Polyprotic Acids and Bases____________Ch 10-1 – 10-5

Third midterm exam on Monday, November 22

Today is last quiz (Adrian is grading tonight! Will be posted on web as soon as available)

will omit solubility

put up W13, W14 Week-in-Review

9-5 Review of Buffers
10-1 Diprotic Acids and Bases
10-2 Diprotic Buffers
10-3 Polyprotic Acids and Bases
10-4 Principle Species
10-5 Fractional Composition (omit equations)

Polyprotic Acids and Bases

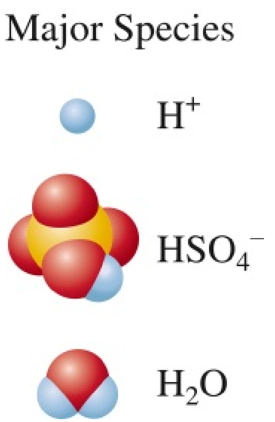
polyprotic acid – capable of donating more than one proton
polyprotic base – capable of accepting more than one proton

EX 1. What is the concentration of all species present in a 1.00 M solution of sulfuric acid where $K_a = 1.2 \times 10^{-2}$?

H_2SO_4 strong acid => [acid] = [H+] = [conjugate base] => **$[H_2SO_4]_o = [H^+] = [HSO_4^-] = 1.00$ M**
[OH-] = $K_w / [H^+] =$ **1.01×10^{-14}**

	$HSO_4^-(aq)$ + $H_2O(l)$	<=>	$H_3O^+(aq)$	+ $SO_4^{2-}(aq)$
I	1.0		1.0	~0
C	$-x$		$+x$	$+x$
E	$1.0 - x$		$1.0 + x$	x

$$K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(1.00 + x)\,x}{1.00 - x} \Rightarrow x = [SO_4^{2-}] = 0.012 \text{ M}$$



100(0.012) = 1.2% OK by 5% rule, not OK by 1% rule, quadratic => x = $[SO_4^{2-}] = 0.0117$ M, $[H^+]_{total} = 1.00 + 0.0117 = 1.01$ M, $[OH^-] = 1.00 \times 10^{-14}$ M

REVIEW FROM MONDAY

EX 2. What is the pH and concentration of all species present in a 5.00 M solution of phosphoric acid?

$K_{a1} = 7.11 \times 10^{-3}$ $H_3PO_4(aq) + H_2O(l) <=> H_3O^+(aq) + H_2PO_4^-(aq)$ $pK_{a1} = 2.1481$

$K_{a2} = 6.34 \times 10^{-8}$ $H_2PO_4^-(aq) + H_2O(l) <=> H_3O^+(aq) + HPO_4^{2-}(aq)$ $pK_{a2} = 7.1979$

$K_{a3} = 4.22 \times 10^{-13}$ $HPO_4^{2-}(aq) + H_2O(l) <=> H_3O^+(aq) + PO_4^{3-}(aq)$ $pK_{a3} = 12.3746$

Polyprotic Acids and Bases

EX 2. What is the pH and concentration of all species present in a 5.00 M solution of phosphoric acid?

100(0.1939)/5.00 = 3.9%,
OK by 5%, not by **1% rule**
quadratic => x = 0.1901
$[H_3O^+] = [H_2PO_4^-] = 0.190$,
$[OH^-] = 5.3 \times 10^{-13}$ M

$K_{a1} = 7.11 \times 10^{-3}$ $\quad H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$

EQ $\quad 5.00 - x \qquad x \qquad x$

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{5.00 - x}$$

=> $x = \mathbf{[H_3O^+] = [H_2PO_4^-] = 0.1939\ M}$

$\mathbf{[H_3PO_4]} = 5.00 - 0.19 = \mathbf{4.81}$, $\mathbf{[OH^-] = 5.2 \times 10^{-13}\ M}$ $\qquad$ **pH = 0.71**

$K_{a2} = 6.34 \times 10^{-8}$ $\quad H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

$$K_{a2} = \frac{[H_3O^+]\mathbf{[HPO_4^{2-}]}}{[H_2PO_4^-]} = \mathbf{6.23 \times 10^{-3}}$$

$$K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{[H_3O^+][PO_4^{3-}]}{K_{a2}}$$

=> $\mathbf{[PO_4^{3-}] = 7.2 \times 10^{-3}\ M}$

Polyprotic Acids and Bases – Intermediate Form

Consider a diprotic acid

$$H_2A(aq) + H_2O(l) \iff H_3O^+(aq) + \boxed{HA^-(aq)}$$ **base**

acid $$\boxed{HA^-(aq)} + H_2O(l) \iff H_3O^+(aq) + A^{2-}(aq)$$

If H_2A is a weak acid its conjugate base, HA^- is amphoteric. It can act as an acid (second equation) or as a base (reverse of first reaction). What is the pH of a solution of HA^- such as NaHA?

Exact Treatment (H pp. 216 - 218) for NaHA

species: H_2A, HA^-, A^{2-}, H^+, OH^-, Na^+ => need 6 equations

charge balance: $[H^+] + [Na^+] = [HA^-] + 2[A^{2-}] + [OH^-]$

material balance: $M_{NaHA} = [Na^+] = [H_2A] + [HA^-] + [A^{2-}]$

equilibria: $K_{a1} = \dfrac{[H^+][HA^-]}{[H_2A]}$ $\quad K_{a2} = \dfrac{[H^+][A^{2-}]}{[HA^-]}$ $\quad K_w = [H^+][OH^-]$

One can show that

$$\boxed{[H^+]^2 = \frac{K_{a1}K_{a2}[HA^-] + K_{a1}K_w}{K_{a1} + [HA^-]}}$$ **exact relation**

Polyprotic Acids and Bases – Intermediate Form

$$[H^+]^2 = \frac{K_{a1}K_{a2}[HA^-] + K_{a1}K_w}{K_{a1} + [HA^-]}$$

1. when the major species is HA^- => $[HA^-] = M_{HA^-}$ (F_{HA^-})

$$\approx \frac{K_{a1}K_{a2}M_{NaHA} + K_{a1}K_w}{K_{a1} + M_{NaHA}} = \frac{K_{a1}(K_{a2}M_{NaHA} + K_w)}{K_{a1} + M_{NaHA}}$$

2. often $\boxed{K_w \ll K_{a2}M_{NaHA}}$

$$\approx \frac{K_{a1}K_{a2}M_{NaHA}}{K_{a1} + M_{NaHA}}$$

3. and $\boxed{K_{a1} \ll M_{NaHA}}$ this often needs to be checked

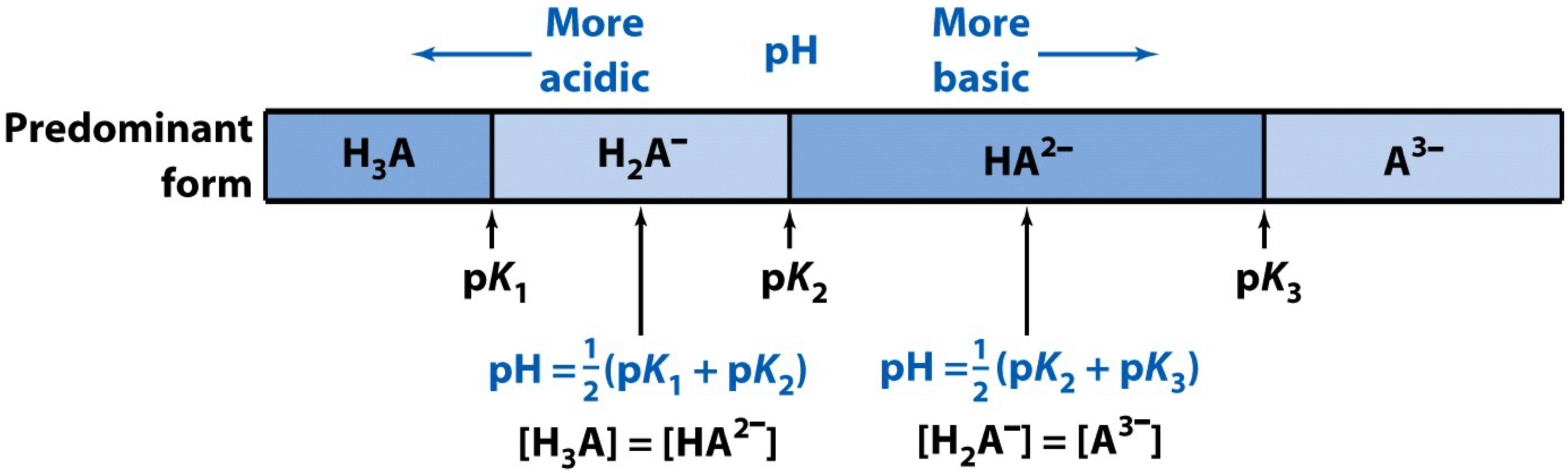
$$\approx \frac{K_{a1}K_{a2}M_{NaHA}}{M_{NaHA}} = K_{a1}K_{a2}$$

or

$$\boxed{pH = \frac{1}{2}(pK_{a1} + pK_{a2})}$$

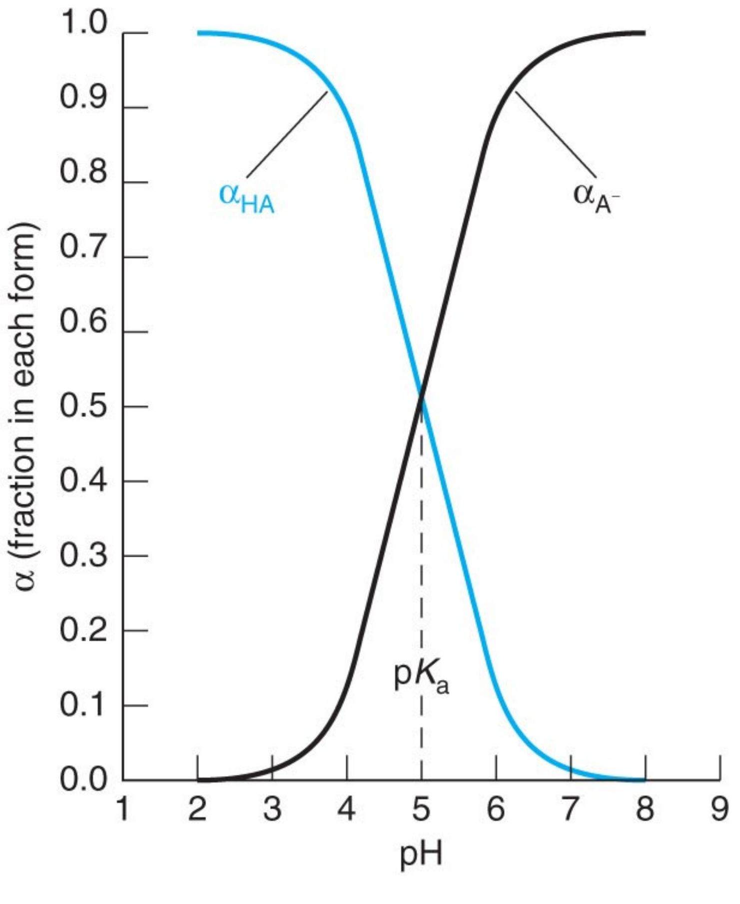
Polyprotic Acids and Bases – Predominant Species

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log_{10}\frac{[\mathrm{B}]}{[\mathrm{A}]}$$

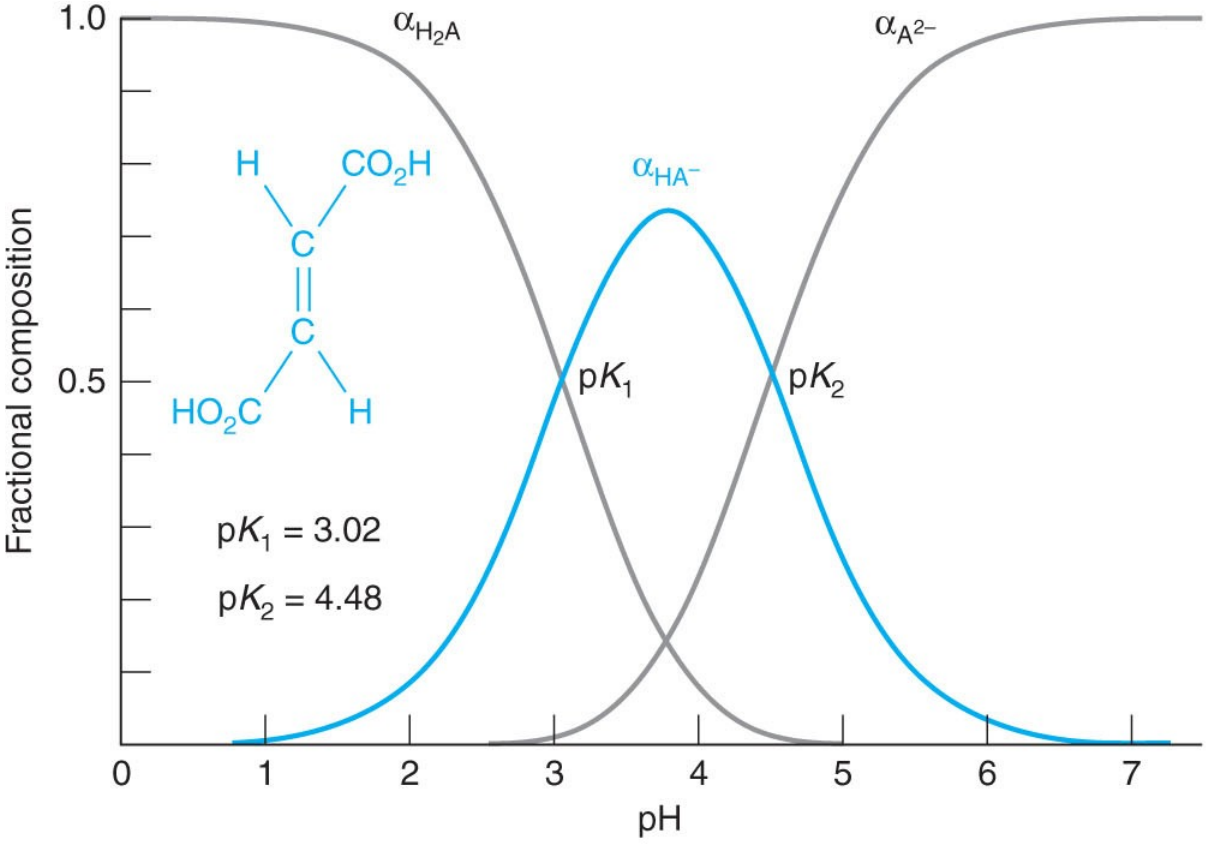


H_3PO_4 2.148 7.197 12.374

Fractional Composition Diagrams, α versus pH



monoprotic acid, HA



diprotic acid, H_2A

Z Chapter 6 (Chemical Equilibrium)

equilibrium constant
- law of mass action
- activity/activity coefficient
- K (molarity)
- K_P (partial pressures)
- reaction quotient, Q
- mathematics
  - multiply reaction by n
  - reverse reaction
  - add reactions
  - subtract reactions

solving equilibrium problems
- homogeneous/heterogeneous reactions
- approximation for small K
- using quadratic formula

Le Chatelier's Principle, change of
- temperature
- total pressure
- concentrations/partial pressures

Z Chapter 7.1 – 7.4, 7.6 (Strong Acids and Bases)

Bronsted Lowry

- definition of acid/base
- conjugate acid/conjugate base
- autoionization
- know 7 common strong acids
- know soluble strong bases
- strength of acids/bases

pH scale

- depends upon water autoionization
- temperature dependence
- meaning of neutrality, acidity, basicity

H Chapter 9 (Monoprotic Acid-Base Equilibria)

systematic treatment of equilibrium
- mass balance
- charge balance
- why and when needed
- for strong acids/bases
- for weak acids/bases [$K = x^2/(F - x)$]

acidity/basicity of salt solutions
- strong acids/bases
- conjugates
- meaning of neutrality, acidity, basicity

buffers
- what are they
- identify them
- quantitative response to added H^+, OH^-
- preparation
  - moles of acid/conjugate
  - molarities of acid/conjugate
  - strong acid + base
  - strong base + acid
- Henderson-Hasselbalch
- setting up and using an ICE table

H Chapter 10 (Polyprotic Acid-Base Equilibria)

polyprotic acids and bases

- write acid reactions
- identify amphoteric species
- intermediate form
  - **how to determine pH from √**
  - pH = ½ (pK_{a1} + pK_{a2})

principle species

buffers

fractional composition

not for Exam III