Topics in the November 2008 Exam Paper for CHEM1102

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- Crystal Structures

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- Hydrolysis of Metal Ions
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Marks • Briefly explain how the concept of electronegativity can rationalise the existence of 3 acidic, basic and amphoteric oxides. Oxides of the *least* electronegative elements (the most electropositive elements the metals) are very ionic. They consist of a cation and the oxide, O^{2-} , ion. The oxide ion is *extremely* basic. For example, it will react rapidly with water: $O^{2}(aq) + H_2O(l) \rightarrow 2OH^{-}(aq)$ Dissolution of the oxide of an element of low electronegativity will result in a strongly basic solution. The oxides of the *most* electronegative elements (the non-metals) are covalent and contain E=O bonds (where E is the electronegative element). They react with water to form acids. For example, sulfur trioxide reacts with water to produce sulfuric acid which rapidly ionizes to give an acidic solution: $SO_3(aq) + H_2O(l) \rightarrow H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$ Elements with intermediate electronegativity form oxides which react with both acids and bases. As a result, they are classified as being amphoteric. Aluminium oxide is an example. It will dissolve in acidic and in alkaline solutions according to the reactions: reacting as a base: $Al_2O_3(s) + 6H^+(aq) + 3H_2O(l) \rightarrow 2[Al(OH_2)_6]^{3+}$ reacting as an acid: $Al_2O_3(s) + 2OH(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]$ You would *not* have needed to remember these reactions of SO₃ or Al₂O₃ to get full marks on this question. They are given here as examples. 2 Draw the face-centred cubic unit cell. The face-centred cubic unit cell has one atom on each corner of the cube and one atom on each face. They are no atoms at the centre of the cube.

A solution is prepared that is 0.10 M in potassium bromide and 0.10 M in potassium

Marks

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chromate. A concentrated aqueous solution of silver nitrate is added with stirring. What is the concentration of $Ag^{+}(aq)$ ions when silver bromide first appears? $K_{\rm sp}$ of AgBr = 5.0 × 10⁻¹³ When precipitation occurs, the following equilibrium is established and $[Ag^{+}(aq)]$ and $[Br^{-}(aq)]$ are controlled by the value of the solubility product: $AgBr(s) \iff Ag^{+}(aq) + Br^{-}(aq)$ $K_{\rm sp} = [{\rm Ag}^+({\rm aq})][{\rm Br}^-({\rm aq})] = 5.0 \times 10^{-13}$ As the solution is 0.10 M in KBr, [Br(aq)] = 0.10 M: $[Ag^{+}(aq)] \times (0.10) = 5.0 \times 10^{-13}$ so $[Ag^{+}(aq)] = 5.0 \times 10^{-12} M$ Answer: 5.0×10^{-12} M What is the concentration of $Ag^{+}(aq)$ ions when silver chromate first appears? $K_{\rm sp}$ of Ag₂CrO₄ = 2.6 × 10⁻¹² When precipitation occurs, the following equilibrium is established and $[Ag^{+}(aq)]$ and $[CrO_{4}^{2-}(aq)]$ are controlled by the value of the solubility product: $Ag_2CrO_4 \implies 2Ag^+(aq) + CrO_4^{2-}(aq)$ $K_{sp} = [Ag^+(aq)]^2[CrO_4^{2-}(aq)] = 2.6 \times 10^{-12}$ As the solution is 0.10 M in K_2CrO_4 , $[CrO_4^{2-}(aq)] = 0.10$ M: $[Ag^{+}(aq)]^{2} \times (0.10) = 2.6 \times 10^{-12}$ so $[Ag^{+}(aq)] = 5.1 \times 10^{-6} M$ Answer: 5.1×10^{-6} M What is the concentration of Br⁻(aq) ions when silver chromate first appears? [Br⁻(aq)] is control by the K_{sp} for AgBr and so when [Ag⁺(aq)] = 5.1 × 10⁻⁶ M, $K_{\rm sp} = [{\rm Ag}^+({\rm aq})][{\rm Br}^-({\rm aq})] = 5.0 \times 10^{-13}$ $(5.1 \times 10^{-6}) \times [Br(aq)] = 5.0 \times 10^{-13}$ so $[Br(aq)] = 9.8 \times 10^{-8} M$ Answer: 9.8×10^{-8} M ANSWER CONTINUES ON THE NEXT PAGE

• Calculate the equilibrium constant for the following reaction.

$$AgI(s) + 2CN(aq) \implies [Ag(CN)_2](aq) + \Gamma(aq)$$

Data: K_{stab} of $[\text{Ag}(\text{CN})_2]^- = 3 \times 10^{20}$; K_{sp} of $\text{AgI} = 8.3 \times 10^{-17}$

The equations for the dissolution of AgI and the stability constant of the complex $[Ag(CN)_2]^-$ are, respectively:

$$AgI(s) \iff Ag^{+}(aq) + I^{-}(aq) \qquad K_{sp} = [Ag^{+}(aq)][I^{-}(aq)]$$
$$Ag^{+}(aq) + 2CN^{-}(aq) \iff [Ag(CN)_{2}]^{-}(aq) \qquad K_{stab} = \frac{[[Ag(CN)_{2}]^{-}(aq)]}{[Ag^{+}(aq)][CN^{-}(aq)]^{2}}$$

Addition of these reactions gives the required reaction and so the equilibrium constant for the reaction is the product of the individual equilibrium constants:

$$AgI(s) + 2CN^{-}(aq) \iff [Ag(CN)_{2}]^{-}(aq) + \Gamma(aq)$$

$$K = K_{sp} \times K_{stab} = [Ag^{+}(aq)][\Gamma(aq)] \times \frac{[[Ag(CN)_{2}]^{-}(aq)]}{[Ag^{+}(aq)][CN^{-}(aq)]^{2}}$$

$$= \frac{[[Ag(CN)_{2}]^{-}(aq)][\Gamma^{-}(aq)]}{[CN^{-}(aq)]^{2}}$$

Hence,

$$K = K_{\rm sp} \times K_{\rm stab} = (8.3 \times 10^{-17}) \times (3 \times 10^{20}) = 2 \times 10^4$$

Answer: 2×10^4

• Which of the cations, $[Fe(OH_2)_6]^{3+}$ and $[Fe(OH_2)_6]^{2+}$, has the larger p K_a ? Briefly explain why.

Solutions containing both cations are acidic due to the equilibria: $[Fe(OH_2)_6]^{2+}(aq) \iff [Fe(OH_2)_5(OH)]^{+}(aq) + H^{+}(aq)$ $[Fe(OH_2)_6]^{3+}(aq) \iff [Fe(OH_2)_5(OH)]^{2+}(aq) + H^+(aq)$ The Fe^{2+} and Fe^{3+} cations polarize the Fe-OH₂ bond, pulling electron density from the oxygen. The oxygen, in turn, pulls electron density away towards itself in the O-H bond, causing H^+ to be produced. Fe³⁺ has a higher charge and is smaller than Fe²⁺: it is more polarizing and so $[Fe(OH_2)_6]^{3^+}$ is more acidic. The equilibrium is further to the right for $[Fe(OH_2)_6]^{3^+}$ than it is for $[Fe(OH_2)_6]^{2^+}$ so K_a ($[Fe(OH_2)_6]^{3^+}$) > K_a ($[Fe(OH_2)_6]^{2^+}$). As $pK_a = -\log_{10}K_a$, a higher K_a means a *lower* pK_a . Thus, $[Fe(OH_2)_6]^{3+}$ is the more acidic of the two cations and has the lower pK_a value. Consider the compound $[CrCl(OH_2)_4(NCS)]Cl \cdot 2H_2O$. ٠ The complex ion is [CrCl(OH₂)₄(NCS)]⁺. This contains Cr³⁺ bonded to Cl⁻, 4H₂O and one NCS⁻. For each ligand, the donor atom is listed *first*. What is the oxidation state of the transition metal ion? +3 or (III) What is the coordination number of the transition metal ion? 6 How many *d*-electrons in the transition metal ion? Cr is in group 6 so Cr(III) is d^3 List all the ligand donor atoms. $C\Gamma$, 4 × O and N • Consider the complexes cis-[PtCl₂(NH₃)₂] and trans-[PtCl₂(NH₃)₂]. Draw the structures of the two isomers, clearly illustrating the stereochemistry. The platinum is bonded to four ligands $(2 \times C\Gamma \text{ and } 2 \times NH_3)$. With four ligands, two geometries are possible - tetrahedral and square planar. Of these, only square planar gives rise to cis and trans-isomers and so the complexes must be square planar: NH₃ CI NH₃ NH_3

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trans-diamminedichloridoplatinum(II)

3

Briefly suggest why *cis*-[PtCl₂(NH₃)₂] is an effective anti-cancer drug, but *trans*-[PtCl₂(NH₃)₂] is not.

cis-[PtCl₂(NH₃)₂] is believed to act by binding the *cis*-Pt(NH₃)₂ group to two nearby nitrogen atoms on the bases of a strand of DNA. This can only be achieved by the *cis* isomer – the *trans* form has 180° between the vacant sites of the Pt(NH₃)₂ group and is not able to bind in this way.

The coordination of the platinum to the DNA causes a kink in the α -helix of the DNA and this prevents its replication.

Marks • Buffers made of mixtures of $H_2PO_4^-$ and HPO_4^{2-} are used to control the pH of soft 5 drinks. What is the pH of a 350 mL drink containing 6.0 g of NaH₂PO₄ and 4.0 g of Na₂HPO₄? For phosphoric acid, H_3PO_4 , $pK_{a1} = 2.15$, $pK_{a2} = 7.20$ and $pK_{a3} = 12.38$. The formula masses of NaH₂PO₄ and Na₂HPO₄ are: $M(\text{NaH}_2\text{PO}_4) = (22.99 \text{ (Na)} + 2 \times 1.008 \text{ (H)} + 30.97 \text{ (P)} + 4 \times 16.00 \text{ (O)}) \text{ g mol}^{-1}$ $= 119.976 \text{ g mol}^{-1}$ $M(Na_2HPO_4) = (2 \times 22.99 (Na) + 1.008 (H) + 30.97 (P) + 4 \times 16.00 (O)) \text{ g mol}^{-1}$ $= 141.958 \text{ g mol}^{-1}$ Hence, the number of moles of each present are: $n(NaH_2PO_4) = mass / formula mass$ $= 6.0 \text{ g} / 119.976 \text{ g mol}^{-1} = 0.050 \text{ mol}$ $n(\text{Na}_2\text{HPO}_4) = 4.0 / 141.958 \text{ g mol}^{-1} = 0.028 \text{ mol}$ As both are present in the same solution, the ratio of their concentrations is the same as the ratio of these amounts. There is no need to calculate the concentrations, although it does not change the answer. The relevant equilibrium for this buffer is $H_2PO_4^-(aq) \iff HPO_4^{2-}(aq) + H^+(aq)$ This corresponds to the second ionization of H_3PO_4 so pK_{a2} is used with the base acid being $H_2PO_4^-$ (from NaH₂PO₄) and the base being HPO₄²⁻ (from Na₂HPO₄). The pH can be calculated using the Henderson-Hasselbalch equation: $pH = pK_a + log([base]/[acid])$ $= pK_{a2} + \log([HPO_4^{2}]/[H_2PO_4]) = 7.20 + \log(0.028/0.050) = 6.95$ Briefly describe how this buffer system functions. Use equations where appropriate. The buffer contains an acid $(H_2PO_4^{-})$ and its conjugate base (HPO_4^{-2}) and is able to resist changes in pH when H⁺ or OH⁻ is added. If H⁺ is added, the base reacts with it to remove it according to the equilibrium: $HPO_4^{2-}(aq) + H^+(aq) \implies H_2PO_4^{-}(aq)$ ANSWER CONTINUES ON THE NEXT PAGE

If OH⁻ is added, the acid reacts with it to remove it according to the equilibrium:

 $H_2PO_4(aq) + OH(aq) \iff HPO_4(aq) + H_2O(l)$

As long the amounts of the acid and base present are not exceeded, the changes in pH will be small.

Is this buffer better able to resist changes in pH following the addition of acid or of base? Explain your answer.

Maximum buffering occurs when equal amounts of base and acid are present. This buffer has less base than acid present. As a result, it is less able to resist cope with the addition of H^+ .

Larger changes in pH result from the addition of acid.



Marks Addition of salt to water raises its boiling point and lowers its melting point. Sketch 3 the phase diagram for water containing salt, showing how it relates to the phase diagram for water (shown as dotted lines below). The melting point is lowered so the solid – liquid boundary is shifted to lower temperature. The boiling point is raised so the liquid – gas boundary is shifted to higher temperature. D liquid Pressure (not to scale) solid gas Temperature (not to scale) In terms of the relative entropies of all relevant species, explain why the boiling point of salt water is higher than that of pure water. Boiling water leads to a large increase in its entropy: $\Delta_{sys}S > 0$. Because boiling requires breaking bonds, it is endothermic and requires energy from the surroundings. This lowers the entropy of the surroundings: $\Delta_{surr} S < 0$. The boiling $\Delta_{univ}S$ to be positive. The boiling point is the temperature at which the gain in the entropy of the water is larger than the loss in the entropy of the surroundings. When salt water is boiled, the $Na^+(aq)$ and $C\Gamma(aq)$ ions form NaCl(s). This greatly reduces their entropy. Hence, when salt water boils the entropy gain is much smaller than when pure water boils. Because $\Delta_{sys}S$ is less positive for boiling salt water, a *higher* temperature is

required before it is larger than the loss in the entropy of the surroundings.

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CHEM1102

• The following data were obtained for the reaction between gaseous nitric oxide and chlorine at -10 °C:

 $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

Experiment Number	Initial P _{NO} (atm)	Initial P _{Cl2} (atm)	Initial Reaction Rate (atm s ⁻¹)
1	2.16	2.16	0.065
2	2.16	4.32	0.130
3	4.32	4.32	0.518

Derive an expression for the rate law for this reaction and calculate the value of the rate constant.

Between experiments (1) and (2), the partial pressure of NO is kept constant and the partial pressure of Cl_2 is doubled. This leads to a doubling of the rate so the reaction is first order with respect to Cl_2 .

Between experiments (2) and (3), the partial pressure of Cl_2 is kept constant and the partial pressure of NO is doubled. This leads to the rate quadrupling. The reaction is second order with respect to NO.

Overall,

rate = $kP_{NO}^2 P_{Cl_2}$ or rate = $k'[NO(g)]^2[Cl_2(g)]$

As the partial pressure is proportional to the concentration. Either form is acceptable.

Using experiment (1), rate = 0.065 atm s⁻¹ when P_{NO} = 2.16 atm and P_{Cl_2} = 2.16 atm. Hence,

0.065 atm s⁻¹ = $k \times (2.16 \text{ atm})^2 \times (2.16 \text{ atm})$

 $k = 0.0064 \text{ atm}^{-2} \text{ s}^{-1}$

The units of *k* are obtained by ensuring that those in the equation balance:

atm s⁻¹ = (units of k) × (atm)² × (atm) so k has units of atm⁻² s⁻¹.

Rate law: rate = $kP_{NO}^2 P_{Cl_2}$ or rate = $k'[NO(g)]^2[Cl_2(g)]$

Rate constant: $k = 0.0064 \text{ atm}^{-2} \text{ s}^{-1}$

Marks 2

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The mechanism for th	is reaction has been postulated to	be that below.	Mark 1
2NO(g	$N_2O_2(g)$	fast	-
$N_2O_2(g$	g) + $Cl_2 \rightarrow 2NOCl(g)$	slow	
Work out the rate law consistent with the ex	expected for this mechanism and perimental rate law and the chem	hence show that it is ical equation.	
The rate determinin its rate law can be v	ng step is the slow, second step. A vritten down from its stoichiom	As this is an elementary step, etry:	
rate = $k_2[N_2O_2$	(g)][Cl ₂ (g)]		
where <i>k</i> ² is the rate	constant for this step.		
This rate law involv cannot be controlle	es the reactive intermediate N ₂ 0 d so this rate law cannot be expe	O ₂ . The concentration of this erimentally tested.	
The first reaction is backward elementa	a fast equilibrium. The rate lav ry reactions are:	vs for the forward and	
rate of forwar rate of backwa	d reaction = $k_1[NO(g)]^2$ ard reaction = $k_{-1}[N_2O_2(g)]$		
where k_1 and k_{-1} are respectively.	e the rate constants for the forwa	ard and backward reactions,	
At equilibrium, the	rate of the forward and backwa	ard reactions are equal so	
$k_1[\mathrm{NO}(\mathbf{g})]^2 = k$	$-1[N_2O_2(g)]$		
$[N_2O_2(g)] = \frac{k}{k}$	$\frac{1}{1}$ [NO(g)] ² and $\frac{[N_2O_2(g)]}{[NO(g)]^2} =$	$=\frac{k_1}{k_{-1}}=K_{\rm c}$	
Substituting this va	lue into the rate law for the seco	ond step gives,	
rate = $k_2[N_2O_2$.(g)][Cl ₂ (g)]		
$=k_2\frac{k_1}{k_{-1}}$ [$NO(g)]^{2}[Cl_{2}(g)] = k'[NO(g)]^{2}[Cl_{2}(g)]$	2(g)] with $k' = k_2 \frac{k_1}{k_{-1}} = k_2 K_c$	
This rate law is seco Cl ₂ , just as in the ex proposed mechanis	ond order with respect to NO an perimentally determined rate la m is thus consistent with the exp	nd first order with respect to aw in 2008-N-8. The periment.	
<u> </u>	ANSWER CONTINUES ON TI	HE NEXT PAGE]

The reaction is exothermic. Draw the potential energy *vs* reaction coordinate diagram for this mechanism, labelling all species that can be isolated.







ANSWER CONTINUES ON THE PAGE

When G is reacted with dilute sulfuric acid, a further product, H, is formed. H has a peak at 3300 cm^{-1} in its IR spectrum. Draw the structure of product **H**.



CHEM1102	2008-N-12	November 2008
• Consider the compour	nd J below.	Marks 5
What is the systematic	J name for compound J.	
(E)-hex-2-ene		
Draw a constitutional	isomer of J .	
Constitutional isomo constitutional isome	ers have different atomic connectiv rs include those below:	vities. Possible
/		
/		
/		\sim
~		\sim
Draw a configurationa	l isomer of J .	
Configurational ison arrangements of the double bond, the fol	ners have the same atomic connect atoms. Because of the restricted r lowing compound is a configuratio	tivity but different spatial otation about a C=C onal isomer of J:
Draw the structure of hydrogen gas (H ₂) and	the product formed when compound a palladium on carbon (Pd/C) cataly	J is reacted with yst.
Treatment with H ₂ a bond:	a Pd/C catalyst will lead to addition	n of H-H across the C=C
	\sim	



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