

*Instructors  
Key*

***Questions and Answers***

***Practice Test***

***AP Chemistry  
Free Response 4***

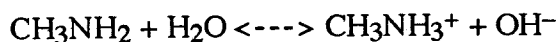
***Acid Base and Solubility Equilibrium***

1.

Discuss the roles of indicators in the titration of acids and bases. Explain the basis of their operation and the factors to be considered in selecting an appropriate indicator for a particular titration.

- An indicator changes color at the endpoint of a titration, thus signaling the point at which the moles acid = moles base.
- An indicator is a weak acid (or weak base) whose conjugate acid base forms are different colors.
- Let  $\text{HIn} \equiv$  acid form of indicator and  $\text{In}^- \equiv$  the base form of the indicator.
- Color change occurs when  $[\text{In}^-] \approx [\text{HIn}]$   
$$\text{pK}_{\text{a HIn}} \approx \text{pH} + \log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} + \log(1) = \text{pH}$$
- Thus color change occurs when the pH of the solution being titrated  $\approx$  the  $\text{pK}_{\text{a}}$  of the indicator.
- Therefore pick an indicator whose  $\text{pK}_{\text{a}}$  is approximately equal to the pH of the solution at the endpoint of the titration.

2.



Methylamine,  $\text{CH}_3\text{NH}_2$ , is a weak base that reacts according to the equation above. The value of the ionization constant,  $K_b$ , is  $5.25 \times 10^{-4}$ . Methylamine forms salts such as methylammonium nitrate,  $(\text{CH}_3\text{NH}_3^+)(\text{NO}_3^-)$ .

- (a) Calculate the hydroxide ion concentration,  $[\text{OH}^-]$ , of a 0.225-molar aqueous solution of methylamine.
- (b) Calculate the pH of a solution made by adding 0.0100 mole of solid methylammonium nitrate to 120.0 milliliters of a 0.225-molar solution of methylamine. Assume no volume change occurs.
- (c) How many moles of either NaOH or HCl (state clearly which you choose) should be added to the solution in (b) to produce a solution that has a pH of 11.00? Assume that no volume change occurs.
- (d) A volume of 100. milliliters of distilled water is added to the solution in (c). How is the pH of the solution affected? Explain.

$$a) K_b = 5.25 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{x^2}{.225 - x} \approx \frac{x^2}{.225}$$

$$[\text{OH}^-] = \sqrt{K_b(.225)} = \sqrt{(5.25 \times 10^{-4})(.225)} = \boxed{0.0109 = [\text{OH}^-]}$$

$$(.0109 / .225) \times 100 = 4.8\% < 5\% \text{ so approximation is OK}$$

b)  $\text{MeNH}_3\text{NO}_3$  is a strong electrolyte

$$[\text{MeNH}_3^+]_i = 0.0100 / .120 = 0.0833 \text{ M}$$

$$[\text{MeNH}_2]_i = 0.225 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{MeNH}_2]}{[\text{MeNH}_3^+]} = -\log \left( \frac{10^{-14}}{5.25 \times 10^{-4}} \right) + \log \left( \frac{.225 + x}{.0833 - x} \right) = 10.720 + \log \left( \frac{.225}{.0833} \right) = \boxed{11.15 = \text{pH}}$$

Note: you can use  $\text{pH} = \text{p}K_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)$  or  $\text{pOH} = \text{p}K_b + \log \left( \frac{[\text{acid}]}{[\text{base}]} \right)$

c) We want the pH to decrease therefore **HCl** must be added.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{MeNH}_2]}{[\text{MeNH}_3^+]} \right)$$

$$11 = 10.720 + \log \left( \frac{.225 - x}{.0833 + x} \right)$$

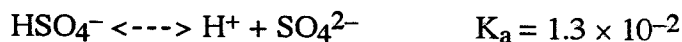
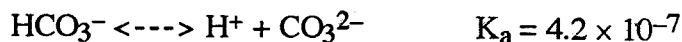
$$0.280 = \log \left( \frac{.225 - x}{.0833 + x} \right) \Rightarrow 10^{.28} = \frac{.225 - x}{.0833 + x} \Rightarrow \overset{1.905}{(0.0228)} (.0833 + x) = 0.225 - x$$

$$\Rightarrow 0.0663 = 2.905x \Rightarrow x = \text{mol H}^+ \text{ added} = 0.0228 \text{ M} \Rightarrow \frac{0.0228}{.120} = \boxed{0.00274 \text{ mol H}^+ \text{ added}}$$

d)  $\text{pH}$  is not affected  $\text{pH} = \text{p}K_a + \log \left( \frac{\text{base}_i / (.120 + .100)}{\text{acid}_i / (.120 + .100)} \right) = \text{p}K_a + \log \frac{[\text{base}]_i}{[\text{acid}]_i}$   
 ratio  $[\text{base}] / [\text{acid}]$  doesn't change.

3.

The equations and constants for the dissociation of three different acids are given below.



- From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. Explain your choice.
- Explain briefly how you would prepare the buffer solution described in (a) with the conjugate pair you have chosen.
- If the concentrations of both the acid and the conjugate base you have chosen were doubled, how would the pH be affected? Explain how the capacity of the buffer is affected by this change in concentrations of acid and base.
- Explain briefly how you could prepare the buffer solution in (a) if you had available the solid salt of the only one member of the conjugate pair and solution of a strong acid and a strong base.

a)  $\text{HCO}_3^- \quad pK_a = 6.376$   
 $\text{H}_2\text{PO}_4^- \quad pK_a = 7.208$   
 $\text{HSO}_4^- \quad pK_a = 1.886$

$\text{HPO}_4^{2-} / \text{H}_2\text{PO}_4^-$  is the best conjugate pair because  $pK_a$  is closest to 7.2

b) Take a solution of  $\text{NaH}_2\text{PO}_4$  and titrate to first endpoint with  $\text{NaOH}$ .

OR

Dissolve equal numbers of moles of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  in water.

OR

Take a solution of  $\text{Na}_2\text{HPO}_4$  and titrate to the first endpoint with  $\text{HCl}$ .

c) The pH would not change because  $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}\right)$   
 and  $\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$  does not change with dilution.

d) Same as b

4.

At 25°C the solubility product constant,  $K_{sp}$ , for strontium sulfate,  $SrSO_4$ , is  $7.6 \times 10^{-7}$ . The solubility product constant for strontium fluoride,  $SrF_2$ , is  $7.9 \times 10^{-10}$ .

- (a) What is the molar solubility of  $SrSO_4$  in pure water at 25°C?  
 (b) What is the molar solubility of  $SrF_2$  in pure water at 25°C?  
 (c) An aqueous solution of  $Sr(NO_3)_2$  is added slowly to 1.0 litre of a well-stirred solution containing 0.020 mole  $F^-$  and 0.10 mole  $SO_4^{2-}$  at 25°C. (You may assume that the added  $Sr(NO_3)_2$  solution does not materially affect the total volume of the system.)
- Which salt precipitates first?
  - What is the concentration of strontium ion,  $Sr^{2+}$ , in the solution when the first precipitate begins to form?
- (d) As more  $Sr(NO_3)_2$  is added to the mixture in (c) a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?

$$a) K_{sp} = 7.6 \times 10^{-7} = [Sr^{+2}][SO_4^{2-}] = (sol)(sol) = sol$$

$$\sqrt{7.6 \times 10^{-7}} = sol$$

$$8.7 \times 10^{-4} \frac{mol}{L} = sol \text{ } SrSO_4$$

$$b) K_{sp} = 7.9 \times 10^{-10} = [Sr^{+2}][F^-]^2 = (sol)(2sol)^2 = 4sol^3$$

$$\sqrt[3]{(7.9 \times 10^{-10})/4} = sol$$

$$5.8 \times 10^{-4} \frac{mol}{L} = sol \text{ } SrF_2$$

c)  $[F^-] = 0.020 M$      $[SO_4^{2-}] = 0.10 M$

ppt of  $SrSO_4$  occurs when  $[Sr^{+2}] = K_{sp}/[SO_4^{2-}] = (7.6 \times 10^{-7})/0.10 = 7.6 \times 10^{-6} M$

ppt of  $SrF_2$  occurs when  $[Sr^{+2}] = K_{sp}/[F^-]^2 = (7.9 \times 10^{-10})/(0.020)^2 = 2.0 \times 10^{-6} M$

1)  $SrF_2$  will precipitate first when

2)  $[Sr^{+2}] = 2.0 \times 10^{-6} M$

d) The anion of the first ppt. is  $F^-$  when the second ppt ( $SrSO_4$ ) forms  $[Sr^{+2}] = 7.6 \times 10^{-6} M$  (see part c)

at that point  $[F^-] = \sqrt{K_{sp} SrF_2 / 7.6 \times 10^{-6}} = \sqrt{(7.9 \times 10^{-10}) / (7.6 \times 10^{-6})}$

$$= 1.02 \times 10^{-2}$$

$$\% F^- \text{ remaining} = \left( \frac{1.02 \times 10^{-2}}{0.020} \right) \times 100 = 51\%$$

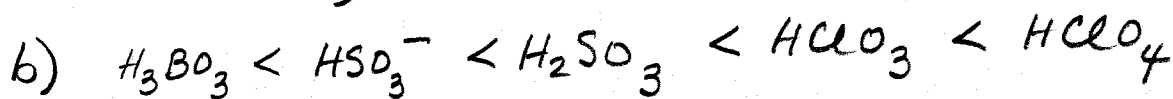
5.



Oxyacids, such as those above, contain an atom bonded to one or more oxygen atoms; one or more of these oxygen atoms may also be bonded to hydrogen.

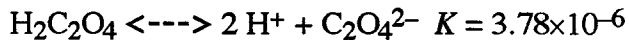
- (a) Discuss the factors that are often used to predict correctly the strengths of the oxyacids listed above.
- (b) Arrange the examples above in the order of increasing acid strength.

- a) ● For an oxyacid, the acidity increases with the number of nonprotonated oxygens bonded to the central atom.
- As the electronegativity of the central atom of an oxyacid increases the acidity increases.
- For a polyprotic acid conjugate pair, the anion will be a weaker acid (negative charge makes it more difficult to remove the  $\text{H}^+$ ).



6.

The overall dissociation of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is represented below. The overall dissociation constant is also indicated.

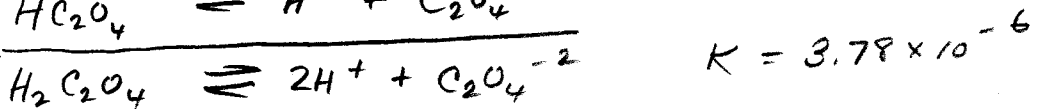
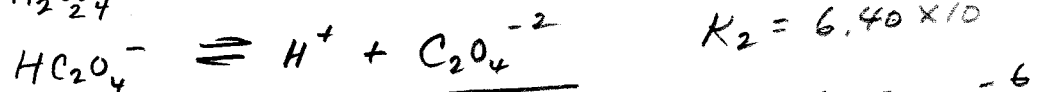
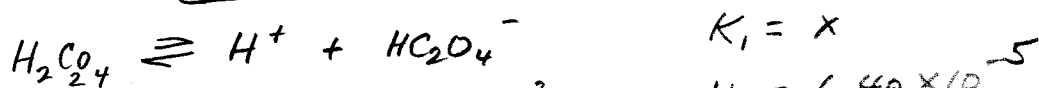


- (a) What volume of 0.400-molar NaOH is required to neutralize completely a  $5.00 \times 10^{-3}$ -mole sample of pure oxalic acid?
- (b) Give the equations representing the first and second dissociations of oxalic acid. Calculate the value of the first dissociation constant,  $K_1$ , for oxalic acid if the value of the second dissociation constant,  $K_2$ , is  $6.40 \times 10^{-5}$ .
- (c) To a 0.015-molar solution of oxalic acid, a strong acid is added until the pH is 0.5. Calculate the  $[\text{C}_2\text{O}_4^{2-}]$  in the resulting solution. (Assume the change in volume is negligible.)
- (d) Calculate the value of the equilibrium constant,  $K_b$ , for the reaction that occurs when solid  $\text{Na}_2\text{C}_2\text{O}_4$  is dissolved in water.

$5.00 \times 10^{-3}$  mol oxalic acid requires  $2(5.00 \times 10^{-3} \text{ mol}) \text{ NaOH}$   
 $= 1 \times 10^{-2} \text{ mol NaOH}$

$$1 \times 10^{-2} \text{ mol} = \frac{0.400 \text{ M}}{x \text{ L}}$$

$$0.025 \text{ L} = x = \text{volume NaOH}$$



$$K_1 K_2 = K \quad \Rightarrow \quad x(6.40 \times 10^{-5}) = 3.78 \times 10^{-6}$$

$$x = 5.9 \times 10^{-2} = K_1$$

use  $K = \frac{[\text{H}^+]^2 [\text{C}_2\text{O}_4^{2-}]}{[\text{H}_2\text{C}_2\text{O}_4]} = 3.78 \times 10^{-6}$       $[\text{H}^+] = 10^{-0.5} = 0.316$

$$3.78 \times 10^{-6} = \frac{(0.316)^2 (x)}{0.015 - x} \approx \frac{(0.316)^2 x}{0.015}$$

$$x = \frac{(3.78 \times 10^{-6})(0.015)}{(0.316)^2} = 5.67 \times 10^{-7} = [\text{C}_2\text{O}_4^{2-}]$$



$$K_b = \frac{[\text{HC}_2\text{O}_4^-][\text{OH}^-]}{[\text{C}_2\text{O}_4^{2-}]}$$

$$K_b = K_w / K_2 (\text{HC}_2\text{O}_4^-) = 10^{-14} / (6.4 \times 10^{-5})$$

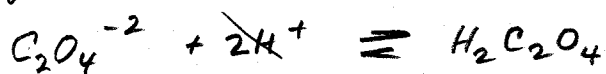
$$= 1.56 \times 10^{-10}$$

Note on Problem # b d

If we were asked to calculate  $K_f$  for



we would add the following reactions and multiply their equilibrium constants:



$1/K$



$K_w^2$



$$K_{eq} = \frac{K_w^2}{K}$$

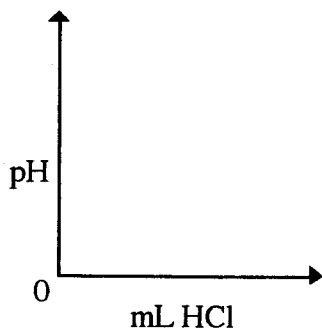
$$= (10^{-14})^2 / 3.78 \times 10^{-6} = 2.65 \times 10^{-23}$$



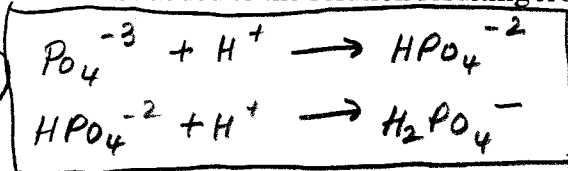
7.

A chemical reaction occurs when 100. milliliters of 0.200-molar HCl is added dropwise to 100. milliliters of 0.100-molar Na<sub>3</sub>PO<sub>4</sub> solution.

- Write the two net ionic equations for the formation of the major products.
- Identify the species that acts as both a Brønsted acid and as a Brønsted base in the equation in (a), Draw the Lewis electron-dot diagram for this species.
- Sketch a graph using the axes provided, showing the shape of the titration curve that results when 100. milliliters of the HCl solution is added slowly from a buret to the Na<sub>3</sub>PO<sub>4</sub> solution. Account for the shape of the curve.



- Write the equation for the reaction that occurs if a few additional milliliters of the HCl solution are added to the solution resulting from the titration in (c).



b)  $\text{H}_2\text{PO}_4^-$  acts as both a Brønsted acid and base

$P = 5$   
 $4 \times O = 24$   
 $2 \times H = 2$   
 $(-) = \frac{1}{32} \div 2 = 16 \text{ pairs electrons}$

