



<u>Le Chatelier's</u> <u>Princ. at</u> <u>Work every</u> <u>day!</u>

Effect of acid rain on erosion of limestone/marble Calcite---CaCO_{3(s)} <----> Ca⁺² + CO₃⁻² $CO_3^{-2} + H^+ <---> HCO_3^-$

acid rain---shifts calcite equilibrium to right!

Tooth decay--same princple (now acid from lactic acid--produced by bacteria---degrades hydroxyapatite) :

 $Ca_{10}(PO_4)_6(OH)_2 + 14 H^+ < ---> 10 Ca^{+2} + 6H_2PO_4^- + 2H_2O$

Polyprotic acids/bases---Chapter 10 ECA

 $HA < ----> H^+ + A^- pK_1$

 $H_2A < ----> H^+ + HA^- < ----> H^+ + A^{-2}$; pK_1 and pK_2

 $H_3A < ----> H^+ + H_2A^{-2} < ----> HA^{-2} + H^+ < ----> A^{-3} + H^+; pK_1, pK_2, pK_3$

•Can have also species where acidic protons come as a result of amine sites----so with proton---site is + charge---loss of proton gives neutral species: $RNH_3^+ < ----RNH_2 + H^+ pK_a$

•Can have combination of both types of protonated sites in same structure--Amino



Let's look at a real amino acid---which is triprotic---three different pK_a values---



from a titration standpoint---and also to calculate the pH, given a specific concentration of one form of the molecule! K_a and K_b relationships for such species---

Diprotic--
$$H_2A < ----> H^+ + HA^ K_{a1}$$

 $HA^- + H_2O < ----> H_2A + OH^ K_{b2}$ -the weaker conjugate base

$$H_2O < H^+ + OH^- K_w$$

therefore: $K_{a1} K_{b2} = K_w$

$$\begin{array}{c} HA^{-} < --- > H^{+} + A^{-2} & K_{a2} \\ A^{-2} + H_2O < --- > HA^{-} + OH^{-} & K_{b1} \\ \end{array}$$
stronger $H_2O < --- > H^{+} + OH^{-} & K_w \\ conj. \\ base \qquad \text{therefore: } K_{a2} K_{b1} = K_w \end{array}$

Similarly---can derive--relationships for triprotic system: $K_{a1} K_{b3} = K_w$; $K_{a2} K_{b2} = K_w$; and $K_{a3} K_{b1} = K_w$ <u>Diprotic case in more detail</u>---what is pH of solution?---let's use simple diprotic amino acid as generic example:

 $H_3N^+C(R)COOH \leq H_3N^+C(R)COO^- \leq H_2NC(R)COO^-$

$$H_2L^+ < ----> HL < -----> L^-$$

 $pK_{a1} = 2.329 pK_{a2} = 9.747$

thus---L⁻ + H₂O <----> HL + OH⁻
$$\mathbf{K}_{b1}$$

HL + H₂O <---> HL⁺ + OH⁻ \mathbf{K}_{b2}

What is pH of solution of H_2L^+ salt--at 0.05 M?

$$pK_{a1} = pK_1 = 2.329; K_a = 4.69 \times 10^{-3}$$

HL is much weaker acid--- $K_a = 1.79 \times 10^{-10}$ ---So--H₂L⁺ will dissociate slightly to generate H⁺ in solution--but the contribution by further dissociation of HL <---> H⁺ is negligible so pH can be calculated treating H_2L^+ as monoprotic acid--

$$K_1 = x^2 / (F-x)$$
; $F = 0.05 \text{ M}$; $x = 1.31 \text{ x} 10^{-2} \text{ M} = [HL] = [H^+]$

Therefore: $pH = -log (1.31 \times 10^{-2}) = 1.88$

What is concentration of L⁻ in such a solution? We know that $K_2 = ([L^-] [H^+]) / [HL]$; $[L^-] = (K_2[HL]) / [H^+]$

 $[L^{-}] = (1.79 \text{ x } 10^{-10}) (1.31 \text{ x } 10^{-2}) / (1.31 \text{ x } 10^{-2}) = 1.79 \text{ x } 10^{-10} \text{ M} = K_2$

as long as $K_1 > K_2$ by at least 1-2 orders of magnitude---the assumption to neglect second dissociation reaction in calculating proton concentration is OK!

If solution contained L⁻ only at 0.05 M to start--what would be pH?

weak base problem---Need K_{b1} value ; $K_{b1} = K_w / K_2 = 5.59 \times 10^{-5}$

OH⁻ produced from small amount of HL that forms would be negligible--since $K_{b2} = K_w / K_1 = 10^{-14} / 4.69 \text{ x} 10^{-3} = 2.13 \text{ x} 10^{-12}$ ----very very weak base!

So pH is based only on K_{b1} value:

 $K_{b1} = x^2 / F-x$; 5.59 x 10⁻⁵ = x² /(0.05-x); x = 4.84 x 10⁻² M =[OH⁻] = [HL]

$$[H^+] = K_w / [OH^-] = 10^{-14} / 4.84 \text{ x } 10^{-2} = 6.08 \text{ x } 10^{-12} \text{ M}$$

therefore: **pH = 11.22**

<u>Finally--what about a 0.05 M solution of HL --What is pH?</u> more complex--since HL is intermediate form--it can be both a base and acid (an **amphiprotic** species!!!!)

 $\begin{array}{ll} HL <----> H^+ + L^- & K_2 = 1.79 \ x \ 10^{-10} \\ HL + H_2O <---> H_2L^+ + OH^- & K_{b2} = 2.13 \ x \ 10^{-12} \\ \text{since } K_2 > K_{b2} \ \text{; expect solution of HL to be acidic!} \end{array}$

Determing pH of solution containing HL alone--is perfect example of solving more complex simultaneous equilibria type problems in chemistry!

best starting point---use "charge balance" equation

must have <u>charge neutrality in solution</u>--therefore the total concentration of all positively charged species = total concentration of all negatively charged species in solution!

 $[H^+] + [H_2L^+] = [L^-] + [OH^-]$

or $[H_2L^+] - [L^-] + [H^+] - [OH^-] = 0$

but we have relationships that we can substitute for each of these species: $\frac{[HL][H^+]}{K_1} - \frac{[HL]K_2}{[H^+]} + [H^+] - \frac{K_w}{[H^+]} = 0$ Can solve for [H⁺] (see ECA--p. 217)

$$[H^{+}] = \sqrt{\frac{K_{1}K_{2}[HL] - K_{1}K_{w}}{K_{1} + [HL]}}$$

everything is known except [HL]-----but we know that while HL is both an acid and base---it is weak--and hence the concentration of [HL] at equilibrium is going to be very close to the formal concentration that you add to the solution--F; thus:

$$[H^+] = \sqrt{\frac{K_1 K_2 F - K_1 K_w}{K_1 + F}}$$
 recall we said that
F = 0.05 M to start!

 K_1K_w is usually $<<< K_1K_2F$; and $K_1 << F$

$$[H^{+}] = \sqrt{\frac{K_{1}K_{2}F - K_{1}K_{w}}{K_{1} + F}} \longrightarrow [H^{+}] = \sqrt{K_{1}K_{2}}$$

take log of both sides:

 $\log [H^+] = 1/2 \log (K_1 K_2)$ $\log [H^+] = 1/2(\log K_1 + \log K_2)$ multiply by sides by -1: $-\log [H^+] = 1/2(-\log K_1 - \log K_2)$ $pH = 1/2 (pK_1 + pK_2)$

so the pH of the solution of 0.05 M HL = 1/2 (2.329 + 9.747)

pH = 6.04

note---pH of the HL solution is independent of concentration!

once you know the pH---you can then go back and calculate how much of H_2L^+ and L^- from the equilibrium constant expressions!

turns out that the concentrations are very low ----approx. 10⁻⁵ M-compared to 0.05 M of HL that was added to solution!

Example---what is pH of 0.05 M KHP?



Potassium hydrogen phthalate = K^+HP^-

pH = 1/2 (2.950 + 5.408) = 4.18

Principal species in solution?

reported as α values vs. pH of solution!----where α is the fraction of total polyprotic acid in a given form---

can estimate α values from log term in HH equation----if ratio is 10; (log (10/1)---then base form is approx. 90% fraction---if log (100/1) then base form is 99% fraction!





 $[H_3A] = [HA^{2-}]$ $[H_2A^{-}] = [A^{3-}]$

Blood-Gas Transfer During Respiration



$$CO_{2} + H_{2}O <----> H_{2}CO_{3} <----> HCO_{3}^{-} + H^{+} <---> CO_{3}^{-2} + H^{+} pK_{1} = 6.35 \qquad pK_{2} = 10.33$$

controls pH of blood--- If your lungs are not working well to get rid of CO_2 --- pH of blood decreases (more carbonic acidpresent)

In clinical labs they measure P_{CO2} = partial pressure of CO_2 in blood and also total CO_2 species---sum of $[CO_2] + [HCO_3^-]$ (CO_3^{-2} --too low to contribute appreciably to total carbon dioxide species present)!





<u>pI values</u>----pH of solution where polyprotic species is neutral! called isoelectric pH value!









Titration of diprotic acid with strong base---shape depends on values of pK_1 and pK_2



titration of 50 mL of 0.02 M Na₂CO₃ with 0.1 M HCl

