Topics in the November 2007 Exam Paper for CHEM1102

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- Weak Acids and Bases

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- Weak Acids and Bases
- Calculations Involving pKa
- Periodic Trends in Aqueous Oxide

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• Solubility Equilibrium

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Synthetic Strategies

CHEM1102	2007-N-2	November 2007
• Often pH is used to c	characterise acidic solutions. Give a b	prief definition of pH. Marl 5
pH is a measure of using the equation	the $H^+(aq)$ ion concentration in a so	olution and is defined
$\mathbf{pH} = -\mathbf{log}_{10}[\mathbf{H}^+($	aq)]	
Describe the differen	ice between a strong acid and a weak	acid.
A strong acid disso	ciates completely in water. For example	mple:
$\mathrm{HCl}(\mathrm{aq}) \rightarrow \mathrm{H}^{-1}$	[⊬] (aq) + Cl [–] (aq)	
A weak acid dissoc	iated only slightly in water. For exa	imple:
HF(aq)	$\mathbf{H}^{+}(\mathbf{aq}) + \mathbf{F}^{-}(\mathbf{aq})$	
The pH of a solution acid can give a high a low concentration	on of a strong acid depends on its co h pH (corresponding to low [H ⁺ (aq) n.	ncentration and a strong]) if the acid is present in
In general, can pH be	e used to define the strength of an acid	d? Explain your answer.
No.		
The pH of a solution of a 0.1 M solution	on of a strong acid depends on its co of HCl is 1.0 and the pH of a solution	ncentration. Thus, the pH on of 10 ⁻⁶ M HCl is 6.0.
A low pH can arise solution of a weak	from a solution of a strong acid or acid.	a more concentrated
A high pH can aris solution of a weak	e from a weak solution of a strong a acid.	acid or from a stronger
THE REMAINDE	R OF THIS PAGE IS FOR ROUG	H WORKING ONLY.

• Rank H ₂ O(l), H ₂ S(aq) and HF(aq) in order of their Brønsted acid strengths. Explain your reasoning.		
$HF(aq) > H_2S(aq) > H_2O(l)$		
The H–F bond is more polar than H–O so is easier to break HF into H^+ and F^- than to break H_2O into H^+ and OH^- . Hence HF is stronger acid than H_2O .		
S is much larger atom than O, so the H–S bond is much longer and weaker than H–O; hence H ₂ O is weaker acid than H ₂ S.		
HF is stronger than H ₂ S because the small F ⁻ ion bonds more strongly to the water molecules than does the larger HS ⁻ ion.		
• Buffer systems are frequently used in chemistry. Briefly describe a buffer system and how it functions? Use equations where appropriate.	4	
Buffer systems resist changes in pH. They consist of a weak acid (HA) and its conjugate base (A ⁻) in high concentrations.		
If H ⁺ is added, it is consumed by the A ⁻ ions:		
$H^{+}(aq) + A^{-}(aq) \rightarrow HA(aq)$		
If OH is added, it is consumed by the acid present: $OH^{-}(ag) + HA(ag) \rightarrow H_{0}O + A^{-}(ag)$		
If the amount of H^+ or OH^- added is too great, there may be insufficient HA or A^- present and so the buffer may not work.		
What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 4.00? The K_a of acetic acid is 1.8×10^{-5} M.		
The pH of a buffer can be calculated using the Henderson-Hasselbalch equation can be used:		
$\mathbf{pH} = \mathbf{pK}_{\mathbf{a}} + \log_{10} \left(\frac{[\mathbf{base}]}{[\mathbf{acid}]} \right)$		
For acetic acid, $pK_a = -log_{10}K_a = -log_{10}(1.8 \times 10^{-5}) = 4.74$. Thus to achieve pH 4.00, the ratio of base to acid must be:		
$4.00 = 4.74 + \log_{10} \left(\frac{[CH_3COO^-]}{[CH_3COOH]} \right)$		
$\log_{10}\left(\frac{[CH_{3}COO^{-}]}{[CH_{3}COOH]}\right) = -0.74 \text{ or } \frac{[CH_{3}COOH]}{[CH_{3}COO^{-}]} = 5.6$		
Answer: $CH_3COOH : CH_3COO^- = 5.6$		

- Marks
 - 4
- Barium sulfate is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, K_{sp} , for BaSO₄, given that a maximum of 1.167×10^{-8} g will dissolve in 500 mL of water?

The formula mass of BaSO₄ is 137.34 (Ba) + 32.07 (S) + 4 × 16.00 = 233.41 g mol⁻¹. 1.167 × 10⁻⁸ g therefore corresponds to:

number of moles = $\frac{\text{mass}}{\text{formula mass}} = \frac{1.167 \times 10^{-8}}{233.41} = 5.000 \times 10^{-11}$

Barium sulfate dissolves according to the equilibrium:

BaSO₄(s)
$$\implies$$
 Ba²⁺(aq) + **SO**₄²⁻(aq) $K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$

As 5.000×10^{-11} mol dissolves in 500 mL,

 $[Ba^{2+}(aq)] = [SO_4^{2-}(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{5.000 \times 10^{-11}}{0.500} = 1.00 \times 10^{-10} \text{ M}$

Hence,

$$K_{\rm sp} = (1.00 \times 10^{-10}) \times (1.00 \times 10^{-10}) = 1.00 \times 10^{-20}$$

Answer: **1.00** × **10**⁻²⁰

What advantage would there be in administering $BaSO_4$ as a slurry that also contains 0.5 M Na_2SO_4 ?

As indicated by the very small solubility above, the equilibrium

 $BaSO_4(s) \implies Ba^{2+}(aq) + SO_4^{2-}(aq)$

lies far to the left. Adding more $SO_4^{2-}(aq)$ ions pushes it further to the left.

This acts to remove $Ba^{2+}(aq)$ ions from solution. This is advantageous as barium ions are highly toxic.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

4

• What is a chelate ligand?

A chelate is a ligand with more than one donor atom that can bond to the same metal ion.

Draw all possible isomers of $[CoCl_2(en)_2]$. en = ethylenediamine = NH₂CH₂CH₂NH₂

cis and *trans* geometric isomers are possible. The *cis*-isomer can exist as non-superimposable mirror images (enantiomers).



• Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3} M, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9} M.

2

The Fe^{3+} ion has a higher charge and is smaller than the Fe^{2+} ion – it has a higher charge density. The higher charge density withdraws electron density from the oxygen and leading to a more polarised O–H bonds that are more easily broken.

- Marks
 - 3

1

• You may recall from a lecture demonstration or your laboratory work that solid CO₂ sublimes under ambient conditions while ice melts. Define the terms sublimation and melting.

Sublimation is a phase change from solid to gas without passing through the liquid phase.

Melting is a phase change from solid to liquid.

What is a triple point (*e.g.* in the phase diagram of CO_2 or H_2O)?

The triple point is the temperature and pressure at which all three phases (solid, liquid and gas) coexist in equilibrium.

What does the different behaviour of ice and solid CO₂ indicate about the relative positions of their respective triple points?

The triple point of CO₂ is above ambient pressure.

The triple point of H₂O is below ambient pressure.

• Carbon has a number of allotropes, the two major ones being graphite and diamond. The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions?

Graphite is more stable at room temperature and pressure. Diamond has a more compact structure than graphite and becomes more stable than graphite at very high pressures. Under very high pressures, graphite can be converted into diamond.

When the pressure is released, the reverse process is favourable. However, the structural rearrangement required is considerable and the activation energy is very high. Thus, at low temperatures, the diamond \rightarrow graphite conversion is extremely slow and diamonds can exist for many thousands of years.

Marks • Hydrogenation of nitric oxide to nitrogen and water is a potential means of reducing 3 smog-forming NO_x gases: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0) . Rate / kPa s^{-1} $P_0(H_2) / kPa$ P_0 (NO) / kPa Run 1 53.3 40.0 0.137 2 53.3 20.3 0.033 3 38.5 53.3 0.213 4 19.6 53.3 0.105 Derive an expression for the rate law for this reaction. Between Run 1 and 2, P_0 (H₂) is constant and P_0 (NO) is halved. This causes the rate to be reduced by a factor of four. The rate is second order with respect to NO. Between Run 3 and 4, P_0 (H₂) is halved and P_0 (NO) is constant. This causes the rate to be reduced by a factor of two. The rate is first order with respect to H₂. Overall, rate = $k \times P(H_2) \times P^2(NO)$ Answer: rate = $k \times P(H_2) \times P^2(NO)$ Calculate the value of the rate constant. Using Run 1, rate = 0.137 kPa s^{-1} when $P(H_2) = 53.3 \text{ kPa and } P(NO) = 40.0 \text{ kPa}$: $0.137 \text{ kPa s}^{-1} = k \times 53.3 \text{ kPa} \times (40.0 \text{ kPa})^2$ $k = 1.61 \times 10^{-6} \text{ kPa}^{-2} \text{ s}^{-1}$ Answer: $k = 1.61 \times 10^{-6} \text{ kPa}^{-2} \text{ s}^{-1}$ What is the order of the reaction? $1 (H_2) + 2 (NO) = 3 (third order)$

Marks

3

• Hemochromatosis or "iron overload" is a potentially fatal disorder in which excess iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide. It can be treated by administration of desferioxamine B (Desferal), a natural substance isolated from fungi. HNIH



Desferal is taken over 8-12 hour periods up to six times per week. A value of $\log K = 30.6$ is associated with the following equilibrium:

 $Fe^{3+} + LH_3^+ \implies FeL^+ + 3H^+ \text{ where } LH_3^+ = Desferal$

Briefly describe the chemical basis for the use of *Desferal* in iron overload therapy.

The solubility of Fe₂O₃ is very small - the equibrium for the reaction below lies far to the left:

 $Fe_2O_3(s) + excess H_2O \implies 2Fe^{3+}(aq) + 6OH^{-}(aq)$

Complexation of Fe³⁺ ions with Desferal is very favourable – the equilibrium for the reaction below lies far to the right (as K for this reaction is $10^{30.6}$):

 $Fe^{3+} + LH_3^+ \implies FeL^+ + 3H^+$ where $LH_3^+ = Desferal$

The Desferal complexes all free Fe³⁺(aq) ions, so more Fe₂O₃ must dissolve to reestablish the first equilibrium (le Chatelier's principle). Eventually all the Fe₂O₃ will dissolve.



• Complete the following table.			Marks 5
Starting material	Reagents / Conditions	Major organic product(s)	
ОШСОН	SOCl ₂		
	HCl	Cl	
H	1. NaBH ₄ 2. H [⊕] / H ₂ O	ОН	
Br	hot conc. KOH ethanol (solvent)		
	CN	CN	

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5





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