Lecture Notes U: Acid-Base Chemistry VIII
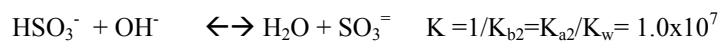
1) Polyprotic acids

$H_2SO_4 + H_2O \leftrightarrow H_3O^+ + HSO_4^-$ $K_{a1} = 1000$ $pK_{a1} = -2$
$HSO_4^- + H_2O \leftrightarrow H_3O^+ + SO_4^=$ $K_{a2} = 1.2 \times 10^{-2}$ $pK_{a2} = 1.92$

$H_2SO_3 + H_2O \leftrightarrow H_3O^+ + HSO_3^-$ $K_{a1} = 1.54 \times 10^{-2}$ $pK_{a1} = 1.81$
$HSO_3^- + H_2O \leftrightarrow H_3O^+ + SO_3^=$ $K_{a2} = 1.02 \times 10^{-7}$ $pK_{a2} = 6.91$

$H_2S + H_2O \leftrightarrow H_3O^+ + HS^-$ $K_{a1} = 9.1 \times 10^{-8}$ $pK_{a1} = 7.04$
$HS^- + H_2O \leftrightarrow H_3O^+ + S^=$ $K_{a2} = 1.1 \times 10^{-12}$ $pK_{a2} = 11.9$

$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^-$ $K_{a1} = 4.3 \times 10^{-7}$ $pK_{a1} = 6.37$
$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^=$ $K_{a2} = 4.8 \times 10^{-11}$ $pK_{a2} = 10.32$

$H_3PO_4 + H_2O \leftrightarrow H_3O^+ + H_2PO_4^-$ $K_{a1} = 7.52 \times 10^{-3}$ $pK_{a1} = 2.12$
$H_2PO_4^- + H_2O \leftrightarrow H_3O^+ + HPO_4^{-2}$ $K_{a2} = 6.23 \times 10^{-8}$ $pK_{a2} = 7.21$
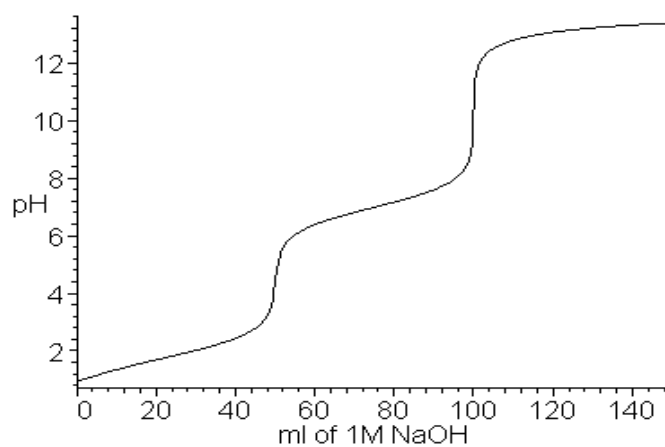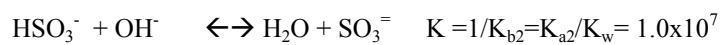$HPO_4^{-2} + H_2O \leftrightarrow H_3O^+ + PO_4^{-3}$ $K_{a3} = 2.2 \times 10^{-13}$ $pK_{a1} = 12.67$

2) Titration of a polyprotic acid

The following shows the result of titrating 50ml of 1M H_2SO_3 with 1M NaOH.
The relevant reactions are:

$H_2SO_3 + OH^- \leftrightarrow H_2O + HSO_3^-$ $K = 1/K_{b1} = K_{a1}/K_w = 1.5 \times 10^{12}$

$HSO_3^- + OH^- \leftrightarrow H_2O + SO_3^=$ $K = 1/K_{b2} = K_{a2}/K_w = 1.0 \times 10^7$

$H_2SO_3 + OH^- \quad \longleftrightarrow \quad H_2O + HSO_3^- \quad K=1/K_{b1}=K_{a1}/K_w= 1.5 \times 10^{12}$

$HSO_3^- + OH^- \quad \longleftrightarrow \quad H_2O + SO_3^= \quad K =1/K_{b2}=K_{a2}/K_w= 1.0 \times 10^7$

The following shows the result of titrating 50ml of a weak acid solution with 1M NaOH.
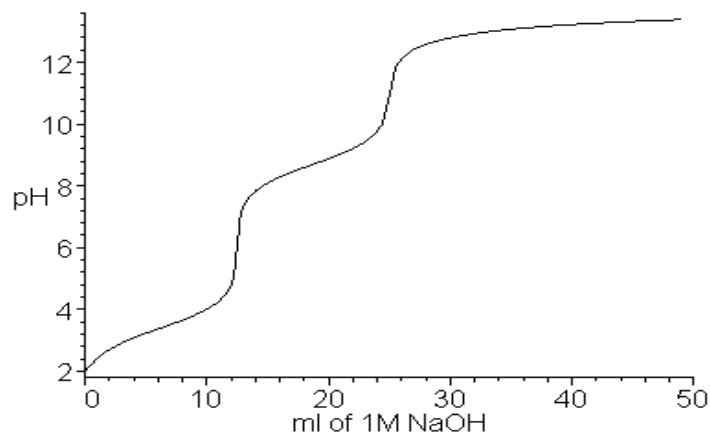
What is the pK_{a1} and pK_{a2} of this acid?

What is the concentration of this acid?

3) *Buffers made with polyprotic acids*

What is the pH of a solution formed by mixing 50ml of 1.0M H_2SO_3 with 50ml of 1.0M $NaHSO_3$?

$$H_2SO_3 + \quad H_2O \quad \longleftrightarrow \quad H_3O^+ + \quad HSO_3^- \qquad K_{a1} = 1.54 \times 10^{-2} \quad pK_{a1} = 1.81$$

In the above buffer solution, what is the concentration of $SO_3^=$?

What is the pH of a solution formed by mixing 50ml of 1.0M $NaHSO_3$ with 50ml of 1.0M Na_2SO_3?

HSO_3^- + H_2O ←→ H_3O^+ + $SO_3^=$ K_{a2} =1.02 x 10^{-7} pK_{a2} = 6.91

In the above buffer solution, what is the concentration of H_2SO_3?

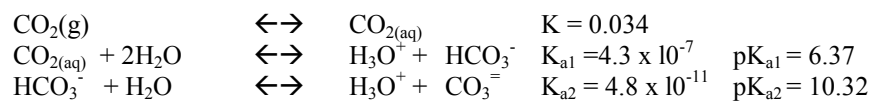*Concept*
Which of the following would give me a buffer with pH=7.2?
a)   50ml of 1M H_3PO_4 and   50ml of 1M NaH_2PO_4

b)   50ml of 1M NaH_2PO_4 and   50ml of 1M NaOH

c)   50ml of 1M NaH_2PO_4 and   25ml of 1M NaOH

d)   25ml of 1M NaH_2PO_4 and   50ml of 1M NaOH

Concept
You have a sample of water containing phosphoric acid. The pH of the sample is 12.3. Which protonation states of phosphoric acid are present in significant amounts?

H_3PO_4 $H_2PO_4^-$ $HPO_4^=$ PO_4^{-3}

4) pH of solutions containing multi-protic weak acids?

$$CO_2(g) \quad\longleftrightarrow\quad CO_{2(aq)} \qquad K = 0.034$$

$$CO_{2(aq)} + 2H_2O \quad\longleftrightarrow\quad H_3O^+ + HCO_3^- \quad K_{a1} = 4.3 \times 10^{-7} \quad pK_{a1} = 6.37$$

$$HCO_3^- + H_2O \quad\longleftrightarrow\quad H_3O^+ + CO_3^= \quad K_{a2} = 4.8 \times 10^{-11} \quad pK_{a2} = 10.32$$

The partial pressure of CO_2 in the atmosphere is 3.55×10^{-4} atm. What is the pH of water in equilibrium with air?

Suppose a can of soda contains a gas mixture for which the partial pressure of CO_2 is 1atm. What is the pH of the soda?

5) *General solution of aqueous equilibria*

What is the pH of 1.0×10^{-5}M HCN?