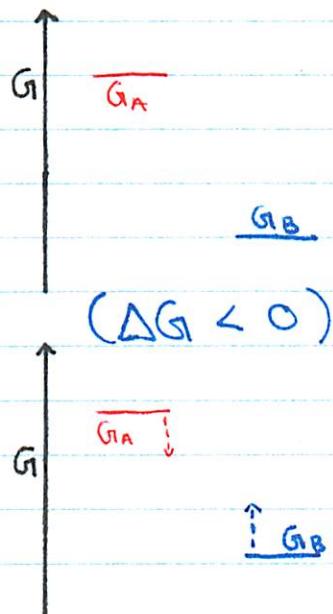
$$Q \gg 1 \quad \therefore RT \ln(Q) \gg 0 \quad \therefore \Delta G > 0$$

non-spontaneous : total free energy decrease
reverse spontaneous as rxn \rightarrow reverse

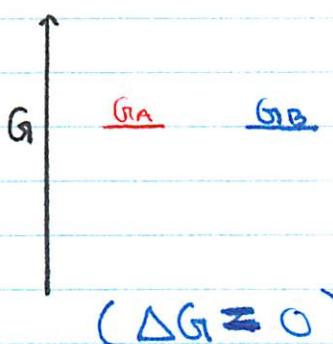
* At min. free energy composition,
 \rightarrow system is at equilibrium ($Q = K$)

- The equil. composition persists indefinitely unless
the system is disturbed (Châtelier)

Free Energy and Equilibrium



initial free energies of $A(g)$ and $B(g)$.



As $A(g)$ changes to $B(g)$
 → P_A is decreasing
 ∴ Free energy decreases
 → P_B is increasing
 ∴ Free energy increases

$G_A = G_B \Rightarrow$ equilibrium position
 • No longer a driving force
 to change A to B
 or B to A, so the
 sys. remains at this position.

$$\Delta G_{rxn} = G_{products} - G_{reactants}$$

At equilibrium: $\underline{\Delta G = 0}$, $\underline{Q = K}$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$0 = \Delta G^\circ + RT \cdot \ln(K)$$

$$\therefore \boxed{\Delta G^\circ = -RT \ln(K)}$$

$K = K_c$ or K_p
 (equil constant)

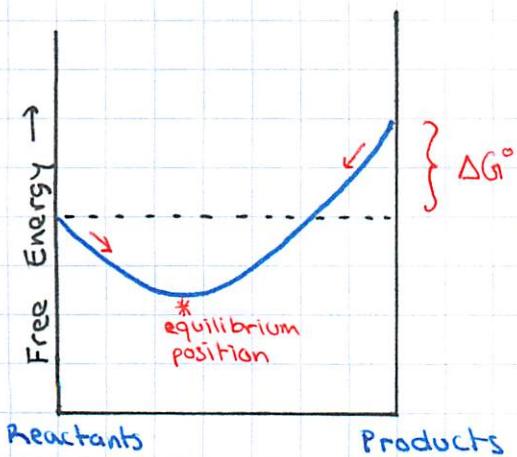
- for K_c : concentrations expressed in M
- for K_p : concentrations expressed in P_A (atm)

ΔG° and the Equilibrium Constant (K)

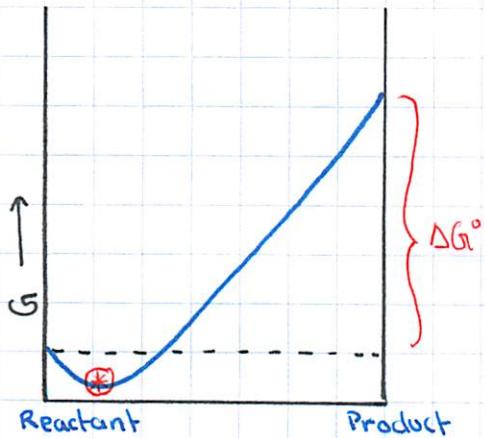
→ The equilibrium position represents the lowest free-energy value available to a particular rxn system.



(i)



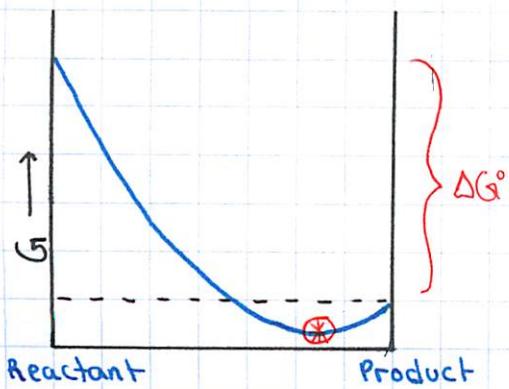
(ii)



$$K < 1, \Delta G^\circ > 0$$

- equilibrium lies closer to reactants
- rxn doesn't go far

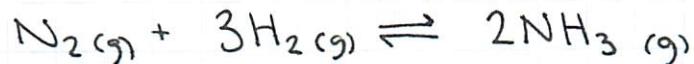
(iii)



$$K > 1, \Delta G^\circ < 0$$

- equilibrium lies closer to products
- rxn spontaneously goes far ($\Delta G^\circ < 0$)

ex: Consider the synthesis of ammonia:



- (i) Calculate ΔG_f at 298 K for a rxn mixture that consists of: 1 atm N_2 , 3 atm H_2 , 0.5 atm NH_3 with $\Delta G_f^\circ = -33.3 \text{ kJ}$.

$$\Delta G_f = \Delta G_f^\circ + RT \ln(Q)$$

$$= -33.3 \times 10^3 \text{ J} + (8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}})(298\text{K}) \cdot \ln \left[\frac{(0.5)^2}{(1) \cdot (3)^3} \right]$$
$$= \boxed{-44.9 \times 10^3 \text{ J/mol rxn}}$$

more spontaneous than at standard (smaller than ΔG_f°)

- (ii) Calculate the equilibrium constant at 298 K

$$\text{At eq. } \Delta G_f = 0$$

$$0 = \Delta G_f^\circ + RT \ln(K)$$

$$\Delta G_f^\circ = -RT \ln(K)$$

$$\ln(K) = -\frac{\Delta G_f^\circ}{RT}$$

$$e^{-\frac{\Delta G_f^\circ}{RT}} = K$$

$$K = e^{-\left(\frac{-33.3 \times 10^3 \text{ J}}{8.314 \cdot 298}\right)}$$

$$\boxed{K = 7 \times 10^5, \text{ at } 298 \text{ K}}$$

Relationship between temp. and K

- Le Châtelier's principle is used to predict the qualitative effect of temp. on the equilibrium constant.
- Quantitative:

$$\ln(K) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

Derive: $\Delta G^\circ = -RT \ln(K) = \Delta H^\circ - T\Delta S^\circ$

$$\ln(K) = \frac{\Delta H^\circ}{-RT} - \frac{T\Delta S^\circ}{-RT}$$

T in (K)

$$R = 8.314 \frac{\text{J}}{\text{K}\cdot\text{mol}}$$

$\Delta H, \Delta S$ in J/mol of rxn

$$\ln(K) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

$$y = m x + b$$

Graph : $\ln(K)$ Y vs $(\frac{1}{T})$ X

$$\rightarrow \text{slope} = -\frac{\Delta H}{R} \Rightarrow \Delta H = -(\text{slope})(R)$$

The Van't Hoff Equation

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

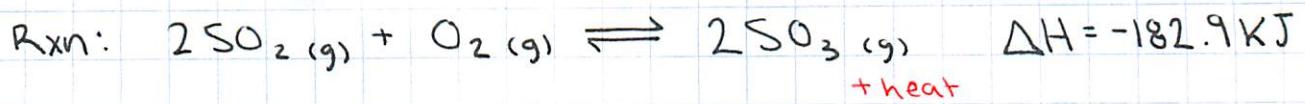
Derive: $\ln K_1 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1}\right) + \frac{\Delta S^\circ}{R}$

$\ln K_2 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2}\right) + \frac{\Delta S^\circ}{R}$

$$\ln K_1 - \ln K_2 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1}\right) + \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ}{R} \left(-\frac{1}{T_1} + \frac{1}{T_2}\right)$$

ex: Estimate the temperature at which $K_p = 1 \times 10^6$
 if at $\frac{800}{T_2}$, $K_p = 9.1 \times 10^2$



$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln\left(\frac{10^6}{9.1 \times 10^2}\right) = -\frac{182.9 \times 10^3 \text{ J}}{8.314} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$-3.18 \times 10^{-4} = \frac{1}{800 \text{ K}} - \frac{1}{T_1}$$

$$T_1 = 638 \text{ K}$$

Verify using le Chatelier:

$T_1 \rightarrow T_2$: temp increase

- ∴ reverse rxn occurs (consume heat)
- ∴ consume product
- ∴ K decrease from $1 \rightarrow 2$ ✓

Note: $K = \frac{[SO_3]^2}{[SO_2]^2 \cdot [O_2]}$ ∴ $K \downarrow$

Acids and Bases

Arrhenius (limited to aqueous sol'n)

- Acid - substance that increases the conc. of H^+ ions dissolved in H_2O .
- Base - substance that increases the conc. of OH^- ions dissolved in H_2O .

Brønsted-Lowry (more general)

- Acid = proton (H^+) donor.
- Base = proton (H^+) acceptor.

Acids

- monoprotic acid (HX) : 1 acidic proton

ex: HCl , HBr , HI , CH_3COOH

- diprotic acid (H_2X) : 2 acidic protons

ex: H_2SO_4

- triprotic acid (H_3X) : 3 acidic protons

ex: H_3PO_4

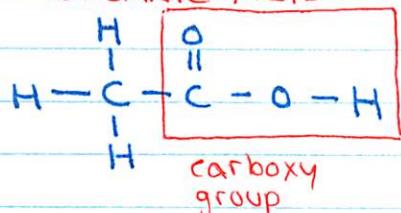
- oxyacid : acidic proton is attached to an oxygen atom.

ex: H_3PO_4 , HNO_3 (nitrous acid),
 $HOCl$ (hypochlorous acid)

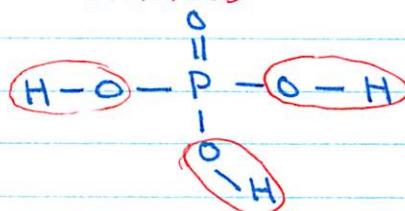
- organic acid: contain carboxyl = $COOH$,

ex: CH_3COOH , C_6H_5COOH

ORGANIC ACID



OXYACID



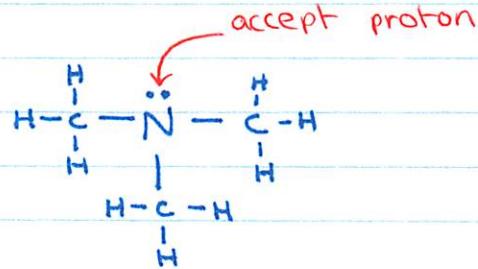
Bases

- metal hydroxides : $M_x(OH)_y$
- metal oxides : $M_x(O)_y$

ex: $NaOH$, $Mg(OH)_2$, CaO

- ammonia and amines (nitrogen attached to 3 groups of atoms)

ex: NH_3 , $N(CH_3)_3$, RNH_2 (R = chain containing C and H)



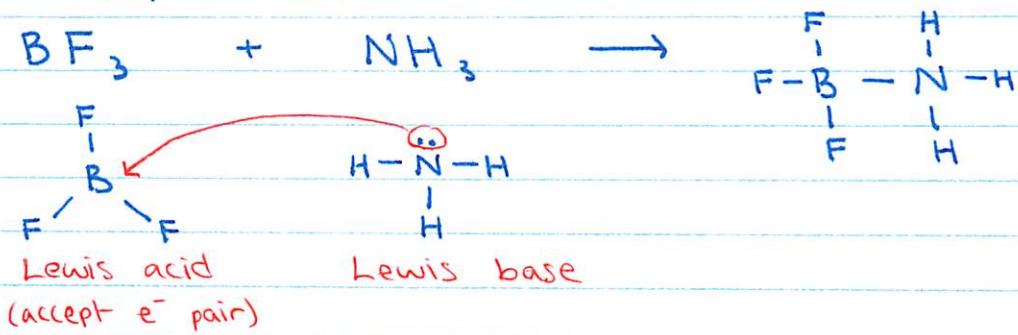
Lewis Acid and Base

→ Lewis acid = species that can form a covalent bond by accepting an e^- pair.
(Has an empty orbital)

→ Lewis base = species that can form a covalent bond by donating an e^- pair
(Has a lone pair of e^- available).

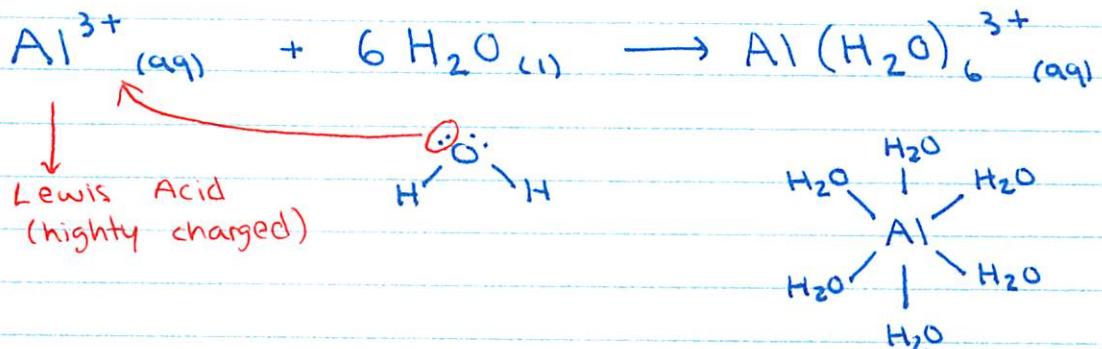
Lewis Acid Examples:

- molecules with incomplete octets have ~~incomplete / full~~ empty orbitals (AlCl_3 , BF_3)



- compounds with multiple bonds: can rearrange e^- to obtain empty orbitals

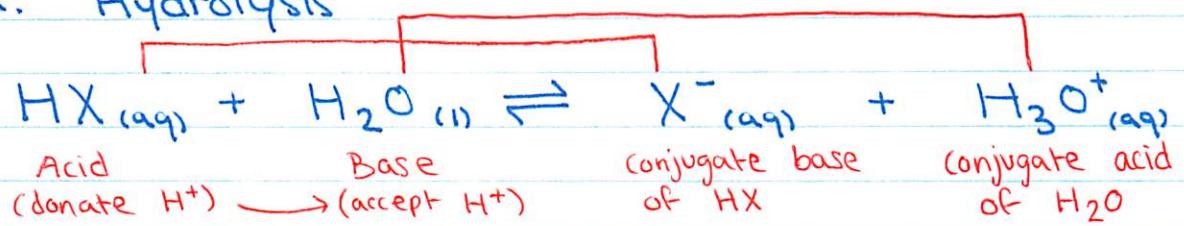
- cations such as highly charged metal ions (Al^{3+} , Fe^{3+} , ...) that lost e^- have empty orbitals.



Conjugate Acid-Base Pair

- when acid or base is dissolved in H_2O
= hydrolysis (dissociation or ionization rxn)
- conjugate acid-base pair = 2 substances related to each other by the donating or accepting of a single proton.

ex: Hydrolysis



forward: HX donates proton to H_2O

reverse: H_3O^+ donates proton to X^-

Acid Dissociation Constant

- strength of acid measured by its tendency to ionize (lose proton).
- equilibrium constant = acid dissociation constant (K_a)



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

Strong acid

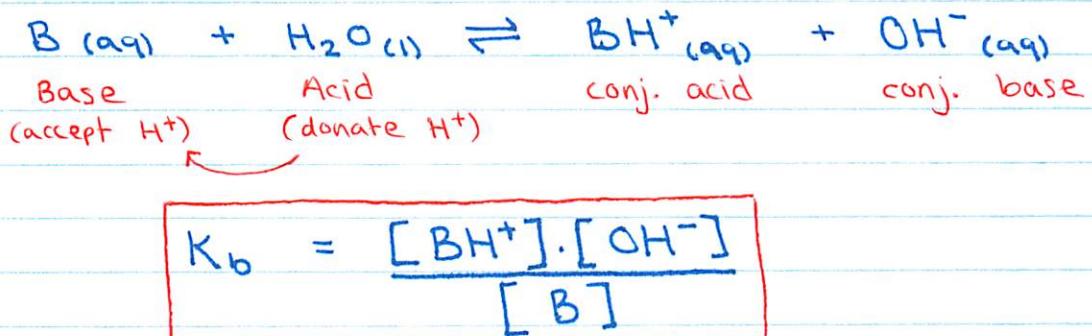
- large K_a ($K_a \gg 1$)
 - ionization goes far to the right (complete)
 - Yields a weak conjugate base (weaker than H_2O)
- 6 strong acids: HCl , HBr , HI
 HNO_3 , H_2SO_4 , HClO_4

Weak acid

- small K_a ($K_a \ll 1$)
 - smaller K_a , weaker the acid
 - ionization equil. lies far to the left
- exists in mixture as mix of the acid and its conjugate base. \rightleftharpoons
- The weaker the acid, the stronger its conjugate base. (stronger than H_2O)

Base Dissociation Constant

- unlike strong bases that contain OH, most weak bases produce OH⁻ by accepting a proton from H₂O
- base dissociation constant (K_b)



Strong base

- K_b value is large (K_b ≫ 1)
- ionization lies far to the right (complete) →
- Yields a weak conjugate acid (weaker acid than H₂O)

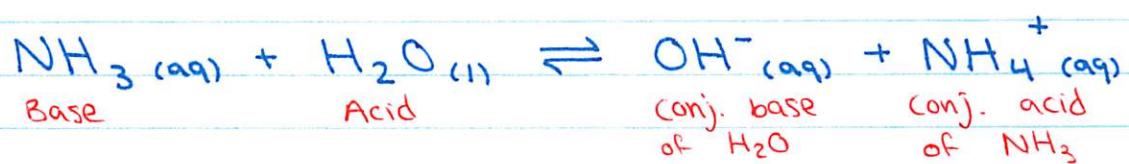
Strong bases: M_x(OH)_y where M is alkali (gr. I) or alkali-earth (gr. 2)



Weak base

- small K_b (K_b ≪ 1)
- ionization equil. lies far left ⇌
- The weaker the base, the stronger its conjugate acid (stronger acid than H₂O)

Weak bases: NH₃, amines



	Acid	Base	
Strongest acids			
	HClO ₄	ClO ₄ ⁻	
	H ₂ SO ₄	HSO ₄ ⁻	
	HI	I ⁻	
	HBr	Br ⁻	
	HCl	Cl ⁻	
	HNO ₃	NO ₃ ⁻	
	*H ₃ O ⁺	*H ₂ O	
	HSO ₄ ⁻	SO ₄ ²⁻	
	H ₂ SO ₃	HSO ₃ ⁻	
	H ₃ PO ₄	H ₂ PO ₄ ⁻	
	HNO ₂	NO ₂ ⁻	
	HF	F ⁻	
	HC ₂ H ₃ O ₂	C ₂ H ₃ O ₂ ⁻	
	Al(H ₂ O) ₆ ³⁺	Al(H ₂ O) ₅ OH ²⁺	
	H ₂ CO ₃	HCO ₃ ⁻	
	H ₂ S	HS ⁻	
	HClO	ClO ⁻	
	HBrO	BrO ⁻	
	NH ₄ ⁺	NH ₃	
	HCN	CN ⁻	
	HCO ₃ ⁻	CO ₃ ²⁻	
	H ₂ O ₂	HO ₂ ⁻	
	HS ⁻	S ²⁻	
Weakest acids	*H ₂ O	*OH ⁻	Strongest bases
			Weakest bases

A strong acid yields a weak base
(weaker base than H₂O)

A weak acid yields a strong base
(stronger base than H₂O)

Quantifying the strength

→ of an acid: • the greater the value of K_a , stronger the acid.

$$pK_a = -\log(K_a)$$

∴ the smaller the value of pK_a , the stronger the acid.

ex:

	K_a	pK_a	
A_1	1×10^{-2}	2	
A_2	1×10^{-9}	9	↑ increasing strength.

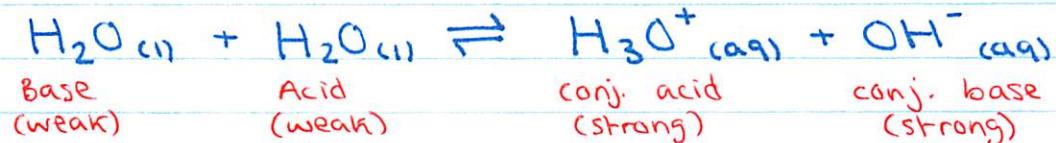
→ of a base: • K_b and pK_b

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

Water

→ amphoteric : can behave as an acid or a base
(other examples: HSO_4^- , HCO_3^-)

→ can undergo autoionization: transfer a proton from one H_2O to another



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

At 25°C , $K_w = 1 \times 10^{-14}$ (so small ∴ go left)

Note: if different temp. use "Van't Hoff"

No matter what the sol'n contains,
 $[\text{H}_3\text{O}^+] \times [\text{OH}^-]$ must always equal to
 1.0×10^{-14} (at 25°C).

$$\left\{ \begin{array}{ll} [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} & \text{neutral sol'n} \\ & \hookrightarrow \text{in distilled water} \\ [\text{H}_3\text{O}^+] > [\text{OH}^-] & \text{acidic sol'n} \\ [\text{H}_3\text{O}^+] < [\text{OH}^-] & \text{basic sol'n} \end{array} \right.$$

In each case (at 25°C):

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14}$$

Relationship between K_a and K_b

- The product of K_a for an acid and K_b for its conjugate base equals K_w
- ∴ As the strength of an acid increases (larger K_a), the strength of its conjugate base decreases (smaller K_b)

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

$$pK_a + pK_b = pK_w \quad 14$$



$$K_a \times K_b = K_w \\ = [\text{OH}^-][\text{H}_3\text{O}^+]$$

pH and pOH

→ $[H_3O^+]$ and $[OH^-]$ in sol'n are very small, so we use a different scale.

$$pH = -\log [H_3O^+]$$

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

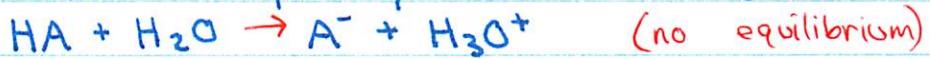
* As pH decreases, $[H_3O^+]$ increases.

Note: $pH + pOH = 14 = pK_w$ at $25^\circ C$

- pH = 7 : $[H_3O^+] = 1 \times 10^{-7} M$: neutral sol'n
- pH > 7 : $[H_3O^+] < 1 \times 10^{-7} M$: basic sol'n
- pH < 7 : $[H_3O^+] > 1 \times 10^{-7} M$: acidic sol'n

Calculating pH : strong acid

→ strong acids completely ionize in sol'n



- Acid is usually the only source of H_3O^+ ions

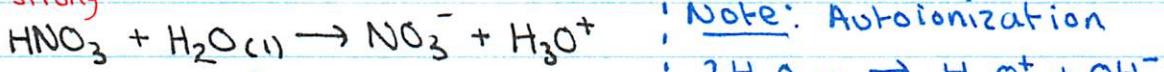
- * Autoionization still takes place

- usually conc. from autoionization can be neglected.

- if conc. of acid is 10^{-6} M or less, we also consider H_3O^+ ions that result from the autoionization of H_2O .

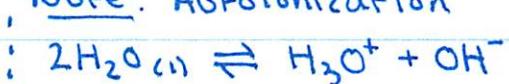
Calculate pH of 0.1 M HNO_3

strong



Before: 0.1 M

0 0



After: 0

0.1M

0.1 M

$1 \times 10^{-7} M$

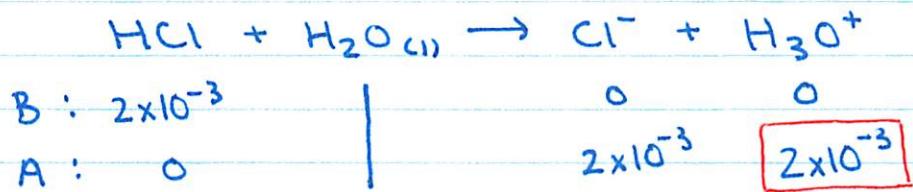
neglect bc so small compared to...

Major species: H_2O , H_3O^+ , NO_3^-

$$\therefore pH = -\log[H_3O^+] = -\log[0.1] = 1$$

ex: consider aqueous sol'n 2×10^{-3} M HCl

Major species: H_2O , Cl^- , H_3O^+



$$\therefore \text{pH} = -\log [2 \times 10^{-3}] = 2.7$$

ex: consider a 1.5×10^{-11} M HCl sol'n

Note: bc the concentration is so small ($< 10^{-6}$ M)
the amount of H_3O^+ coming from H_2O autoionization is significant.

$$[\text{H}_3\text{O}^+] \text{ from autoionization of } \text{H}_2\text{O} = 1.0 \times 10^{-7} \text{ M}$$

$$[\text{H}_3\text{O}^+] \text{ from dissociation of HCl} = \underbrace{1.5 \times 10^{-11} \text{ M}}_{\text{neglect: so small}}$$

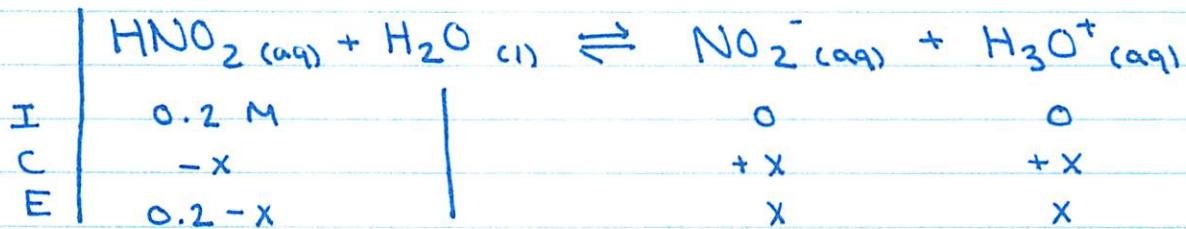
$$\therefore \text{pH} = -\log (1 \times 10^{-7} \text{ M}) = 7$$

Calculating pH: weak acid

- weak acids only partially ionize in sol'n
 - USE equilibrium constant K_a
 - we can use K_a to find eq. conc. of H_3O^+ and find pH.

1. List major species in sol'n
2. Species that can produce H_3O^+
 - write balanced equations
3. Decide which equilibrium will dominate the production of H_3O^+ . (based on K_a values).
4. ICE table
5. Solve for x
 - assume $[\text{HA}]_i - x = [\text{HA}]_i$
 - use 5% rule
6. Calculate pH.

ex: Calculate pH of 0.2 M soln of nitrous acid (HNO_2), $K_a = 4.6 \times 10^{-4} < 1$ ∴ weak
 Major species: H_2O , HNO_2



$$K_a \times 400 < 0.2 \\ \therefore \text{approximate } \approx 0.2$$

$$K_a = \frac{x^2}{0.2} = 4.6 \times 10^{-4}$$

$$\boxed{x = 9.6 \times 10^{-3} \text{ M}}$$

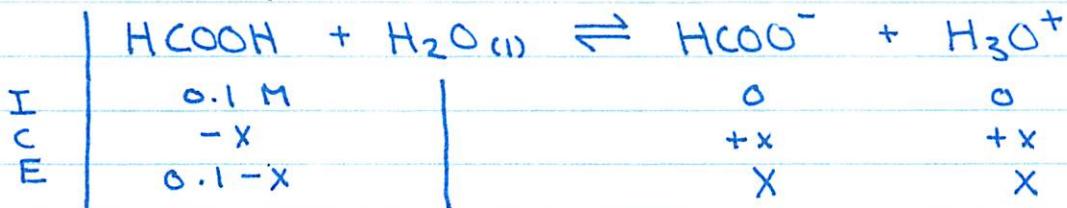
$$\underline{\text{Validate: }} \frac{9.6 \times 10^{-3}}{0.2} \times 100 < 5\% \quad \checkmark$$

$$[\text{H}_3\text{O}^+] = 9.6 \times 10^{-3} \text{ M} \quad \underline{\text{Note: }} > 1 \times 10^{-7} \text{ M from autoionization}$$

$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+]_{\text{eq}} = -\log (9.6 \times 10^{-3}) = 2.02$$

ex: 0.1 M HCOOH has pH of 2.38 at 25°C.

Calculate K_a :



Solve for x

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$10^{-\text{pH}} = [\text{H}_3\text{O}^+] = x$$

$$10^{-2.38} = x$$

$$\boxed{x = 4.2 \times 10^{-3}}$$

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

$$= \frac{(4.2 \times 10^{-3})^2}{(0.1 - 4.2 \times 10^{-3})}$$

$$= \boxed{1.8 \times 10^{-4}}$$

Percent Dissociation (Ionization)

→ measure of strength of acid

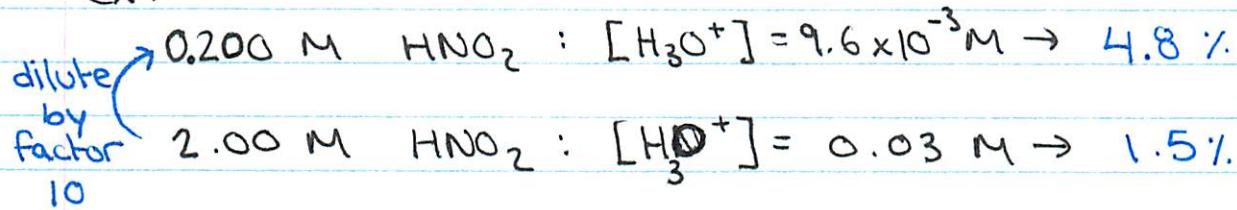
- The stronger the acid, the greater the percent dissociation

$$\text{Percent dissociation} = \frac{\text{amount dissociated}}{\text{initial concentration}} \times 100$$

$$\text{Percent dissociation for acid} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_i} \times 100$$

* The percent dissociation of a weak acid decreases with increasing concentration of weak acid

ex:



$$Q_a = \frac{\left(\frac{1}{10} \text{ H}_3\text{O}^+\right) \cdot \left(\frac{1}{10} \text{ NO}_2^-\right)}{\left(\frac{1}{10} \text{ HNO}_2\right)}$$

After dilution

$$Q_a = \frac{1}{10} K_a$$

∴ rxn shifts to the right
⇒ more product
⇒ more dissociation

Polyprotic Acid

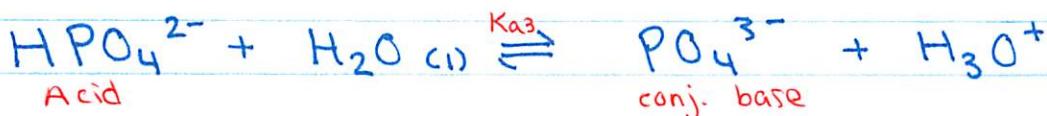
- Acids can furnish more than 1 proton
→ dissociate stepwise (1 proton at a time).
- * Conjugate base of the first dissociation equilibrium, becomes the acid in the second step.
- It is always easier to remove the first proton from a polyprotic acid than to remove the second.
For a typical weak polyprotic acid:



→ K_{a_1} forms the most ions (stronger acid)

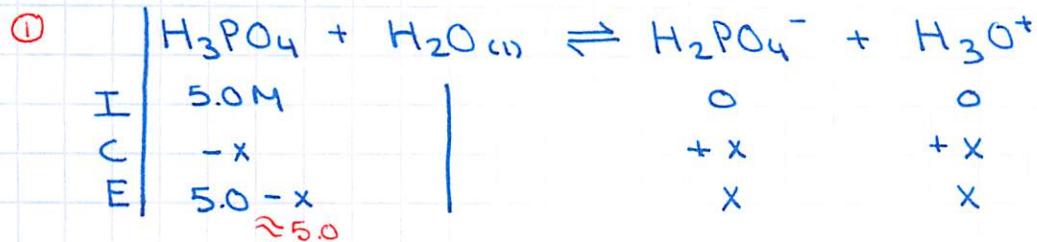
- * For a typical polyprotic acid, only the first dissociation step is important to calculate the pH of the sol'n.

ex. ionization of phosphoric acid:



ex. Calculate pH of 5.0 M H_3PO_4 and determine equilibrium conc. of H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} ($K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, $K_{a_3} = 4.8 \times 10^{-13}$)
 only consider K_{a_1} for pH bc much greater than K_{a_2} and K_{a_3}

Major Species: H_2O , H_3PO_4



$$K_{a_1} = 7.5 \times 10^{-3} = \frac{x^2}{5.0}$$

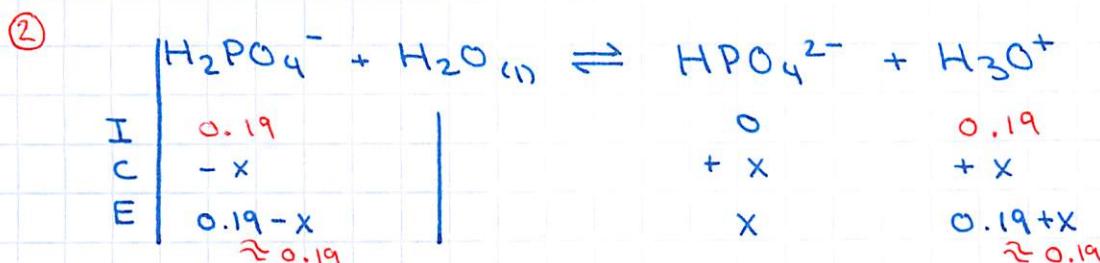
$$x = 0.19$$

Validate

$$\frac{0.19}{5.0} \times 100 = 3.8\% < 5\%$$

$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log (0.19) = 0.72 = \text{pH}$$

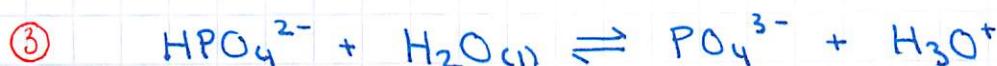


$$K_{a_2} = 6.2 \times 10^{-8} = \frac{x(0.19)}{(0.19)}$$

$$x = 6.2 \times 10^{-8}$$

Validate

$$\frac{6.2 \times 10^{-8}}{0.19} \times 100 < 5\%$$



$$K_{a_3} = 4.8 \times 10^{-13} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]}$$

$$\rightarrow 0.19$$

$$\rightarrow 6.2 \times 10^{-8}$$

$$[\text{PO}_4^{3-}] = 1.6 \times 10^{-19} \text{ M}$$

$$[\text{H}_3\text{PO}_4] = 4.81 \text{ M}$$

$$[\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$$

$$[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$$

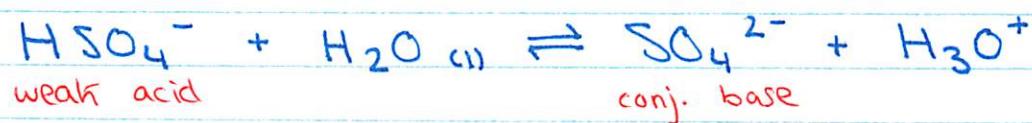
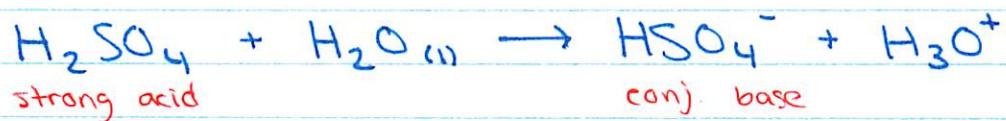
$$[\text{PO}_4^{3-}] = 1.6 \times 10^{-19} \text{ M}$$

Sulfuric Acid (a unique polyprotic)

→ H_2SO_4 is a strong acid

→ second step \Rightarrow become weak acid

- For 1.0 M or more
the large concentration of H_3O^+ comes from the first step and the contribution of step 2 is neglected.
 - For dilute = smaller 0.1 M
the second step will make a significant contribution to H_3O^+



ex: calculate pH of 2.0 M H_2SO_4 soln
 $2.0 \text{ M} \therefore \text{concentrate 1}$



B:	2.0 M		0	0
A:	0		2.0 M	2.0 M

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2)$$

$$\therefore \boxed{\text{pH} = -0.3} \quad \text{neg. pH value}$$

ex: calculate pH for $1 \times 10^{-2} \text{ M}$ sol'n H_2SO_4
 $(K_{a_2} = 1.2 \times 10^{-2})$.



B:	$1.0 \times 10^{-2} \text{ M}$		0	0
A:	0		$1 \times 10^{-2} \text{ M}$	$1 \times 10^{-2} \text{ M}$

{ eq₁ = initial₂ }

	$\text{HSO}_4^- + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+$
I	$1 \times 10^{-2} \text{ M}$
C	$-x$
E	$1 \times 10^{-2} - x$

NO APPROXIMATION

bc initial conc. is small (similar to K_{a_2})

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{x (10^{-2} + x)}{(10^{-2} - x)}$$

$$x^2 + (0.022)x - 1.2 \times 10^{-4} = 0$$

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

$$\boxed{x = 4.5 \times 10^{-3}}$$

$$[\text{H}_3\text{O}^+] = 10^{-2} + (4.5 \times 10^{-3}) \\ = 0.0145$$

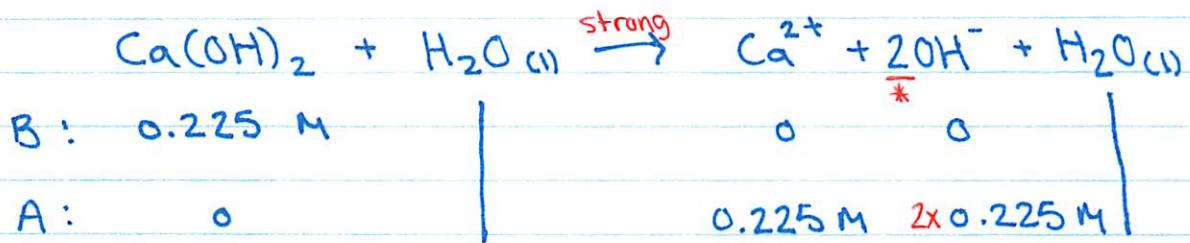
$$\text{pH} = -\log (0.0145)$$

$$\therefore \boxed{\text{pH} = 1.84}$$

Calculate pH : Strong base

- strong base will completely dissociate
- strong base = $M\text{OH}$ or $M(\text{OH})_2$
where $M = 1\text{A}$ metal or 2A metal
- * Unlike diprotic acids, which ionize in 2 steps, bases containing 2 OH^- ions dissociate in 1 step.

ex: calculate the pH of 0.225 M $\text{Ca}(\text{OH})_2$
major species: H_2O , OH^- , Ca^{2+}



2 ways to calculate pH:

① $\text{pH} + \text{pOH} = 14$

$$\begin{aligned}\text{pOH} &= -\log [\text{OH}^-] \\ &= -\log (2 \times 0.225) \\ &= 0.347\end{aligned}$$

$$\begin{aligned}\text{pH} &= 14 - \text{pOH} \\ &= 14 - 0.347 \\ &= 13.65\end{aligned}$$

② calculate $[\text{H}_3\text{O}^+]$

$$\begin{aligned}\text{K}_w &= [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 10^{-14} \\ [\text{H}_3\text{O}^+] \cdot (0.225 \times 2) &= 10^{-14} \\ [\text{H}_3\text{O}^+] &= 2.22 \times 10^{-14}\end{aligned}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.22 \times 10^{-14}) = \boxed{13.65}$$

Calculate pH : weak base

→ unlike strong base that contain OH^- , common weak bases produce OH^- ions by accepting a proton from H_2O .

- Quantify the extent of ionization of a weak base with K_b

$$\text{percent dissociation for base} = \frac{[\text{OH}^-]_{\text{eq}}}{[\text{B}]_{\text{i}}} \times 100$$

ex: calculate pH for 0.1M NH_3 ($K_b = 1.76 \times 10^{-5}$)

	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
I	0.1 M
C	-x
E	0.1 - x ≈ 0.1

$$K_b = \frac{x^2}{0.1} = 1.76 \times 10^{-5}$$

$$x = 1.33 \times 10^{-3} \text{ M}$$

Validate

$$\frac{1.33 \times 10^{-3}}{0.1} \times 100$$

$$= 1.33\% < 5\%$$

$$\text{pOH} = -\log(1.33 \times 10^{-3}) = 2.88$$

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

$$\therefore \text{pH} = 11.12$$

Percent Ionization Note: same as validation

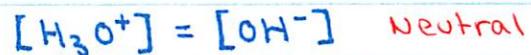
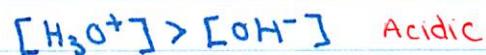
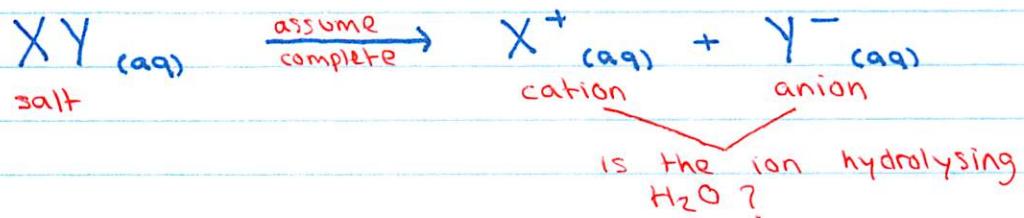
$$= \frac{[\text{OH}^-]_{\text{eq}}}{[\text{NH}_3]_{\text{i}}} \times 100 = \frac{1.33 \times 10^{-3}}{0.1} \times 100 = 1.33\%$$

Acid - Base Property of Salts

- When an ionic compound (salt) dissolves in water, it breaks up into its ions : a cation (+) and a anion (-).
→ These ions can act as acid / base.

* Assume all salts dissociate completely

- Anion and cation can react with H_2O to generate OH^- , H_3O^+ ions.

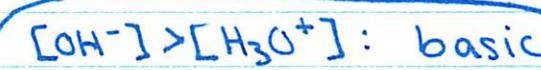
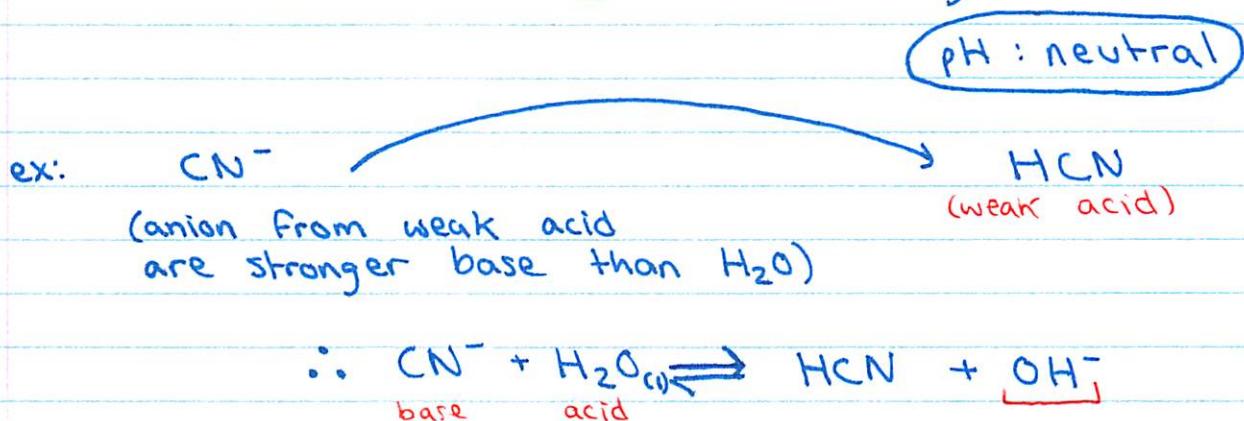
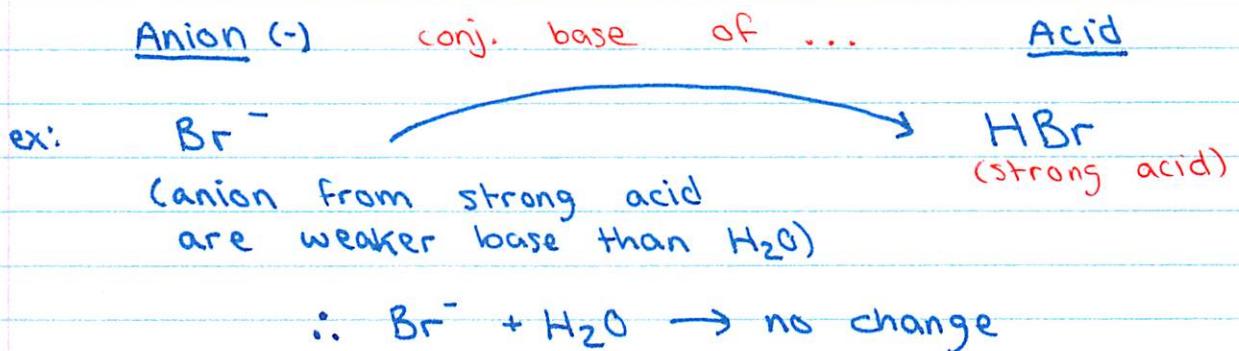


Anion (-) as weak base

• \rightarrow anion = conjugate base of acid



- anion of weak acids can hydrolyse H_2O
 \Rightarrow forms basic sol'n
- anion of strong acids cannot hydrolyse H_2O
 \Rightarrow sol'n stays neutral



Note: even though base is stronger than H_2O
it is still a weak base \therefore equil. \rightleftharpoons

Cation (+) as weak acid

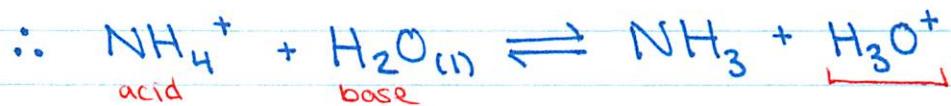
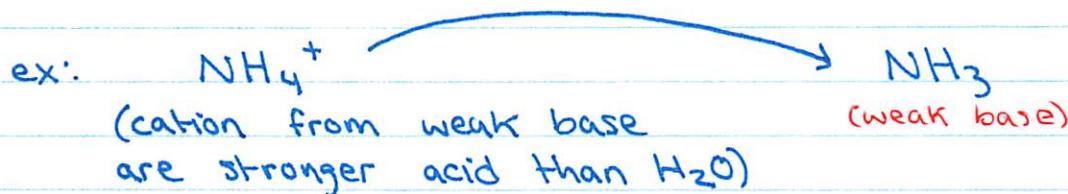
① Cations that are counterions of strong base do not hydrolyse H_2O .

⇒ form neutral sol'n

i.e. Alkaline and Alkaline-earth metals

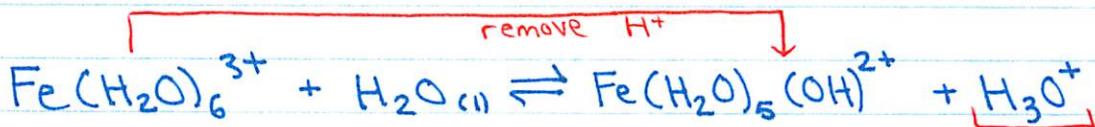
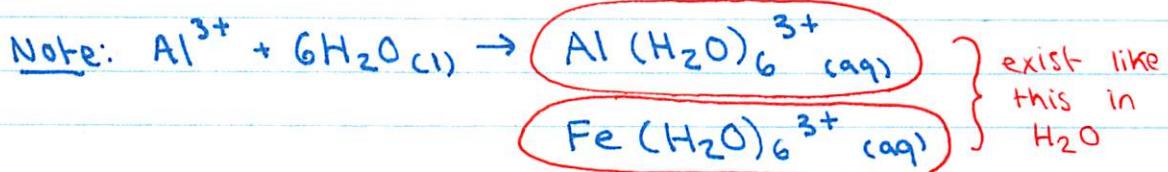
ex: Ca^{2+} , Na^+ ⇒ cannot hydrolyse H_2O

② Cations that are conjugate acid of weak base can hydrolyse H_2O
⇒ form acidic sol'n



$[\text{H}_3\text{O}^+] > [\text{OH}^-]$: acidic

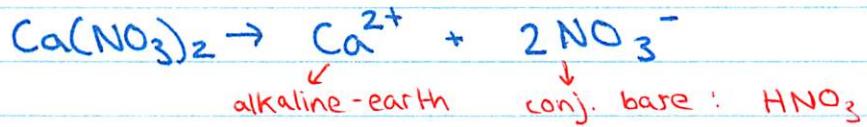
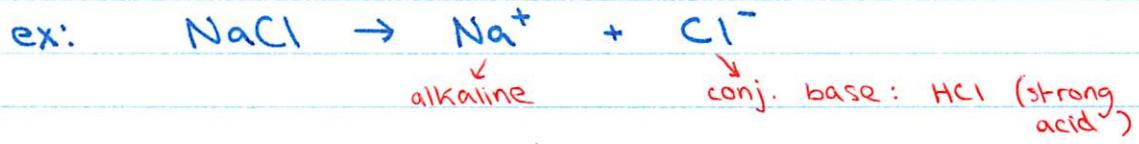
③ Cation: small highly charged metals (Fe^{3+} , Al^{3+} , ...) form weak acidic sol'n.



$[\text{H}_3\text{O}^+] > [\text{OH}^-]$: acidic

Classifying Salts

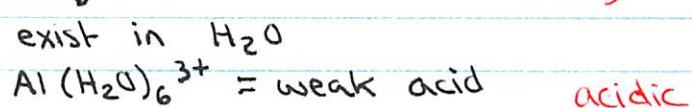
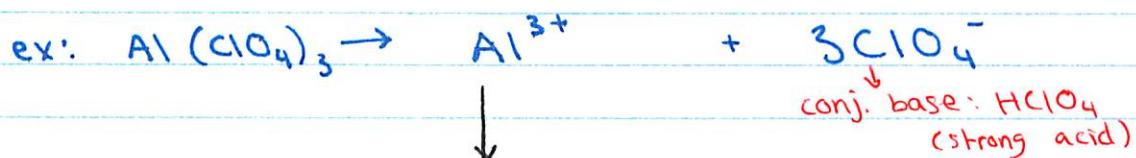
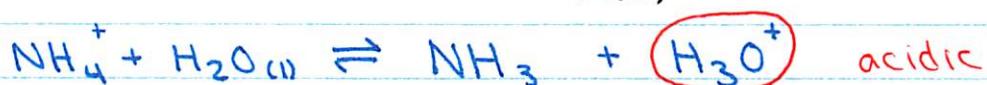
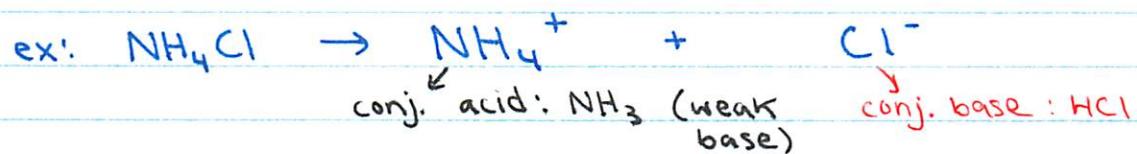
1. Salts in which neither cation / anion can act as base or acid \Rightarrow neutral



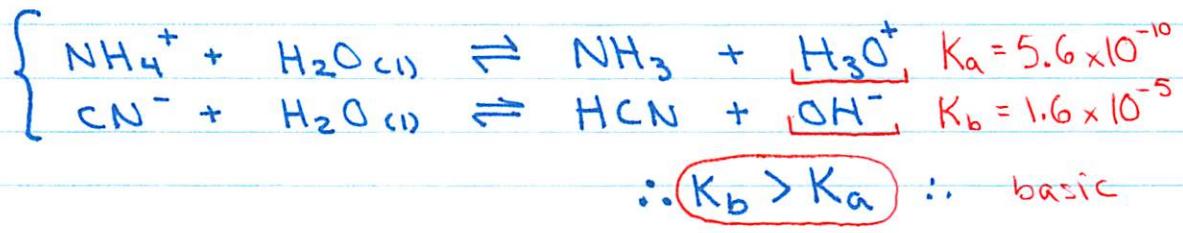
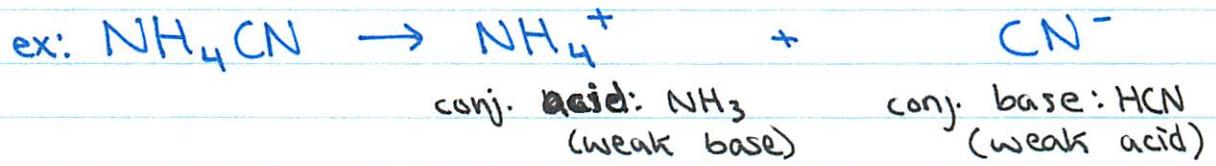
2. Salt: cation does not act as acid , but anion acts as base \Rightarrow basic



3. Salt : cation acts as acid , but anion does not act as base \Rightarrow acidic



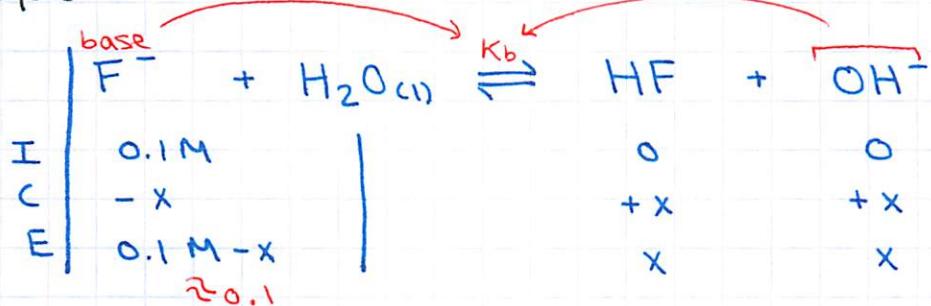
4. Salt: cation acts as acid, anion acts as base \Rightarrow pH depends on strength (K_a , K_b)



ex: Calculate pH of 0.1 M NaF sol'n.
The K_a value of HF is 7.2×10^{-4}



2. Hydrolysis:



Note: Given K_a for HF, want K_b for F^-

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

$$K_b = \frac{10^{-14}}{7.2 \times 10^{-4}}$$

$$K_b = 1.39 \times 10^{-11} = \frac{x^2}{0.1}$$

$$x = 1.18 \times 10^{-6} \text{ M} \quad \text{Validate}$$

$$\frac{1.18 \times 10^{-6}}{0.1} \times 100 < 5\%$$

3. Calculate pH

$$\begin{aligned} \text{(a)} \quad p\text{OH} &= -\log [\text{OH}^-] \\ &= -\log (1.18 \times 10^{-6}) \\ &= 5.93 \end{aligned}$$

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

$$\text{pH} = 8.07$$

$$\text{(b)} \quad [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 10^{-14}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{10^{-14}}{[\text{OH}^-]} \\ &= \frac{10^{-14}}{1.18 \times 10^{-6}} \end{aligned}$$

$$= 8.47 \times 10^{-9} \text{ M}$$

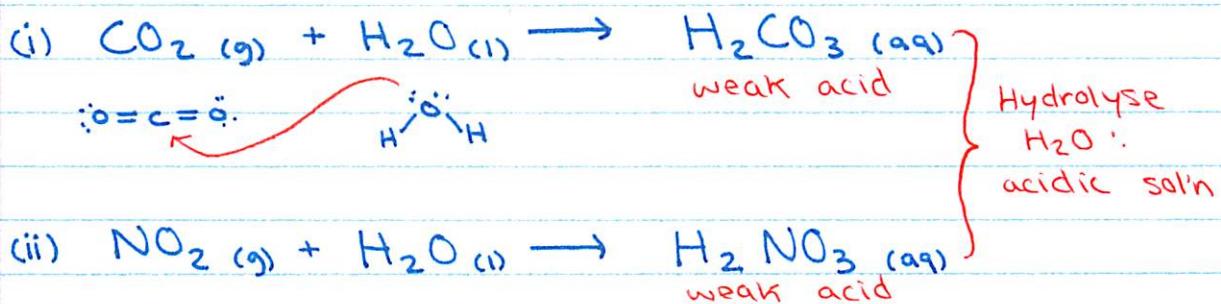
$$\text{pH} = -\log (8.47 \times 10^{-9}) = 8.07$$

Acid/Base properties of Oxides

• Acidic oxides

O-X bond: covalent (with non-metal)

ex: SO_2 , NO_2 , CO_2

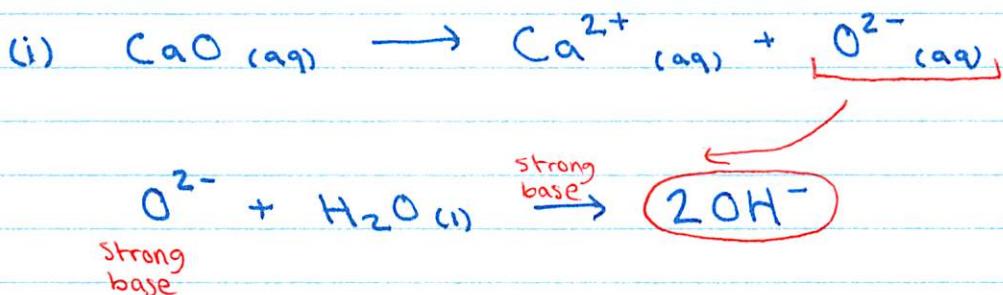


• Basic oxides

O-X bond: ionic (with metal)

O^{2-} = strong base

ex: K_2O , CaO



$[\text{OH}^-] \uparrow \therefore \text{basic}$

Acid Strength and Molecular Structure

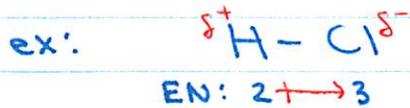
→ Strength of acid depends on the extent to which a proton can be separated from it and transferred to a base.

→ Use molecular structure:

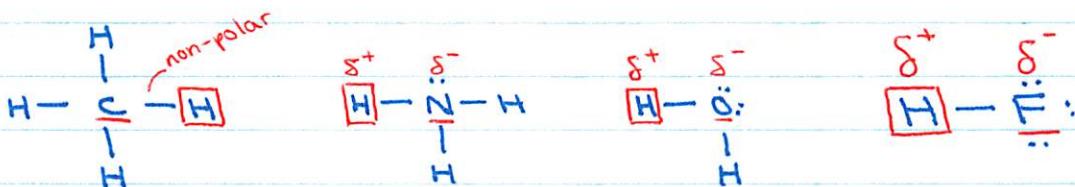
- (a) electronegativity
- (b) size
- (c) effect of charge
- (d) inductive effect.

A Electronegativity: Polarity of H-X bond

- Polarity = distribution of e^- in bond
- Depends on EN difference between atoms
↳ EN = ability to pull an e^- to itself



ex: C N O F → same row (EN increase →)



EN increase (ie. polarity increase) →

∴ bond gets cleaved more easily (breakage) ⇒ already being pulled apart

∴ more dissociation ∴ stronger Acids

B Size of X and Bond strength

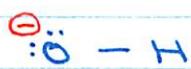
- the stronger the bond, the weaker the acid bc the more tightly the hydrogen atom is held
- strength of H-X bond depends on size of X (atomic radius)
- * As the size of the atom X increases, the strength of the bond decreases giving for a stronger acid.

size increase weaker bond	H-X bond	Bond-Strength	Acid-Strength
	H-F $\leftarrow 2p$	565	Weak
	H-Cl $\leftarrow 3p$	427	Strong
	H-Br $\leftarrow 4p$	363	Strong
	H-I $\leftarrow 5p$	295	Strong

C Effect of charge on Acidity

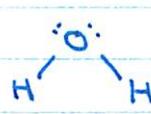
- Acidity increases with increasing positive charge on the atom bearing the acidic hydrogen
- ⇒ bc: neg charge : hard to donate proton

ex: OH^-



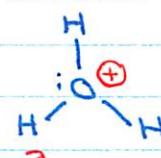
$\text{H}_2\text{O} = \text{conju. acid}$
of OH^-

H_2O



$\text{H}_3\text{O}^+ = \text{conju. acid}$
of H_2O

H_3O^+



acidity increases (easier to donate proton) 

D Inductive effect of Oxyacids

→ Oxyacid = H - O - Y (Y may be bonded to other atoms)

ex: H_2SO_4 , HNO_3 , H_2CO_3 , ...

→ Inductive effect = electronic effect transmitted through sigma bonds when a highly EN atom (Oxygen) is located close to the acidic hydrogen

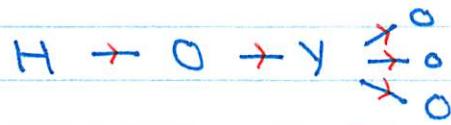


↓
The easier to break this bond,
the stronger the acid

Result: e⁻ density pulled away from H
∴ easy H-O cleave
∴ more dissociation

* The more electronegative the Y group is, the stronger the acid.

- For oxyacids that have the same central atom Y, acid strength increases as the number of O atoms attached to Y increase.



The more O, the more e⁻ is pulled
∴ easy to cleave O-H

Factors that affect acidity:

- EN of element Y
- number of oxygen atoms attached to Y

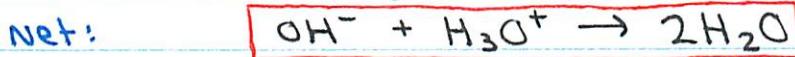
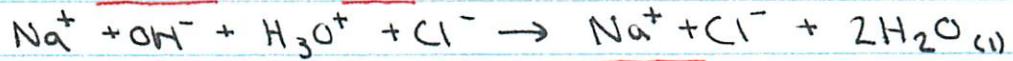
Acid-Base Equilibria

Types of Acid-Base Rxns: neutralization
→ acid-base rxns always favour the formation
of the weaker acid and weaker base.

Note: All rxns have large K ∴ use straight arrow

(a) Rxn: strong acid + strong base

→ equal amounts (mol) ∴ neutral sol'n

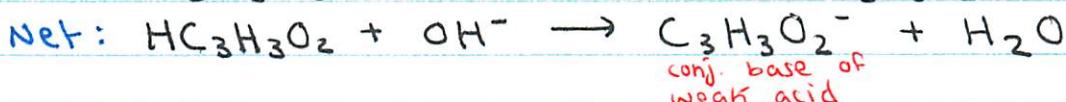


$$\text{Reverse of } K_w \quad \therefore K = \frac{1}{K_w} = \frac{1}{10^{-14}} = 10^{14}$$

large ∴
rxn goes far

(b) Rxn: weak acid + strong base

→ equal amounts (mol) ∴ produce anion which is
conj. base of weak acid ∴ basic: pH depend
on K_b of anion



$$\text{Reverse rxn} = \text{hydrolysis of base} \quad \therefore K = \frac{1}{K_b}$$

(c) Rxn: strong acid + weak base

→ equal amounts (mol) ∴ produce cation which is
conj. acid of weak base ∴ acidic: pH
depend on K_a of cation.

(d) Rxn: weak acid + weak base

→ equal amounts (mol) ∴ produce anion which is
conj. base of weak acid + cation which is
conj. acid of weak base. pH depends on
the relative K_a and K_b values.

Common-Ion Effect

- The effect of adding a solute to a sol'n of a weak acid or base will affect acid/base ionization.
- The common ion effect = the shift in equilibrium position that occurs, caused by the addition of a solute that provides an ion that is already involved in the equilibrium rxn (Le Châtelier).

ex: Add 1.0M NaF to 1.0M HF sol'n.

- initial sol'n: $\text{HF} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+$
weak acid
- addition of NaF (salt \rightarrow dissociates)
= addition of $\boxed{\text{F}^-}$ (already present initially)
⇒ Châtelier: extra F^- ∴ shift left.
 \therefore less H_3O^+
- Sol'n of HF and NaF is less acidic than HF alone (percent dissociation decrease).

ex: Calculate pH and percent dissociation of HF in a sol'n containing 1M HF ($pK_a = 3.14$)
 1M NaF
 (percent diss. of 1M HF = 2.7%) \rightarrow initially 1 M of F^-

(*) Initial amount of F^- (common-ion) is the amount of salt present.

	$HF + H_2O \rightleftharpoons F^- + H_3O^+$
I	1.0 M
C	-x
E	1.0-x

$$pK_a = -\log(K_a)$$

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

$$10^{-3.14} = K_a$$

$$K_a = 7.24 \times 10^{-4}$$

Note: small \therefore approximate!

$$1.0 M \quad 0$$

$$+x \quad +x$$

$$1.0+x \quad x$$

$$K_a = 7.24 \times 10^{-4} = \frac{x(1.0)}{(1.0)}$$

$$x = 7.24 \times 10^{-4} M$$

$$\text{validate: } \frac{7.24 \times 10^{-4}}{0.1} \times 100 = 0.72\% < 5\%$$

$$pH = -\log[H_3O^+]$$

$$= -\log(7.24 \times 10^{-4})$$

$$= 3.14$$

$$\gamma_{\text{dissociation}} = \frac{[H_3O^+]_{\text{eq}}}{[HF]_{\text{i}}} \times 100$$

$$= \frac{7.24 \times 10^{-4}}{0.1} \times 100$$

$$= 0.72\%$$

Buffers

Buffer = sol'n containing a mixture of a weak acid or base with its salt (common ion).

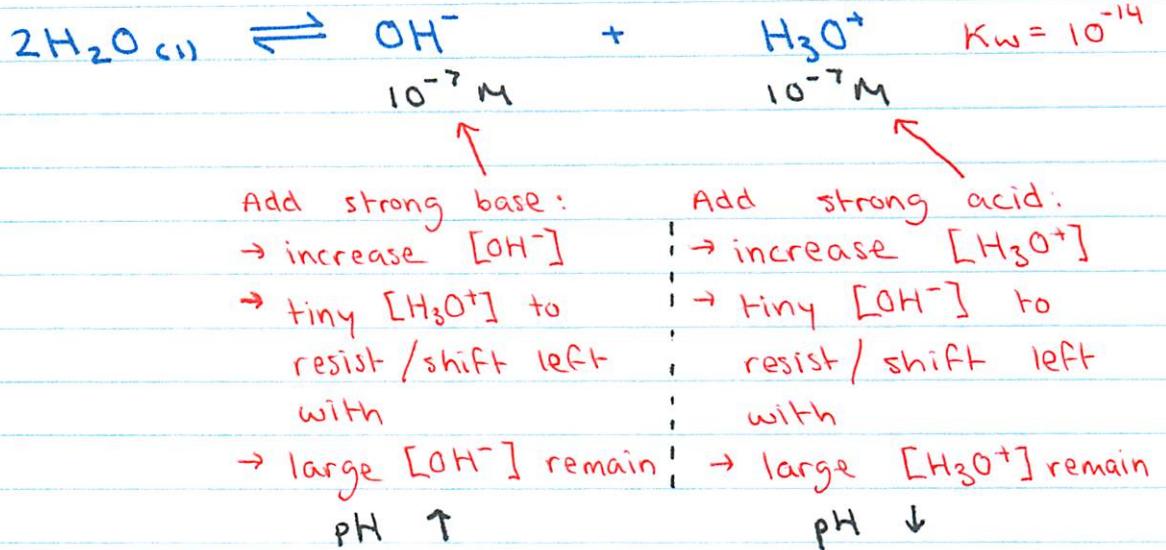
i.e. weak acid-base conjugate pair together in sol'n in significant amount.

- ability to resist changes in pH upon addition of small amounts of strong acids or strong bases.
- sol'n can be buffered at any pH by choosing the appropriate components.

ex:	Water	vs	Buffer
initial pH :	7		7
add 5mL of 0.01 M HCl	: 2.3		≈ 7

resist pH change

Water CANNOT resist pH change



Buffering Action

→ consider a buffer composed of equal amounts of weak acid (HA) and conj. base (A^-).



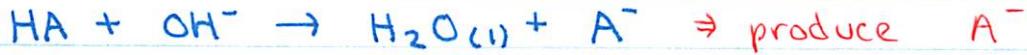
① Add H_3O^+ : react to completion with A^- (conj. base)

→ consume excess H_3O^+

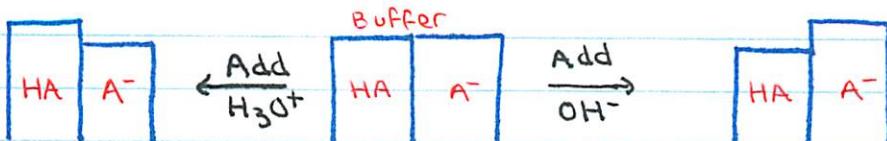


② Add OH^- : react to completion with HA (acid)

→ consume excess OH^-



pH of buffer is determined by ratios of conc. of weak acid and weak base. As long as ratio remains virtually constant: pH virtually constant.
→ will be the case as long as conc. of buffer materials ($\text{HA} + \text{A}^-$ or $\text{B} + \text{BH}^+$) are large compared to the amounts of OH^- and H_3O^+ added.



Buffer Capacity and pH Range.

An effective buffer has:

1. Large concentration of HA, A⁻ or B, BH⁺
→ provides high buffer capacity = the amount of H₃O⁺ or OH⁻ it can neutralize until the pH starts to change.

ex: 0.1 M HA and A⁻ vs. 1M HA and A⁻
higher buffer capacity

2. Equal concentrations of HA, A⁻ or B, BH⁺
→ [HA]:[A⁻] or [B]:[BH⁺] ratio from 1:10 to 10:1 works well (1:1 best)
→ pH range = pH over which the buffer acts effectively
⇒ usually usable range pH = pK_a ± 1

Calculate pH of buffer sol'n (2 ways)

1. Equilibrium problem
 - (a) identify major species
 - (b) identify eq. that is source of H₃O⁺/OH⁻
 - (c) ICE
 - (d) use K to calculate [H₃O⁺]
2. Using Henderson - Hasselbalch equation.

Henderson-Hasselbalch Equation

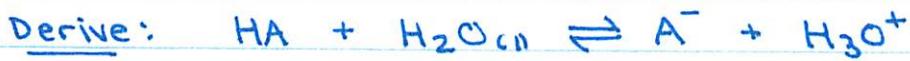
→ use initial concentrations to find pH

* ONLY use for buffers

- For a particular buffer system (conj. A/B pair) all sol'n that have the same ratio: $[A^-]/[HA]$ will have the same pH.
- We can assume that $[HA]$ and $[A^-]$ equilibrium concentrations are the same as the initial concentrations (5% rule) \Rightarrow weak acids

$$pH = pK_a + \log \frac{[A^-]_i}{[HA]_i}$$

$$pOH = pK_b + \log \frac{[BH^+]_i}{[B]_i}$$



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

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

$$-\log(K_a \cdot \frac{[HA]}{[A^-]}) = -\log[H_3O^+]$$

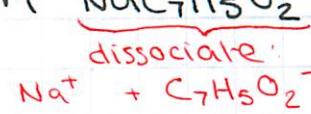
$$pH = -\log(K_a) + -\log \frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

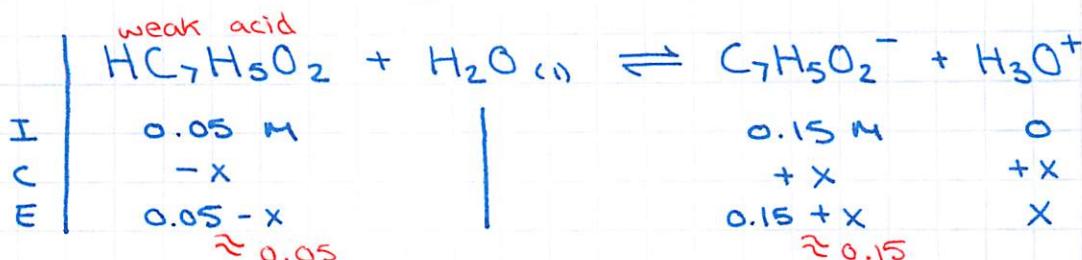
$$\left. \begin{array}{l} \text{if } [A^-]/[HA] = 1 \quad \therefore pH = pK_a \\ \text{if } [A^-]/[HA] = 10 \quad \therefore pH = pK_a + 1 \\ \text{if } [A^-]/[HA] = \frac{1}{10} \quad \therefore pH = pK_a - 1 \end{array} \right\} \begin{array}{l} \text{pH range} \\ \text{of effective} \\ \text{buffer} \\ \text{pH} = pK_a \pm 1 \end{array}$$

ex: Using Equilibrium

Calculate the pH of a buffer sol'n that
is 0.05 M $\text{HC}_7\text{H}_5\text{O}_2$ and 0.15 M $\text{NaC}_7\text{H}_5\text{O}_2$.
(K_a for $\text{HC}_7\text{H}_5\text{O}_2 = 6.5 \times 10^{-5}$)



① Hydrolysis of Acid



$$K_a = 6.5 \times 10^{-5} = \frac{x(0.15)}{(0.05)}$$
$$x = 2.2 \times 10^{-5} \text{ M}$$

validate (use smaller approx value)

$$\frac{2.2 \times 10^{-5}}{0.05} \times 100 = 0.04\% < 5\%$$

$$\text{pH} = -\log (2.2 \times 10^{-5})$$

$$\boxed{\text{pH} = 4.66}$$

ex: Using Henderson-Hasselbalch equation

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

$$= -\log (6.5 \times 10^{-5}) + \log \frac{(0.15 \text{ M})}{(0.05 \text{ M})}$$

$$= \boxed{4.66}$$

Preparing Buffer Sol'n of desired pH.

→ suppose you want buffer sol'n : pH = 5.09

Option A = find weak acid HA, that has $pK_a = 5.09$ and prepare a sol'n with equal molarities of acid HA and its conj. base A^- . (not practical)

Option B = use common weak acid with pK_a close to desired pH. And establish an appropriate $[A^-]/[HA]$ ratio to obtain pH = 5.09.

→ Always verify if 2 options are in fact conj. A/B pair (to be a buffer)
→ only weak acids can be buffer.

ex: Which conj. A/B pair to prepare buffer, pH = 5.09

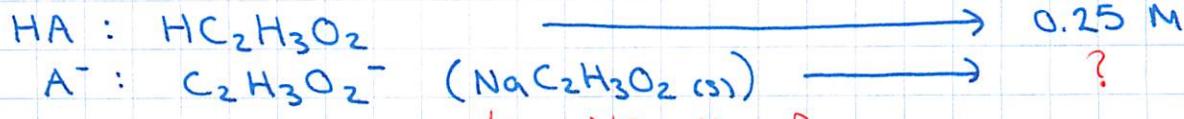
(a) NaCl and HCl → no buffer : strong acid

(b) NH₃ and NH₄Cl ($pK_a = 9.3$)

(c) NaH₂PO₄ and H₃PO₄ ($pK_a = 2.12$)

(d) HC₂H₃O₂ and NaC₂H₃O₂ ($pK_a = 4.74$) ✓

ex: What mass of $\text{NaC}_2\text{H}_3\text{O}_2$ must be dissolved in 0.3 L of 0.25 M $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid) to produce buffer: $\text{pH} = 5.09$ ($\text{pK}_a \text{ HC}_2\text{H}_3\text{O}_2 = 4.74$).



↳ consider Na for mm

(mm = 82.03 g/mol)

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

$$5.09 = 4.74 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$0.35 = \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{0.35}$$

$$[\text{A}^-] = (10^{0.35})(0.25 \text{ M})$$

$$[\text{A}^-] = 0.5597 \text{ M}$$

$$0.3 \text{ L} \cdot \frac{0.5597 \text{ mol}}{\text{L}} \cdot \frac{82.03 \text{ g}}{\text{mol}} =$$

$$= 13.77 \text{ g}$$

of $\text{NaC}_2\text{H}_3\text{O}_2$

ex: Which of these sol'n are buffers when 1.0L of each are mixed?

(a) 0.1 M NH_3 and 0.1 M NH_4Cl
 weak base $\xrightarrow{\text{conj. acid}}$ \Rightarrow buffer

(b) 0.1 M NH_3 and 0.05 M HCl (not conj. pair)

These 2 are not conj. A/B pair

But, if H_3O^+ is limiting reagent (LR), there will be excess NH_3 and produce NH_4^+ \Rightarrow conj. pair

Note: For LR problem / stoichiometry, use mol (NOT M)



B : 0.1 mol 0.05 mol
 -0.05 (LR)

0
 +0.05 mol

A : 0.05 mol 0

0.05 mol

\therefore B is buffer:
 1:1 ratio of
 NH_3 to NH_4^+

(c) 0.1 M NH_3 and 0.1 M HCl



B : 0.1 mol \leftrightarrow 0.1 mol
 stoichiometric
 -0.1 -0.1

0
 +0.1

A : 0 0

\therefore C is NOT :
 no more NH_3

(d) 0.1 M NH_4Cl and 0.05 M NaOH



B : 0.1 mol 0.05 mol
 -0.05 (LR)

0
 +0.05

A : 0.05 mol 0

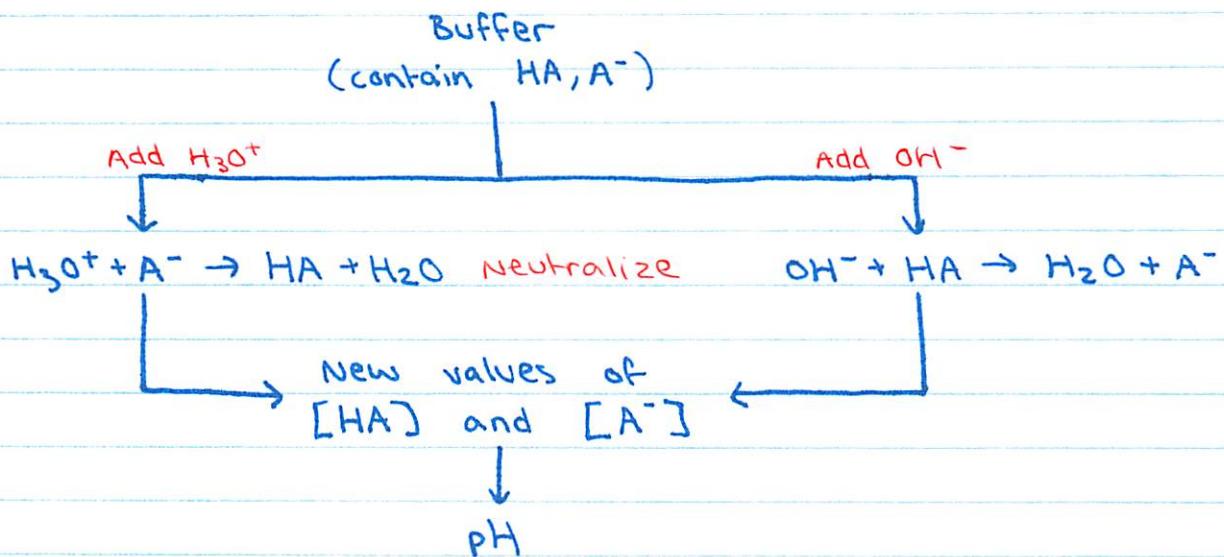
0.05 mol

\therefore D is buffer:
 1:1 ratio of
 NH_4^+ to NH_3

Calculating pH changes in buffer solns

- Buffer resist pH change, but still small change
- 2 parts:

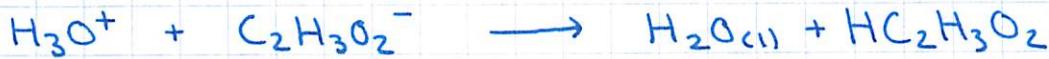
1. Stoichiometric calculation: calculate how addition of A or B changes relative amounts of HA, A⁻ or B, BH⁺
2. Equilibrium Calculation: calculate pH based on new amounts.



ex. What are the effects on pH of 0.3L buffer sol'n
 0.25 M $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid $\rightarrow \text{pK}_a = 4.74$) and
 0.56 M $\text{NaC}_2\text{H}_3\text{O}_2$ having pH = 5.09, by adding:

(a) 50 mL 0.12 M HCl $\Rightarrow \text{H}_3\text{O}^+$ (add Acid)
 will get neutralized using A^-

Note: H_3O^+ must be LR



B:	$0.05 \text{ L} (0.12 \text{ M})$ $= 0.006 \text{ mol}$ <u>LR</u>	$0.3 \text{ L} (0.56 \text{ M})$ $= 0.168 \text{ mol}$ $- 0.006$	$0.3 \text{ L} (0.25 \text{ M})$ $= 0.075 \text{ mol}$ $+ 0.006$ 0.081 mol
A:	0	0.162 mol	

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]_{\text{new}}}{[\text{HA}]_{\text{new}}} \quad \text{since this is ratio}$$

can use $\frac{\text{mol}}{\text{mol}}$ \because same tot. volume

$$\text{pH} = 4.74 + \log \left(\frac{\frac{0.162 \text{ mol}}{\cancel{V_{\text{tot}}}}}{\frac{0.081 \text{ mol}}{\cancel{V_{\text{tot}}}}} \right) = \boxed{5.04}$$

(b) 50 mL 0.12 M NaOH $\Rightarrow \text{OH}^-$ (add base)
 will get neutralized using HA



B:	$0.05 \text{ L} (0.12 \text{ M})$ $= 0.006 \text{ mol}$ <u>LR</u>	$0.3 \text{ L} (0.25 \text{ M})$ $= 0.075 \text{ mol}$ $- 0.006$	$0.3 \text{ L} (0.56 \text{ M})$ $= 0.168 \text{ mol}$ $+ 0.006$ 0.174 mol
A:	0	0.069 mol	

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.069 \text{ mol}}{0.35 \text{ L}}$$

total new volume

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.174 \text{ mol}}{0.35 \text{ L}}$$

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

$$\text{pH} = 4.74 + \log \left(\frac{0.174 \text{ mol}}{0.069 \text{ mol}} \right) = \boxed{5.14}$$

Acid-Base Titration

- procedure for determining the amount of acid or base present by determining the volume of base or acid required to completely react.
- pH meter or indicator.

Equivalence point (stoichiometric point) =

moles of base stoichiometrically equal # moles acid

Endpoint = indicator change color so you can tell equivalence pt. has been reached.

A Strong Acid with Strong Base

B Weak Acid with Strong Base

A) Titration of Strong Acid with Strong Base

Consider the titration of 50 mL of 0.2 M HCl with 0.1 M NaOH.

Note: can find equivalence point with

$$\frac{C_A V_A}{n_A} = \frac{C_B V_B}{n_B}$$

(a) No NaOH added

$$pH = -\log [H_3O^+] = -\log (0.2) = 0.7$$

(b) 50 mL NaOH added



$$\begin{array}{ll} B: & 0.05 L (0.2 M) \\ & = 0.01 mol \\ & - 0.005 mol \end{array} \quad \begin{array}{ll} & 0.05 L (0.1 M) \\ & = 0.005 mol \\ & (LR) \end{array}$$

$$A: \quad 0.005 \text{ mol} \quad 0$$

Major species: H_3O^+ , H_2O

Total new volume

$$\begin{aligned} pH &= -\log [H_3O^+] \\ &= -\log \left(\frac{0.005 \text{ mol}}{(0.05 + 0.05) L} \right) \end{aligned}$$

$$pH = 1.3$$

(c) 100 mL NaOH added



$$\begin{array}{ll} B: & 0.05 L (0.2 M) \\ & = 0.01 mol \\ & (LR) \end{array} \quad \begin{array}{ll} & 0.1 L (0.1 M) \\ & = 0.01 mol \\ & (LR) \end{array}$$

$$A: \quad 0 \quad 0$$

Major species: H_2O

$$pH = 7 \Rightarrow \text{equivalence}$$

(d) 150 mL NaOH added



$$\begin{array}{ll} B: & 0.01 mol \\ & (LR) \end{array} \quad \begin{array}{ll} & 0.15 L (0.1 M) \\ & = 0.015 mol \\ & - 0.01 \end{array}$$

$$A: \quad 0 \quad 0.005 \text{ mol}$$

Major species: OH^- , H_2O

Total new volume

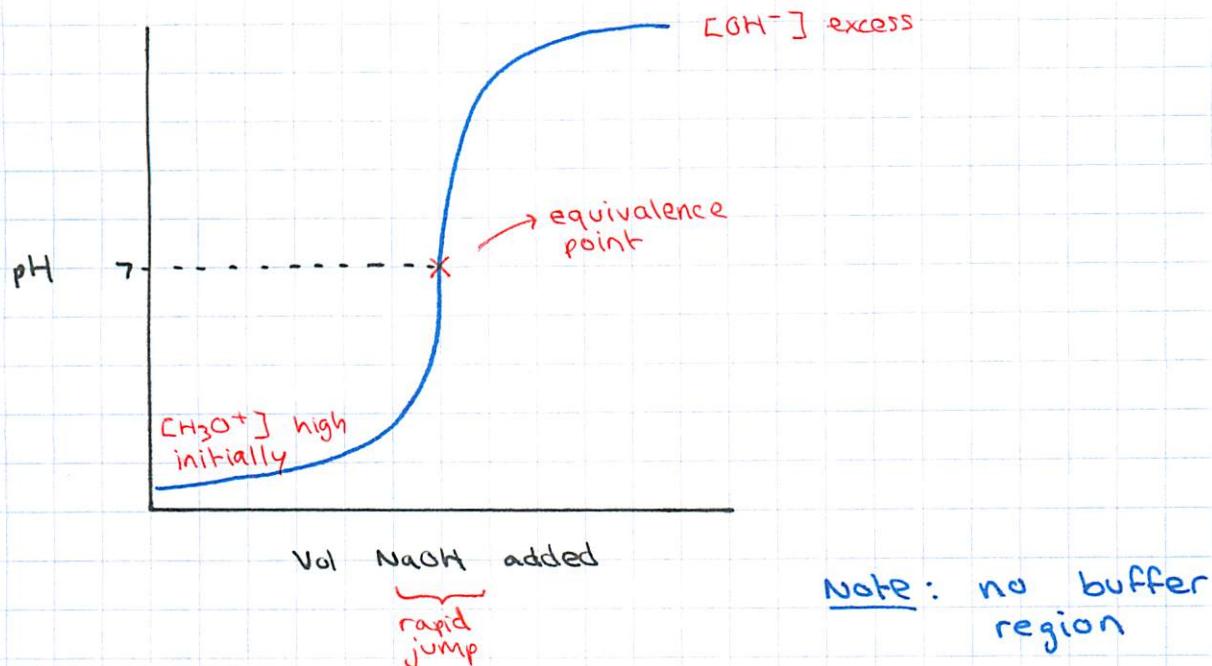
$$\begin{aligned} pOH &= -\log [OH^-] \\ &= -\log \left(\frac{0.005 \text{ mol}}{(0.05 + 0.15) L} \right) \end{aligned}$$

$$pOH = 1.6$$

$$pH = 14 - pOH$$

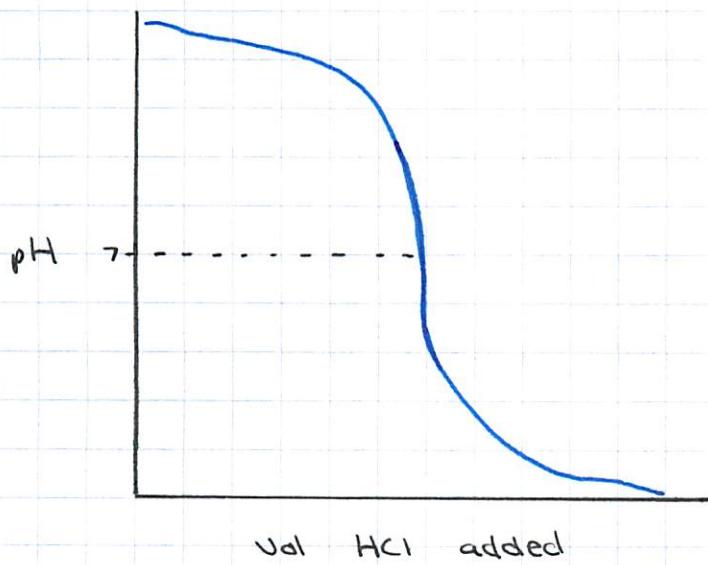
$$pH = 12.4$$

pH curve: strong acid + strong base



pH curve: Titration of 100 mL 0.5 M NaOH
with 1 M HCl

* Curve starts basic



B) Titration of Weak Acid with Strong Base

consider the titration of 50 mL 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) with 0.1 M NaOH .

NaOH titrant

(a) No NaOH added

$$\boxed{\text{pH} = 2.87}$$

(b) 25 mL NaOH added (halfway point)



B:	0.05 L (0.1 M)	0.025 L (0.1 M)		0
	= 0.005 mol	= 0.0025 mol		
	- 0.0025		(ER)	
A:	0.0025 mol	0		+ 0.0025
				0.0025 mol

Note: Buffer: acid + conj. base (1:1)

Buffer so use: $\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$ $\Rightarrow [\text{A}^-] = [\text{HA}]$

$$\text{pH} = \text{pK}_a = -\log (1.8 \times 10^{-5}) = \boxed{4.74}$$

(c) 50 mL NaOH added (equivalence)



B:	0.005 mol	0.005 mol		0
	LR	LR		+ 0.005
A:	0	0		0.005 mol

Major species: H_2O , CH_3COO^- \Rightarrow hydrolysis

Equilibrium calculations:

	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
I	$\frac{0.005 \text{ mol}}{(0.05+0.05) \text{ L}} = 0.05 \text{ M}$
C	-x
E	$0.05 - x \approx 0.05$

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

$$K_b = \frac{10^{-14}}{1.18 \times 10^{-5}} = \frac{x^2}{0.05}$$

$$x = 5.3 \times 10^{-6} \text{ M}$$

$$\text{validate: } \frac{5.3 \times 10^{-6}}{0.05} \times 100 < 5\%$$

$$\text{pOH} = -\log (5.3 \times 10^{-6}) = 5.28$$

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

$$\boxed{\text{pH} = 8.72}$$

(d) 60 mL NaOH added



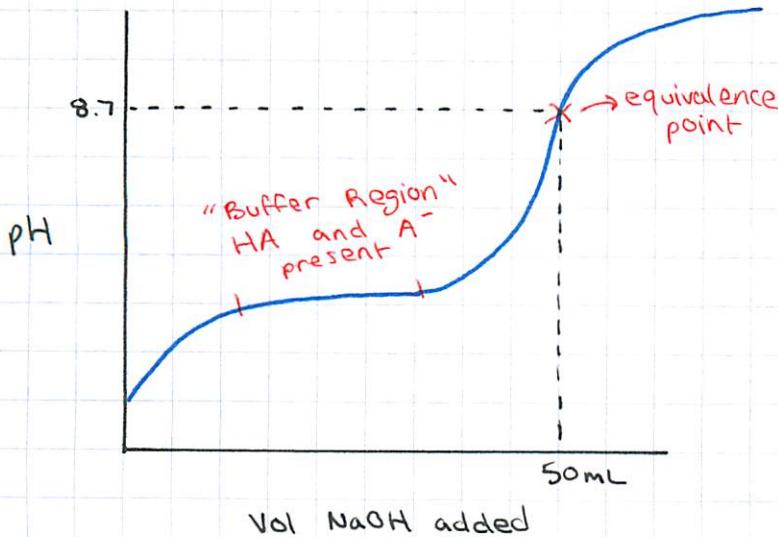
B:	0.005 mol	0.06 L (0.1 M)		0
	LR	= 0.006 mol - 0.005		+ 0.005
A:	0	0.001 mol		0.005 mol

Major species: OH^- , H_2O , CH_3COO^-
Dominant strong base
→ Dictate pH
Hydrolysis neglect.

$$\text{pOH} = -\log \left(\frac{0.001 \text{ mol}}{(0.05 \text{ L} + 0.06 \text{ L})} \right) \quad \text{Total new volume}$$
$$= 2.04$$

$$\text{pH} = 14 - \text{pOH} \quad \Rightarrow \quad \boxed{\text{pH} = 11.96}$$

pH curve: weak acid + strong base



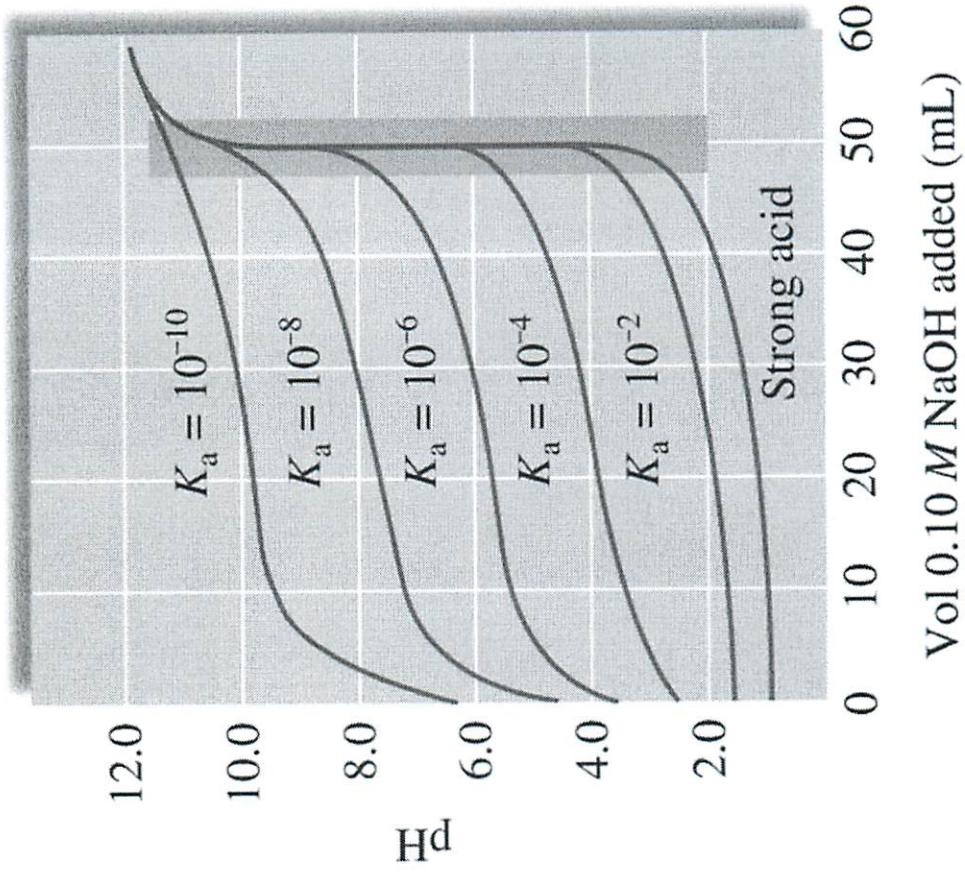
- Between the initial pH and equivalence point, the solution contains the weak acid + conj. base ∴ buffer region

- At half-equivalence point: $\text{pH} = \text{pK}_a$

$$\text{ie: } [\text{A}^-] = [\text{HA}]$$

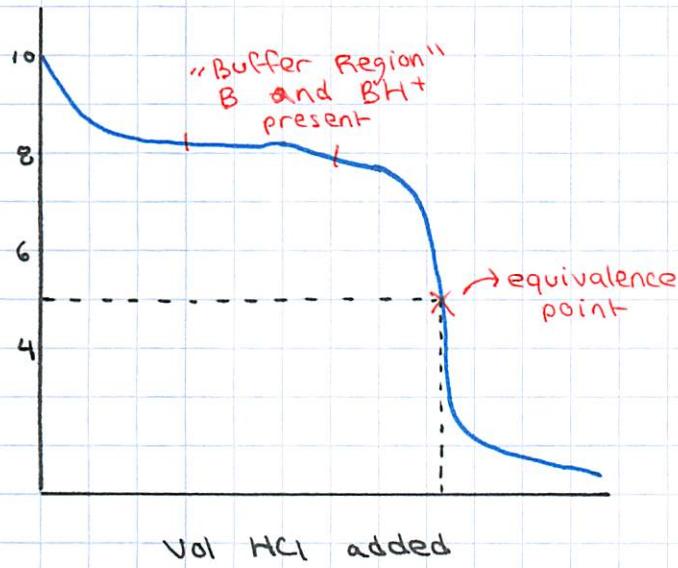
Effect of K_a on Titration Curve

- The solns of weak acids have higher initial pH (more basic) than a soln of strong acid.
- It is the amount of acid (quantity) (NOT strength) that determines equivalence. $\frac{C_A V_A}{n_A} = \frac{C_B V_B}{n_B}$
- pH at equivalence point:
affected by acid strength.
 - $pH = 7$: for strong acid - strong base
 - $pH > 7$: for weak acid - strong base
- pH change at the "rapid-rise" near equivalence is smaller for weak acids than for strong acids.



pH curve for the titration of a weak base + strong acid

consider the titration of 100 mL 0.05 M NH_3 with 0.1 M HCl



At halfway point: $\text{pOH} = \text{pK}_b$

$$\text{pH} = \text{pK}_a$$

or
of the
conj. acid

$\rightarrow K_b$ of NH_3
 $\rightarrow K_a$ of NH_4^+

Note: Halfway point pH gives you:

$$\text{pH} = \text{pK}_a$$

$$\text{pK}_a + \text{pK}_b = \text{pK}_w = 14$$

$$\text{pK}_b = 14 - \text{pK}_a$$

$$\text{pK}_b = -\log(K_b)$$

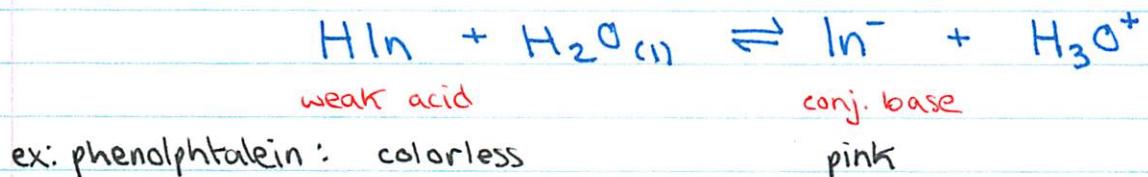
Acid - Base Indicators

- Determine the equivalence point using indicator,
rely on : end point = where indicator color change.
- End point close to equivalence point

Indicator = weak organic acid (HIn) that is
different color from its
conjugate base (In^-)

- Titration of acid with base : color change occur at pH where $[\text{HIn}]:[\text{In}^-]$ is $10:1$
- Titration of base with acid : color change occur at pH where $[\text{HIn}]:[\text{In}^-]$ is $1:10$

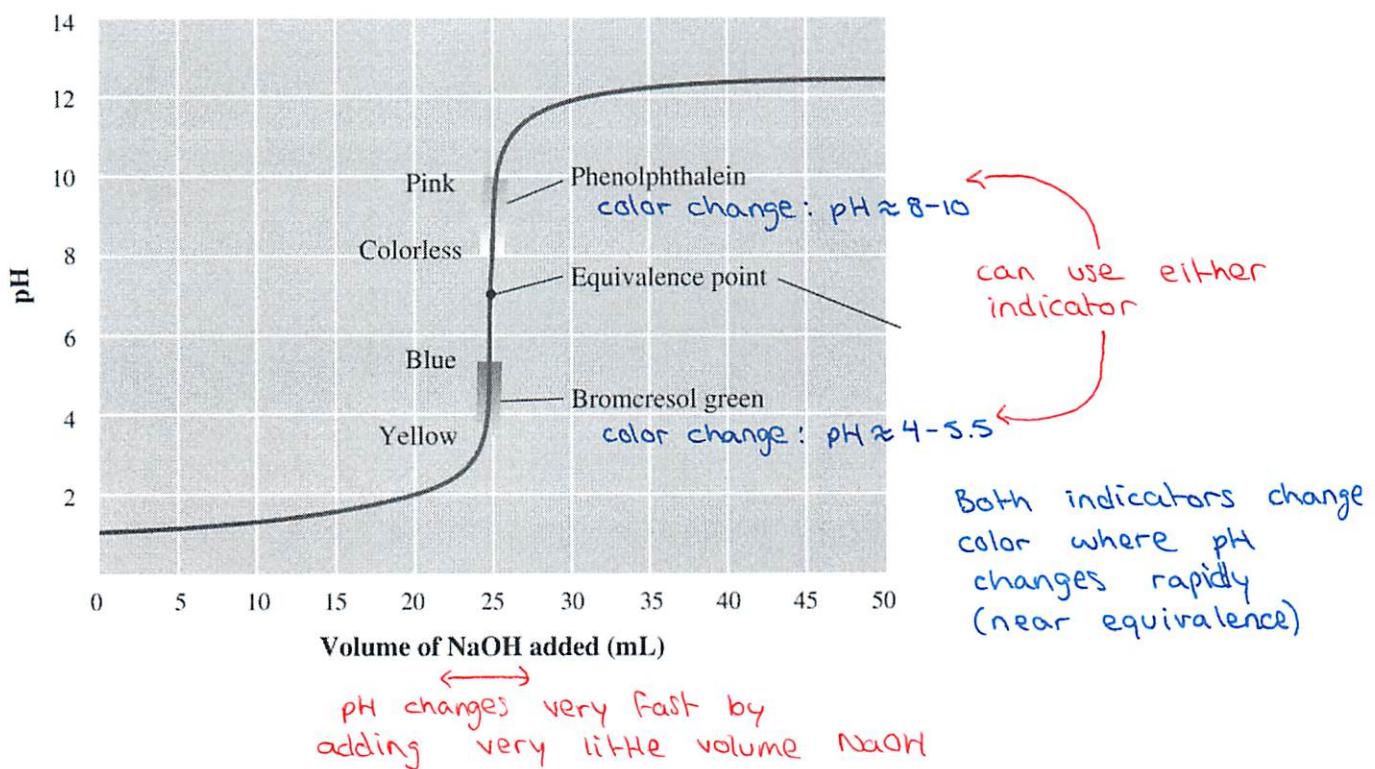
Color of indicator will change over range:
 $\text{pH} = \text{pK}_a \pm 1$ (pKa of HIn)



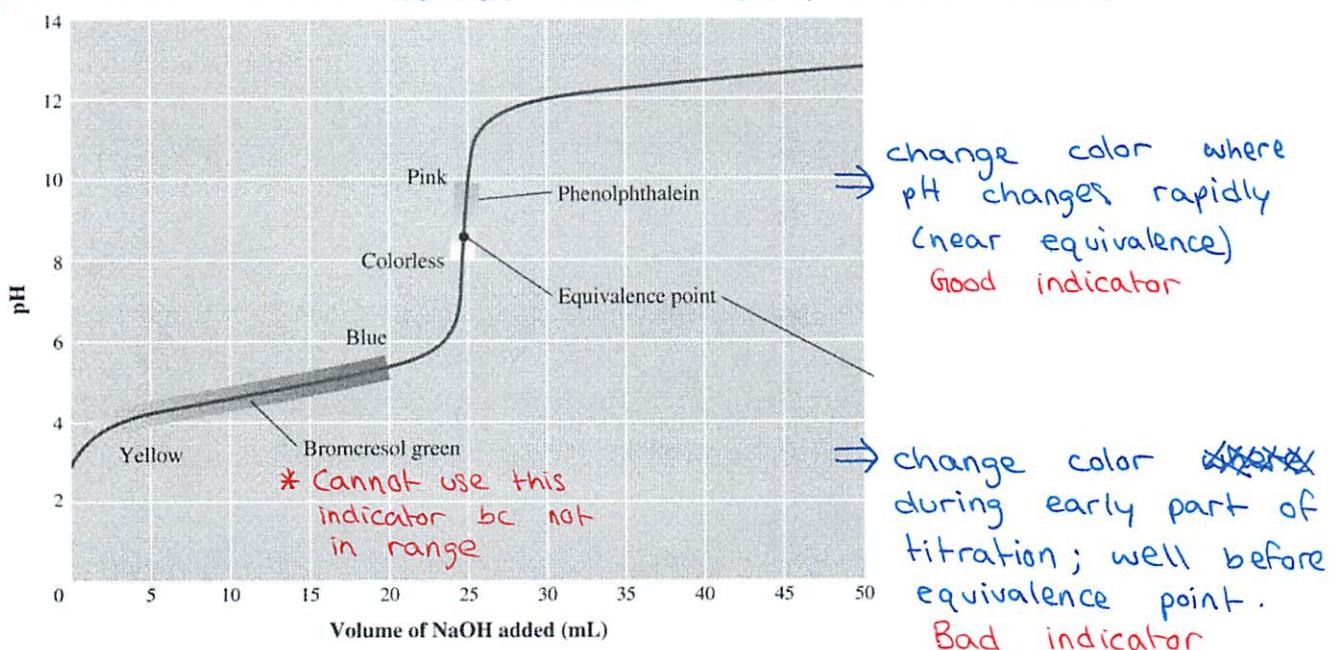
$$\text{K}_a(\text{HIn}) = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$\frac{\text{K}_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{In}^-]}{[\text{HIn}]}$$

pH curve: 0.1M HCl with 0.1M NaOH



pH curve: 0.1M weak acid with 0.1M NaOH



ex: Phenol red = indicator $(K_a = 1.34 \times 10^{-8})$
→ yellow in acidic sol'n
→ red in basic sol'n

(a) Between what pH range will the sol'n be orange (range of color change)?

$$\begin{aligned} \text{pH} &= \text{p}K_a \pm 1 \\ &= -\log(1.34 \times 10^{-8}) \pm 1 \\ &= 7.87 \pm 1 \end{aligned}$$

Range : 6.87 to 8.87 range in pH

(b) Is it a good indicator for a titration of a strong acid with a strong base?

equivalence point = 7

∴ It is a good indicator for strong acid-strong base titration bc it is in the range.