Topics in the June 2007 Exam Paper for CHEM1102

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- Periodic Trends in Aqueous Oxide
- Coordination Chemistry

2007-J-3:

• Coordination Chemistry

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- Weak Acids and Bases
- Calculations Involving pKa

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- Alkynes
- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2007-J-8:

- Alkynes
- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2007-J-9:

- Organic Halogen Compounds
- Synthetic Strategies

2007-J-10:

- Stereochemistry
- Carboxylic Acids and Derivatives

•	• Briefly explain why H ₂ Se is a stronger Brønsted-Lowry acid than H ₂ O and a weaker acid than H ₂ Te.					
	In general, when comparing binary acids within the same group, the strength of the bond E-H between the element (E) and hydrogen determines the acidity:					
	$H_2E(aq) + H_2O(l) \implies EH^-(aq) + H_3O^+(aq)$					
	As the atomic size of E becomes larger, the E-H becomes longer and weaker. Thus H_3O^+ is more readily formed in aqueous solution and acidity increases.					
•	• Compounds of <i>d</i> -block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of V^{3+} .					
	Paramagnetism is associated with the presence of unpaired electron spins. As vanadium is in group 5, V^{3+} has two electrons in its 3d orbitals. These electrons occupy separate orbitals with the same spin to reduce the repulsion between them:					
	\uparrow \uparrow $3d$					
	V ³⁺ thus has two unpaired electrons and is paramagnetic.					

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2007-J-3

• Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)							
Formula	K ₃ [Fe(CN) ₆]	$[Cu(NH_3)_4(H_2O)_2](NO_3)_2$	<i>cis</i> -[CrCl ₂ (en) ₂]Cl				
Oxidation state of transition metal ion	III or +3	II or +2	III or +3				
Coordination number of transition metal ion	$\begin{array}{c} 6 \\ (6 \times \underline{\mathbf{C}} \mathbf{N}^{\text{-}}) \end{array}$	$\begin{array}{c} 6 \\ (4 \times \underline{N}H_3 + 2 \times H_2 \underline{O}) \end{array}$	$\begin{array}{c} 6 \\ (2 \times \underline{\text{CI}} + 2 \times \\ \underline{\text{NH}}_2\text{CH}_2\text{CH}_2\underline{\text{NH}}_2) \end{array}$				
Number of <i>d</i> -electrons in the transition metal ion	5	9	3				
Species formed upon dissolving in water	3K ⁺ [Fe(CN) ₆] ³⁻	$\frac{[Cu(NH_3)_4(H_2O)_2]^{2+}}{2NO_3}$	<i>cis</i> -[CrCl ₂ (en) ₂] ⁺ Cl ⁻				

• Solution A consists of a 0.20 M aqueous solution of formic acid, HCOOH, at 25 °C. Calculate the pH of Solution A. The pK_a of HCOOH is 3.75.

Marks 8

	HCOOH(aq)	$H_2O(l)$	~	HCOO ⁻ (aq)	H ₃ O ⁺ (aq)
start	0.20	large		0	0
change	-x	-X		+x	+x
equilibrium	0.20-x	large		X	x

$$K_{a} = \frac{[\text{HCOO} (aq)][H_{3}O (aq)]}{[\text{HCOOH}(aq)]} = \frac{(x)(x)}{(0.20 - x)} = \frac{x}{(0.20 - x)} = 10^{-3.7}$$

As K_a is very small, x is tiny and $0.20 - x \sim x$. Hence,

$$K_a \sim \frac{x^2}{(0.20)} = 10^{-3.75}$$
 or $x^2 = (0.20) \times (10^{-3.75})$ so $x = [H_3O^+(aq)] = 6.0 \times 10^{-4} M$

As $pH = -log_{10}([H_3O^+(aq)])$:

$$pH = -log_{10}(6.0 \times 10^{-4}) = 2.22$$

Answer: 2.22

ANSWER CONTINUES ON NEXT PAGE

At 25 °C, 1.00 L of Solution B consists of 13.6 g of sodium formate, NaHCO₂, dissolved in water. Calculate the pH of Solution B.

The molar mass of NaHCO₂ is

 $(22.99 (Na)) + (1.008 (H)) + (12.01 (C)) + (2 \times 16.00 (O)) = 68.008$

The solution thus contains $\frac{\text{mass}}{\text{molar mass}} = \frac{13.6}{68.008} = 0.200 \,\text{mol}$

As this is dissolved in 1.00 L, the concentration is 0.200 M. The reaction table is now:

	HCOO ⁻ (aq)	H ₂ O(l)	 HCOOH(aq)	OH ⁻ (aq)
start	0.200	large	0	0
change	-у	-у	+y	+y
equilibrium	0.200-у	large	У	У

As $pK_a + pK_b = 14.00$, $pK_b = 14.00 - 3.75 = 10.25$, $K_b = 10^{-10.25}$ and:

$$K_{b} = \frac{[HCOOH(aq)][OH^{-}(aq)]}{[HCOO^{-}(aq)]} = \frac{(y)(y)}{(0.200 - y)} = \frac{y^{2}}{(0.200 - y)} = 10^{-10.25}$$

Again K_b is very small, y is tiny and $0.200 - y \sim y$. Hence, $y^2 = (0.200) \times (10^{-10.25})$

so y = $[OH^{-}(aq)] = 3.35 \times 10^{-6} \text{ M}$ and pOH = $-\log_{10}([OH^{-}(aq)] = 5.47$

As pH + pOH = 14.00, pH = 14.00 - 5.47 = 8.52

Answer: 8.52

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 $^{\circ}$ C to give Solution C. Calculate the pH of Solution C.

After mixing solution A (1.00 L) and solution B (1.00 L), the total volume is 2.00 L. This halves the concentration of the both the acid and the base.

$$[acid] = \frac{0.20}{2} = 0.10$$
 M and $[base] = \frac{0.200}{2} = 0.100$ M

Solution C contains a weak acid (HCOOH) and its conjugate base (HCOO⁻). It is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation can be used:

pH = pK_a + log₁₀
$$\left(\frac{[base]}{[acid]}\right)$$
 = 3.75 + log₁₀ $\left(\frac{0.100}{0.10}\right)$ = 3.75

Answer: **3.75**

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

[HCOOH] would be increased (the acid)



• The following data were obtained for the reaction between gaseous nitric oxide and chlorine at -10 °C.						Marks 4	
	$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$						
	ExperimentInitial [NO]InitialNumber $(mol L^{-1})$ $(mol L^{-1})$		ial [Cl ₂] nol L^{-1})	Initial Reaction Rate $(mol L^{-1} min^{-1})$			
	1 0.10		0.10	0.18			
2 0.10 (0.20	0.36				
	3	0.20		0.20	1.44		
Deduce the rate law for this reaction and calculate the value of the rate constant.							
RATE L	AW			RATE C	ONSTANT		
Betw [NO] doub	een experime is constant ar led. This doub	nts (1) and (2), nd [Cl ₂] is ples the rate:		Using k -	any of the three experi = rate [Cl,][NO] ²	ments,	
r	ate α [Cl ₂]						
Between experiments (2) and (3), [Cl ₂] is constant and [NO] is doubled. The rate increases by a factor of 4:				For ex	$= \frac{0.18}{(0.10)(0.10)^2} = 180$		
r	ate α [NO] ²			For experiment 2:			
Overall, rate $\alpha [Ch] NO ^2 = k[Ch] NO ^2$				k :	$=\frac{0.36}{(0.20)(0.10)^2}=180$		
			For e	xperiment 3:			
			k :	$=\frac{1.44}{(0.20)(0.20)^2}=180$			
			The u units	nits of k are given by: of k = (concentration u	e nits) ³		
				$=\frac{(\text{mol } L^{-1} \text{ min}^{-1})}{(\text{mol } L^{-1})^3}$ $=\text{mol}^{-2}L^2 \text{ min}^{-1}$			
Answer: $rate = k[Cl_2][NO]^2$				Answer:	180 mol ⁻² L ² min ⁻¹		









June 2007

Marks

7

List the substituents attached to the stereogenic centre of **valine** in order of decreasing priority.

-NH2 -COOH -CH(CH3)2 -H Assign the absolute configuration of the stereoisomer of valine shown above. (S) (anticlocky) Draw a dipeptide formed by the condensation of serine with valine. (H2N-CH-CO-NH-CH-COOH H2N-CH-CO-NH-CH-COOH (H2OH) What are the two key elements of protein secondary structure? The secondary structure describes the orientation of segments of the peptide chain and is defined by the H-bonding between amino acid residues. The most common secondary structures are: - α -helices, right handed coils stabilized by H-bonds between amide I	highest priority	lowest priority						
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Draw a dipeptide formed by the condensation of serine with valine. H ₂ N-CH-CO-NH-CH-COOH CH ₂ OH What are the two key elements of protein secondary structure? The secondary structure describes the orientation of segments of the peptic chain and is defined by the H-bonding between amino acid residues. The most common secondary structures are: α-helices, right handed coils stabilized by H-bonds between amide I 	Assign the absolute shown above.	(S) (anticlockwise)						
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The secondary structure describes the orientation of segments of the peptie chain and is defined by the H-bonding between amino acid residues. The most common secondary structures are: - α-helices, right handed coils stabilized by H-bonds between amide h	What are the two k	What are the two key elements of protein secondary structure?						
 H and C=O groups four residues apart and β-pleated sheets, extended structures stabilized by H-bonds between 								

Marks • A saturated solution of iodine in water contains 0.330 g I₂ per litre, but more than this 4 amount can dissolve in a potassium iodide solution because of the following equilibrium. $I^{-}(aq) + I_{2}(aq) \rightleftharpoons I_{3}^{-}(aq)$ A 0.100 M KI solution dissolves 12.5 g of I₂ per litre, most of which is converted to $I_3(aq)$. Assuming that the concentration of $I_2(aq)$ in all saturated solutions is the same, calculate the equilibrium constant for the above reaction. The molar mass of I_2 is $2 \times 126.90 = 253.8$. As 0.330 g of I_2 dissolves in a litre of water, the concentration of I_2 in the saturated solution of iodine in water is therefore: $[I_2(aq)] = \frac{0.330}{253.8} = 0.0013 \,\mathrm{M}$ 12.5 g of I₂ dissolves in a litre of KI solution, corresponding to $\frac{12.5}{253.8} = 0.0493 \text{ M}$. For the equilibrium, the reaction table is therefore: I^(aq) $I_2(aq)$ $I_3(aq)$ [initial] 0.100 0.0493 0 change -X -X +X [equilibrium] 0.100-x 0.0493-x Х Assuming that $[I_2(aq)]$ is the same as in the saturated solution (as stated in the question), 0.0493 - x = 0.0013 so x = 0.048 giving: $[I'(aq)] = 0.100 - 0.048 = 0.052 \text{ M}, [I_2(aq)] = 0.0013 \text{ M} \text{ and } [I_3'(aq)] = 0.048$ М. The equilibrium constant is therefore: $K_{c} = \frac{[I_{3}^{-}(aq)]}{[I^{-}(aq)][I_{2}(aq)]} = \frac{(0.048)}{(0.052)(0.0013)} = 710$ Answer: 710