CHEMISTRY

TARGET : JEE Advanced - 2023

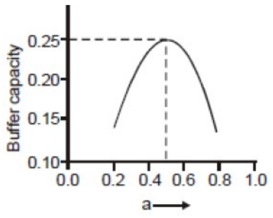
CAPS – 7

Ionic Equilibrium

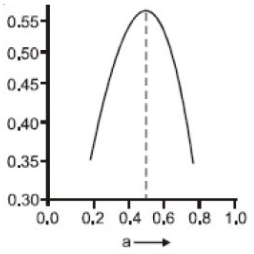
1. At what molar concentration of HCl will its aqueous solution have an $[H^+]$ to which equal contributions come from HCl and H_2O.

(A) $\sqrt{60}\times10^{-7}$ M (B) $\sqrt{50}\times10^{-8}$ M (C) $\sqrt{40}\times10^{-9}$ M (D) $\sqrt{30}\times10^{-8}$ M

2. A buffer solution is prepared by mixing 'a' mole of CH_3COONa and 'b' moles of CH_3COOH into water to make 1 L buffer solution such that (a + b) = 1. If the instantaneous (differential) buffer capacity of this buffer solution is plotted against moles of salt CH_3COONa (a) then the plot obtained will be (to the scale) approximately. (As shown in figure in options)



(A)



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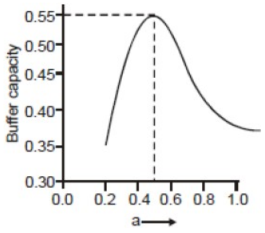

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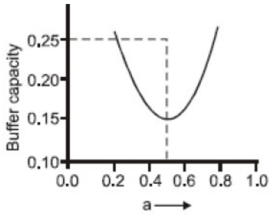


(D)

3. Pure water is added into the following solutions causing a 10% increase in volume of each. The greatest % change in pH would be observed in which case (a), (b), (c) or (d)?

(A) 0.1 M $NaHCO_3$ (B) 0.2 M NaOH

(C) 0.3 M NH_3 – 0.2 M NH_4^+ system (D) 0.4 M CH_3COONH_4

4. Liquid NH_3 dissociation to a slight extent. At a certain temp. itself dissociation constant $K_{SD\,(NH_3)} = 10^{-30}$. The number of NH_4^+ ions are present per 100 cm^3 of pure liquid are:

(A) 10^{-15} (B) 6.022×10^{8} (C) 6.022×10^{7} (D) 6.022×10^{6}

5. 20 mL of 0.1 M weak acid HA ($K_a = 10^{-5}$) is mixed with solution of 10 mL of 0.3 M HCl and 10 mL of 0.1 M NaOH. Find the value of $\frac{[A^-]}{[HA]+[A^-]}$ in the resulting solution:

(A) 2×10^{-4} (B) 2×10^{-3} (C) 2×10^{-3} (D) 0.05

6. Which of the following expression for α of a monoacidic base (BOH) in aqueous solution at appreciable concentration is not correct?

(A) $100\times\sqrt{\frac{K_b}{c}}$ (B) $10^{P_{OH}-P_{Kb}}$ (C) $\frac{K_w\left[H^+\right]}{K_b+K_w}$ (D) $\frac{K_b}{K_b+\left[OH^-\right]}$

7. The simultaneous solubility of AgCN (K_{sp} = 2.5 × 10^{-16}) and AgCl (K_{sp} = 1.6 × 10^{-10}) in 1.0 M NH_3 (aq) are respectively: [Given: $K_f\left[Ag(NH_3)_2^+\right]=10^7$]

(A) 0.037,5.78 × 10^{+8} (B) 5.78 × 10^{-8}, 0.037 (C) 0.04, 6.25 × 10^{-8} (D) 1.58,1.26 × 10^{-5}

8. The $Al(OH)_3$ is involved in the following two equilibria,

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq.) + 30H^-(aq.);K_{sp}$$

$$Al(OH)_3(s) + OH^-(aq.) \rightleftharpoons Al(OH)_4^-(aq.);K_C$$

Which of the following relationship is correct at which solubility is minimum?

(A) $\left[OH^-\right]=\left(\frac{K_{sp}}{K_c}\right)^{1/3}$ (B) $\left[OH^-\right]=\left(\frac{K_c}{K_{sp}}\right)^{1/4}$

(C) $\left[OH^-\right]=\sqrt{\left(\frac{K_{sp}}{K_c}\right)^{1/4}}$ (D) None of these

MULTIPLE CHOICE QUESTIONS

9. If K_{a_1}, K_{a_2} and K_{a_3} be the first, second and third ionization constant of H_3PO_4 and $K_{a_1} >> K_{a_2} >> K_{a_3}$ which is/are correct :

(A) $\left[H^+\right]=\sqrt{K_{a_1}\left[H_3PO_4\right]}$ (B) $\left[H^+\right]=\left[HPO_4^{2-}\right]$

(C) $K_{a_2}=\left[HPO_4^{2-}\right]$ (D) $\left[HPO_4^{2-}\right]=\left[PO_4^{3-}\right]$

10. Which of the following mixtures constitute a buffer ?

(A) HCOOH + HCOONa (B) Na_2CO_3 + $NaHCO_3$

(C) NaCl + HCl (D) NH_4Cl + $(NH_4)_2SO_4$

11. Which of the following statements is/are correct?

(A) The conjugate acid of NH_2^- is NH_3

(B) Solubility product constant increases with increase in concentration of ions

(C) On diluting a buffer solution pH change is negligible

(D) In alkakine buffer solution, If some HCl is added, it's $[OH^-]$ will increase

12. Formic acid is a weak acid and hydrochloric acid is a strong acid. It follows that the :

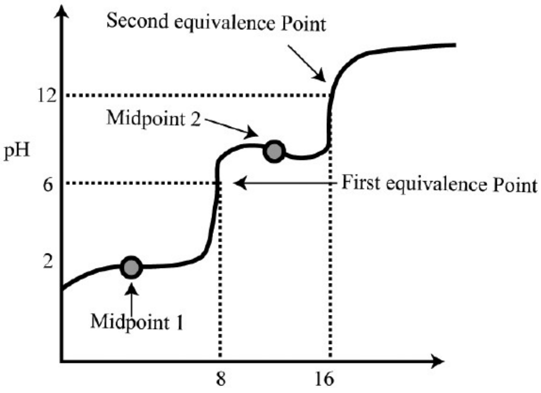
(A) $[OH^-]$ of 0.01 M HCl (aq.) will be less than that of 0.01 M HCOOH (aq.)

(B) solution containing 0.1 M NaOH(aq.) and 0.1 M HCOONa(aq.) is a buffer solution

(C) pH of 10^{-9} M HCl (aq.) will be approximately 7 at 25°C

(D) pH of a solution formed by mixing equimolar quantities of HCOOH and HCl will be less than that of a similar solution formed from HCOOH and HCOONa

13. A weak acid (or base) is titrated against a strong base (or acid), volume v of strong base (or acid) is plotted against pH of the solution (as shown in figure). The weak electrolyte (i.e., acid or base) could be



(A) Na_2CO_3 (B) $Na_2C_2O_4$ (C) $H_2C_2O_4$ (D) $CH_2(COOH)_2$

14. Which of the following statement(s) is/are correct about the ionic product of water

(A) K_i (ionization constant of water) < K_w (ionic product of water)

(B) $pK_i > pK_w$

(C) At 25ºC, $K_i = 1.8 \times 10^{-14}$

(D) Ionic product of water at 10ºC is 10^{-14}

15. H_2A is a weak diprotic acid. If the pH of 0.1M H_2A solution is 3 and concentration of A^{2-} is 10^{-12} at 25ºC.

Select correct statement(s)?

(A) $\left[H^+\right]_{total} \approx \left[H^+\right]$ from first step of ionization of acid H_2A

(B) Concentration of OH^- in solution is 10^{-3} M

(C) The value of K_{a_1} is nearly 10^{-5}

(D) $pK_{a_2} = pK_{a_1} = 9$

16. 0.01 M NH_4Cl (aq.) solution at 25ºC has:

(A) $[Cl^- (aq.)] < 10^{-2}$ M (B) $\left[NH_4^+(aq.) < 10^{-2} M\right]$

(C) pOH > 7 (D) $[H^+] > 10^{-7}$ M

COMPREHENSION # 1 (FOR Q. 17)

17. Potash alum is $KAl(SO_4)_2 \cdot 12H_2O$. As a strong electrolyte, it is 100 % dissociated into K^+, Al^{3+} and SO_4^{2-}. The solution is acidic because of the hydrolysis of Al^{3+}, but not so acidic as might be expected, because the SO_4^{2-} can sponge up some of the H_3O^+ by forming HSO_4^-.

Given a solution made by dissolving 11.85 gm of $KAl(SO_4)_2 \cdot 12H_2O$ in enough water to make 1000 cm^3 of solution. What is $[H_3O^+]$ of the solution if Both Al^{3+} and SO_4^{2-} are hydrolysing.

First hydrolysis constant for Al^{3+} is 1.4×10^{-5}

Acid dissociation constant for HSO_4^- in water is 1.25×10^{-2}

(A) 2.93×10^{-4} M (B) 0.0114 M (C) 5.43×10^{-6} M (D) None of these

18. Match the column

Column I (pH of resultant solution)

(A) 200 ml of H_2SO_4 solution (specific gravity 1.225 containing 25% H_2SO_4 by weight) + 800 ml of 0.525 M strong triacidic base $X(OH)_3$

(B) 50 ml of 0.1 M HCO_3^- + 50 ml of 0.8 M CO_3^{2-}

$\left(H_2CO_3; K_{a_1} = 4 \times 10^{-7}, K_{a_2} = 2 \times 10^{-11}\right)$

(C) 50 ml of 0.2 M HA (aq) (Ka = 10^{-5}) + 50 ml of 0.1 M HCl (aq) + 100 ml of 0.13 M NaOH (aq)

Column II (Exist between Colour transition range of an indicator)

(P) Phenol Red (6.8 to 8.4)

(Q) Propyl red (4.6 to 6.4)

(R) Phenolphthalein (8.3 to 10.1)

(S) Malachite green (11.4 to 13)

SUBJECTIVE ANSWER TYPE

19. An $NH_4^+ - NH_3$ buffer is supposed to keep the pH of the solution constant within 0.3 pH unit during the reaction.

CH_3COOCH_3 (aq.) + $2H_2O$ (aq.) $\rightarrow$ CH_3COO – (aq.) + H_3O^+ (aq.) + CH_3OH (aq.)

If this solution had initial concentrations: $[NH_4^+]_0 = 0.1$ M, $[NH_3]_0 = 0.06$ M, $[CH_3COOCH_3]_0 = 0.02$ M. What would be the initial and final pH of the solution? Is this a satisfactory buffer? [Kb(NH_3) = 1.8×10^{-5}, log 2 = 0.3, log 3 = 0.48].

20. A solution of 0.1 M Cl^-, 0.1 M Br^- and 0.1 M I^- solid $AgNO_3$ is gradually added to this solution. If the addition of $AgNO_3$ does not change the volume. Answer the following:

(i) What conc. of Ag^+ ions will be required to start precipitation of each of the three ions.

(ii) Which ion will precipitate first

(iii) What will be the conc. of this ion when the second ion start precipitating.

(iv) What will be the conc. of both ions when the third ion start precipitating.

Given: K_{sp} (AgCl) = 1.7×10^{-10}, K_{sp} (AgBr) = 5×10^{-13}, K_{sp}(AgI) = 8.5×10^{-17}.

21. Calculate the solubility of AgCN in a buffer solution of pH = 3. Neglect any complexation. Take K_{sp}(AgCN) = 3.2×10^{-16}, K_a(HCN) = 6.4×10^{-10}.

22. If 0.00050 mol $NaHCO_3$ is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms H_2CO_3, HCO_3^- and CO_3^{2-}? For H_2CO_3, $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-13}$.

23. Equilibrium constant for the acid ionization of Fe^{3+} to $Fe(OH)^{+2}$ and H^+ is 6.5×10^{-3}. What is the max. pH, which could be used so that at least 95% of the total Fe^{3+} in a dilute solution exists as Fe^{3+}?

24. Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $KAg(CN)_2$. Given K_{diss} $\left(Ag(CN)_2^-\right) = 4.0 \times 10^{-19} M^2$ and K_{sp} (AgCl) = 2.8×10^{-10} M^2.