

Questions 1 and 2 refer to a solution made by dissolving 0.020 mol of benzoic acid ( $\text{HC}_7\text{H}_5\text{O}_2$ ) and 0.010 moles of sodium benzoate ( $\text{NaC}_7\text{H}_5\text{O}_2$ ) in enough water to make 1.00 L of solution.  $\text{pK}_a$  for  $\text{HC}_7\text{H}_5\text{O}_2$  is 4.20.

1. What is the approximate pH of this solution?

- (A) 4.20      (C) 4.50      (E) 3.10  
 (B) 3.90      (D) 2.96

$$\text{pH} = \text{pK}_a + \log([\text{conjugate base}]/[\text{acid}])$$

$$\text{pH} = 4.20 + \log(0.010/0.020)$$

$$\text{pH} = 4.20 - 0.30 = 3.90$$

2. What is the approximate pH after the addition of 0.010 mol of solid NaOH to the solution (assume no volume change)?

- (A) 5.89      (C) 4.50      (E) 2.96  
 (B) 12.0      (D) 4.20

Since volume is 1 liter, moles and moles/l are the same...

Start with 0.020 M benzoic acid ( $\text{HC}_7\text{H}_5\text{O}_2$ ) and 0.010 M benzoate ( $\text{C}_7\text{H}_5\text{O}_2^-$ ) (Initial)

NaOH ionizes completely to  $\text{Na}^+$  and  $\text{OH}^-$ , then  $\text{OH}^-$  reacts with the acid: (Change)



	$\text{HC}_7\text{H}_5\text{O}_2$	$\text{C}_7\text{H}_5\text{O}_2^-$
Initial	0.020 M	0.010 M
Change	-0.010 M	+0.010 M
Final	0.010 M	0.020 M

$$\text{pH} = \text{pK}_a + \log([\text{conjugate base}]/[\text{acid}])$$

$$\text{pH} = 4.20 + \log(0.020/0.010)$$

$$\text{pH} = 4.20 + 0.30 = 4.50$$

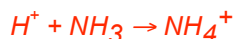
Question 3 refers to a buffer made by dissolving 0.50 moles of  $\text{NH}_3$  and 0.30 moles of  $\text{NH}_4\text{Cl}$  in enough water to form 1.00 L of solution. For  $\text{NH}_3$   $K_b = 1.74 \times 10^{-5}$

3. When a small amount of HCl is added to the original buffer solution, the pH slightly \_\_\_\_\_, the concentration of  $\text{NH}_3$  \_\_\_\_\_, and the concentration of  $\text{NH}_4^+$  \_\_\_\_\_.

pH       $[\text{NH}_3]$        $[\text{NH}_4^+]$

- (A) increases    increases    increases  
 (B) decreases    decreases    increases  
 (C) increases    increases    decreases  
 (D) decreases    increases    decreases  
 (E) decreases    decreases    decreases

Add acid, so pH decreases. The  $\text{H}^+$  from the HCl reacts with  $\text{NH}_3$  (weak base):



4. Which of the solutions below will make a good buffer? (choose one answer)

- (A) 0.10 M HBr + 0.05 M NaBr *strong acid + conjugate base - NO*  
 (B) 0.10 M KNO<sub>2</sub> + 0.05 M NaNO<sub>2</sub> *both salts supply NO<sub>2</sub><sup>-</sup>, a weak base - NO*  
 (C) *0.10 M NaNO<sub>2</sub> + 0.05 M HNO<sub>2</sub> weak acid (HNO<sub>2</sub>) + conj. Base (NO<sub>2</sub><sup>-</sup>) - YES*  
 (D) 0.10 M CH<sub>3</sub>CO<sub>2</sub>H + 0.05 M HClO<sub>4</sub> *weak acid + strong acid - NO*  
 (E) All of the above will make good buffers.

5. When one liter of a 0.50 M CH<sub>3</sub>CO<sub>2</sub>H, 0.50 M CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> buffer solution is diluted to a volume of two liters, the:

- (A) pH is doubled  
 (B) pH is halved  
 (C) [H<sub>3</sub>O<sup>+</sup>] is doubled  
 (D) [H<sub>3</sub>O<sup>+</sup>] is halved  
 (E) *[H<sub>3</sub>O<sup>+</sup>] is nearly constant*

$$pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{acid}]}\right)$$

$$\text{Initially, } \frac{[\text{conjugate base}]}{[\text{acid}]} = \frac{0.50}{0.50} = 1$$

$$\text{After dilution, } \frac{[\text{conjugate base}]}{[\text{acid}]} = \frac{0.25}{0.25} = 1$$

*So, the pH is unchanged (the [H<sub>3</sub>O<sup>+</sup>] is unchanged)*

6. Calculate the [ClO<sup>-</sup>]/[HClO] ratio necessary to give a buffer with a pH = 8.00.

$$K_a \text{ for HClO is } 3.5 \times 10^{-8}$$

- (A) 1.00 (B) 1.07 (C) *3.50* (D) 0.286 (E) 0.932

$$K_a = 3.5 \times 10^{-8}, \text{ so } pK_a = -\log(K_a) = 7.46$$

$$pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{acid}]}\right)$$

$$8.00 = 7.46 + \log\left(\frac{[\text{conjugate base}]}{[\text{acid}]}\right)$$

$$\log\left(\frac{[\text{conjugate base}]}{[\text{acid}]}\right) = 0.54$$

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = 10^{0.54} = 3.50$$

7. Calculate the approximate [H<sub>3</sub>O<sup>+</sup>] in a 0.020 M H<sub>2</sub>S solution.

$$\text{For H}_2\text{S; } K_{a1} = 1.1 \times 10^{-7} \text{ and } K_{a2} = 1.0 \times 10^{-14}$$

- (A) *4.7 x 10<sup>-5</sup>* (C) 1.1 x 10<sup>-21</sup> (E) 1.1 x 10<sup>-7</sup>  
 (B) 2.2 x 10<sup>-9</sup> (D) 3.3 x 10<sup>-11</sup>

	$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$			$K = K_{a1} = 1.1 \times 10^{-7}$
Initial	0.020	0	0	
Change	-x	x	x	
Equilibrium	0.020-x	x	x	

$$\text{So, } K_{a1} = \frac{[H_3O^+][HS^-]}{[H_2S]} = \frac{(x)(x)}{(0.020-x)} = 1.1 \times 10^{-7}$$

Assume x is small, so 0.020-x = 0.02, then

$$(x^2) = 2.2 \times 10^{-9}$$

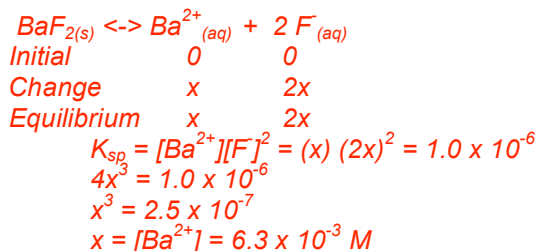
$$x = [H_3O^+] = 4.7 \times 10^{-5} \text{ (and note that } x \text{ is much less than } 0.02)$$

*(You don't need to consider K<sub>a2</sub>, as [H<sub>3</sub>O<sup>+</sup>] >> K<sub>a2</sub>)*

8. What is the [Ba<sup>2+</sup>] in a saturated BaF<sub>2</sub> solution?

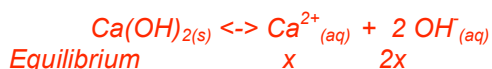
$$K_{sp} = 1.0 \times 10^{-6}$$

- (A)  $1.0 \times 10^{-3} \text{ M}$  (D)  $2.0 \times 10^{-6} \text{ M}$   
 (B)  $6.3 \times 10^{-3} \text{ M}$  (E)  $3.0 \times 10^{-6} \text{ M}$   
 (C)  $1.3 \times 10^{-2} \text{ M}$



9. The molar solubility of calcium hydroxide in water is  $1.3 \times 10^{-4} \text{ M}$ . The solubility product constant ( $K_{sp}$ ) for  $\text{Ca}(\text{OH})_2$  is \_\_\_\_\_ M.

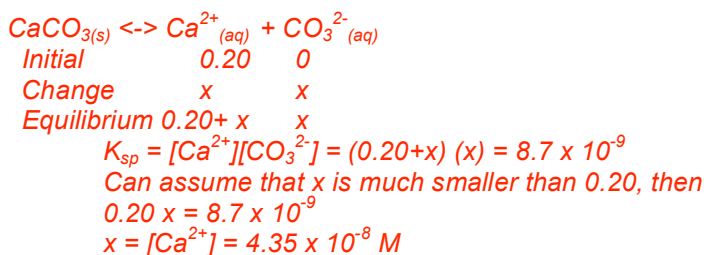
- (A)  $1.3 \times 10^{-4}$  (C)  $2.2 \times 10^{-12}$  (E)  $3.4 \times 10^{-8}$   
 (B)  $1.7 \times 10^{-8}$  (D)  $8.8 \times 10^{-12}$



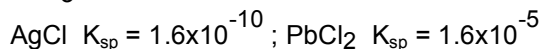
$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^{-}]^2 = (x)(2x)^2 = 4x^3, \text{ but } x = 1.3 \times 10^{-4}, \text{ so } K_{sp} = 8.8 \times 10^{-12}$$

10. The molar solubility of calcium carbonate in 0.20 M calcium nitrate is \_\_\_\_\_ M.  
 For  $\text{CaCO}_3$   $K_{sp} = 8.7 \times 10^{-9}$

- (A)  $8.7 \times 10^{-9}$  (C)  $4.4 \times 10^{-8}$  (E)  $3.2 \times 10^{-3}$   
 (B)  $9.3 \times 10^{-5}$  (D)  $6.3 \times 10^{-3}$



11. If solid NaCl is added to an aqueous solution which is 0.10 M in  $\text{Pb}(\text{NO}_3)_2$  and 0.10 M in  $\text{AgNO}_3$  until the  $[\text{Cl}^{-}]$  is 0.020 M, what will happen? Assume no volume change.



- (A) A precipitate of  $\text{PbCl}_2$  but not of  $\text{AgCl}$  will form.  
 (B) A precipitate of  $\text{AgCl}$  but not of  $\text{PbCl}_2$  will form.  
 (C) Precipitates of both  $\text{AgCl}$  and  $\text{PbCl}_2$  will form.  
 (D) No precipitate will form.  
 (E) A precipitate of  $\text{NaNO}_3$  will form.

Calculate Q for each salt and compare to K<sub>sp</sub>

For AgCl,  $Q = [Ag^+][Cl^-] = (0.10)(0.020) = 2 \times 10^{-3}$ , so  $Q > K_{sp}$ , get precipitate.

For PbCl<sub>2</sub>,  $Q = [Pb^{2+}][Cl^-]^2 = (0.10)(0.020)^2 = 4 \times 10^{-5}$ , so  $Q > K_{sp}$ , get precipitate.

12. CrO<sub>4</sub><sup>2-</sup> is added slowly to a solution that is 1.0 x 10<sup>-2</sup> M in Ag<sup>+</sup>. Assuming no volume change, what is the minimum [CrO<sub>4</sub><sup>2-</sup>] necessary to initiate precipitation of Ag<sub>2</sub>CrO<sub>4</sub>?

The K<sub>sp</sub> of Ag<sub>2</sub>CrO<sub>4</sub> = 2.4 x 10<sup>-12</sup>.

- (A) 2.4 x 10<sup>-10</sup> (C) 1.5 x 10<sup>-6</sup> (E) 8.4 x 10<sup>-5</sup>  
(B) 2.4 x 10<sup>-8</sup> (D) 1.3 x 10<sup>-4</sup>

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (1.0 \times 10^{-2})^2 (x) = 2.4 \times 10^{-12}$$
$$(1.0 \times 10^{-4}) x = 2.4 \times 10^{-12}$$
$$x = [CrO_4^{2-}] = 2.4 \times 10^{-8}$$

Questions 13-16 are worth 2 points each

For the following salts, state whether they will be

- (A) more soluble in 0.1 M HCl than in pure water  
(B) about the same solubility in 0.1 M HCl and pure water  
(C) less soluble in 0.1 M HCl than in pure water

13. AgBr Anion (Br<sup>-</sup>) is neutral, no common ion, (B)

14. AgCl Anion (Cl<sup>-</sup>) is neutral, but add Cl<sup>-</sup> (common ion) (C)

15. Fe(OH)<sub>2</sub> Anion (OH<sup>-</sup>) is basic, so it reacts with acid, increasing solubility (A)

16. CaCO<sub>3</sub> Anion (CO<sub>3</sub><sup>2-</sup>) is basic, so it reacts with acid, increasing solubility (A)

17. What is the concentration of N<sub>2</sub> (in moles/L) in fresh water in equilibrium with air at 25 °C and 1 atm ? The atmosphere is 78% (mole percent) nitrogen. The Henry's Law constant for N<sub>2</sub> in H<sub>2</sub>O is k<sub>H</sub> = 8.42 x 10<sup>-7</sup> M/(mm Hg)

- (A) 6.4 x 10<sup>-4</sup> (B) 5.0 x 10<sup>-4</sup> (C) 6.6 x 10<sup>-5</sup> (D) 8.4 x 10<sup>-7</sup> (E) 6.6 x 10<sup>-7</sup>

$$S_g = k_H P_g$$

P<sub>g</sub> is the pressure of nitrogen. The atmosphere is 78% nitrogen, so the pressure of nitrogen is

$$P_g = 0.78 (760 \text{ mm Hg}) = 592.8 \text{ mm Hg}$$

$$S_g = 8.42 \times 10^{-7} \text{ M/(mm Hg)} \times 592.8 \text{ mm Hg} = 4.99 \times 10^{-4} \text{ M}$$

Use the following information to answer questions 18-20.

12.20 g of sugar (MW= 180.0), a non-electrolyte, is dissolved in 480.0 g water (MW= 18.00) to give a solution with a volume of 488.0 mL. The temperature of the solution is 25.0°C. The vapor pressure of water at 25.0°C is 23.80 mm Hg.

18. The molality of the sugar solution is:

- (A) 0.141 (B) 0.139 (C) 0.0678 (D) 0.158 (E) 0.224

molality = moles solute/kg of solvent

$$\text{moles sugar (solute)} = 12.20 \text{ g}/(180.0 \text{ g/mol}) = 0.0678 \text{ moles}$$

$$\text{molality} = 0.0678 \text{ moles sugar}/0.480 \text{ kg water} = 0.141 \text{ m}$$

(Note: you were asked to calculate the molality, not the molarity, so you don't use the volume information given)

19. The vapor pressure of the sugar solution at 25.0°C in mm Hg is:

- (A) 23.80 (B) 0.997 (C) 23.74 (D) 28.86 (E) 760

$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$ , so need to calculate mole fraction of solvent:

$X_{\text{solvent}} = \text{moles solvent} / (\text{moles solvent} + \text{moles solute})$

Moles solvent = moles water = 480 g water / (18.0 g/mol) = 26.67 moles water

$X_{\text{solvent}} = 26.67 \text{ moles water} / (26.67 \text{ moles water} + 0.0678 \text{ moles sugar})$

$X_{\text{solvent}} = 0.99746$  (note: don't round off until later !)

$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}} = 0.99746 (23.80 \text{ mm Hg}) = 23.74 \text{ mm Hg}$

20. The freezing point of this solution in °C is:

- (A) -0.262° (B) -0.260° (C) -0.186° (D) -0.335° (E) -40.2°

$\Delta T_{\text{fp}} = K_{\text{fp}} m_{\text{solute}} i$

As sugar is a nonelectrolyte,  $i = 1$

$\Delta T_{\text{fp}} = (-1.86 \text{ °C/m})(0.141 \text{ m})(1) = -0.262 \text{ °C}$

Notes: You will be given  $K_{\text{fp}}$  and  $K_{\text{bp}}$  for the solvent. Answering #20 correctly requires answering 18 correctly...for your exam, I'll try to avoid having one question depend on another.

21. Arrange the following aqueous solutions from lowest to highest boiling point: 0.65 m sugar (nonelectrolyte), 0.40 m  $\text{MgCl}_2$ , 0.30 m  $\text{CaSO}_4$ , 0.20 m  $\text{NaNO}_3$ :

(A)  $\text{NaNO}_3 < \text{CaSO}_4 < \text{MgCl}_2 < \text{sugar}$

(B)  $\text{sugar} < \text{NaNO}_3 < \text{CaSO}_4 < \text{MgCl}_2$

(C)  $\text{NaNO}_3 < \text{CaSO}_4 < \text{sugar} < \text{MgCl}_2$

(D)  $\text{MgCl}_2 < \text{sugar} < \text{CaSO}_4 < \text{NaNO}_3$

(E)  $\text{NaNO}_3 < \text{MgCl}_2 < \text{CaSO}_4 < \text{sugar}$

$\Delta T_{\text{bp}} = K_{\text{fp}} m_{\text{solute}} i$ , and for water,  $K_{\text{bp}} = 0.512 \text{ °C/m}$ , so higher boiling point means higher value of  $m_{\text{solute}} i$  (or you can calculate  $\Delta T_{\text{bp}}$  for each solution):

Sugar: nonelectrolyte, so  $i = 1$ ,  $\Delta T_{\text{bp}} = (0.512 \text{ °C/m}) (0.65 \text{ m}) (1) = 0.333 \text{ °C}$

$\text{MgCl}_2$ : electrolyte, with  $i = 3$ , so  $\Delta T_{\text{bp}} = (0.512 \text{ °C/m}) (0.40 \text{ m}) (3) = 0.614 \text{ °C}$  (highest)

$\text{CaSO}_4$ : electrolyte, with  $i = 2$ , so  $\Delta T_{\text{bp}} = (0.512 \text{ °C/m}) (0.30 \text{ m}) (2) = 0.307 \text{ °C}$

$\text{NaNO}_3$ : electrolyte, with  $i = 2$ , so  $\Delta T_{\text{bp}} = (0.512 \text{ °C/m}) (0.20 \text{ m}) (2) = 0.205 \text{ °C}$  (lowest)

22. Cell walls act as semipermeable membranes in living systems. Assume that these membranes are permeable to solvent only. If the ion concentration inside the cell is 0.0043 M and the ion concentration outside of the cell is 0.0025 M you would predict:

(A) Ions would flow from inside the cell to outside.

(B) Water would flow from inside the cell to outside

(C) Ions would flow from outside the cell to inside

(D) Water would flow from outside the cell to inside

(E) Neither water nor ions would flow

Ion concentration inside the cell is higher than outside, so water concentration inside the cell is lower than outside.

This is a semipermeable membrane, so water goes through it, but ions don't.

Water moves from region with higher concentration to region with lower concentration, so from outside the cell to inside.