Topics in the November 2007 Exam Paper for CHEM1902

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- Intermolecular Forces and Phase Behaviour

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- Weak Acids and Bases
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2007-N-12:

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2007-N-13:

• Synthetic Strategies

Marks 2

• In order to reduce the incidence of dental cavities, water is fluoridated to a level of 1 mg L^{-1} . In regions where the water is "hard" the calcium concentration is typically 100 mg L⁻¹. Given that the K_{sp} of calcium fluoride is $3.9 \times 10^{-11} \text{ M}^3$, would it precipitate in these conditions? Show all working.

For the dissolution of $CaF_2(s) \iff Ca^{2+}(aq) + 2F(aq), Q_{sp} = [Ca^{2+}(aq)][F(aq)]^2$. If $Q_{sp} > K_{sp}$, then $CaF_2(s)$ will precipitate. If $Q_{sp} < K_{sp}$, then $CaF_2(s)$ will completely dissolve.

The atomic mass of calcium is 40.08 g mol⁻¹. A 100 mg L⁻¹ solution contains $\frac{100 \times 10^{-3}}{40.08}$ mol and has a concentration of $\frac{100 \times 10^{-3}}{40.08}$ M. [Ca²⁺(aq)] = 2.495×10⁻³ M.

The atomic mass of fluorine is 19.00 g mol⁻¹. A 1 mg L⁻¹ solution contains $\frac{1 \times 10^{-3}}{19.00}$ mol and has a concentration of $\frac{1 \times 10^{-3}}{19.00}$ M. [F⁻(aq)] = 5.263 × 10⁻⁵ M.

Hence, $Q_{sp} = (2.495 \times 10^{-3} \text{ M}) \times (5.263 \times 10^{-5} \text{ M})^2 = 6.911 \times 10^{-12} \text{ M}^3$. As $Q_{sp} < K_{sp}$, calcium fluoride will not precipitate.

Answer: No, it does not precipitate

• Consider the boiling points of the following monosubstituted benzenes.

 C₆H₆
 C₆H₅F
 C₆H₅Cl
 C₆H₅Br
 C₆H₅OH
 C₆H₅I

 b.p.
 80 °C
 85 °C
 132 °C
 156 °C
 182 °C
 188 °C

Explain this order of boiling points.

Phenol (C₆H₅OH) has an anomalously high boiling point compared to the other compounds as it forms strong hydrogen bonds.

The boiling points of the other compounds increase in the expected order, as the halogen increases in atomic number, the size and polarisability of its electron cloud increases and the strength of the intermolecular dispersion forces within the liquid increase.

The strengths of the dipole-dipole forces increase in the opposite order (greatest for C_6H_5F as it contains the most electronegative halogen). This shows that dispersion forces are more important than dipole-dipole forces in this series of compounds.

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• The primary buffering system in blood plasma is represented by the following equation: Marks 5

$$H_2CO_3 \iff HCO_3^- + H^+ \qquad pK_a = 6.1$$

What is the ratio HCO_3 : H_2CO_3 at the normal plasma pH of 7.4?

The Henderson-Hasselbalch equation with $[acid] = [H_2CO_3]$ and $[base] = [HCO_3^-]$ can be used for this buffer system,

 $pH = pK_a + \log_{10} \left(\frac{[base]}{[acid]} \right)$ $= 6.1 + \log_{10} \left(\frac{[base]}{[acid]} \right) = 7.4$ $\frac{[base]}{[acid]} = 10^{(7.4-6.1)} = 10^{1.3} = 20$

Answer: [base] : [acid] = 20 : 1

A typical person has 2 L of blood plasma. If such a person were to drink 1 L of soft drink with a pH of 2.5, what would the plasma pH be if it were not buffered? (Assume all of the H^+ from the soft drink is absorbed by the plasma, but the volume of plasma does not increase.)

As $pH = -log_{10}[H^+]$, the $[H^+]$ in the soft drink is,

$$[H^+]_{soft drink} = 10^{-2.5} M$$

1 L of soft drink therefore contains

number of moles = concentration × volume = $(10^{-2.5} \text{ mol } \text{L}^{-1} \times 1 \text{ L}) = 10^{-2.5} \text{ mol}$

If this amount is present in 2 L of plasma,

$$[H^+]_{plasma} = \frac{number of moles}{volume} = \frac{10^{-2.5}}{2} M$$

Hence the pH of the unbuffered plasma is

$$\mathbf{pH} = -\log_{10}[\mathbf{H}^+] = -\log_{10}\left(\frac{10^{-2.5}}{2}\right) = 2.8$$

Answer: 2.8

ANSWER CONTINUES ON THE NEXT PAGE

What is the pH in this typical person with a normal HCO_3 - concentration of 0.020 M? Ignore any other contributions to the buffering.

Before the addition of the soft drink, $[HCO_3^-] = 0.020$ M and, at pH 7.4, $[H_2CO_3] = [HCO_3^-] / 20 = 0.0010$ M.

As the soft drink has $10^{-2.5}$ mol of H⁺, its concentration when added to the plasma will again be $[H^+] = \frac{10^{-2.5}}{2}$ M before buffering. Adding it will decrease the base concentration and increase the acid concentration so that,

$$[\text{HCO}_{3}^{-}] = (0.020 - \frac{10^{-2.5}}{2}) \text{ M} = 0.018 \text{ M}$$
$$[\text{H}_{2}\text{CO}_{3}] = (0.0010 + \frac{10^{-2.5}}{2}) \text{ M} = 0.0026 \text{ M}$$

Hence,

pH = (6.1) +
$$\log_{10} \left(\frac{0.018}{0.0026} \right) = 7.0$$

Answer: 7.0

two isomeric forms and used this information to predict that the compound had a

Alfred Werner, one of the founders of the field of coordination chemistry, made extensive studies of the metal complex [PtCl₂(NH₃)₂]. He showed that it existed in 6

square-planar molecular geometry. What other molecular geometry would need to be considered for such a complex and on what basis did Werner reject this alternative geometry? As the complex contains 4 ligands bonded to Pt(II) (two Cl⁻ and two NH₃), a tetrahedral geometry also needs to be considered. However, as the angles between all of the bonds in a tetrahedron are the same, tetrahedral $[PtCl_2(NH_3)_2]$ would not give rise to two isomers. Draw and name the two isomers. Cl NH₃ Pt Cl Cl___NH₃ cis-diamminedichloridoplatinum(II) *trans*-diamminedichloridoplatinum(II) Why does platinum(II) form square-planar complexes? There are a number of reasons why platinum(II) forms square-planar rather than tetrahedral complexes. These include: (i) Pt(II) is a relatively big cation and so repulsion between the ligands are not too large. (ii) The Pt-ligands bonds are stronger as, with its $5d^8$ configuration, Pt(II) is able to keep the d_{x2-y2} orbital completely empty allowing the ligands to donate into it. Although the tetrahedral form has less crowding between the ligands, there is no single *d*-orbital which is directed towards, and can bond with, the ligands. Which one of the isomers is biologically active? What is its activity? Describe two features of the complex that play important roles in this biological activity. Only the *cis* isomer is biologically active - it is a potent anti-cancer drug. The cis chloride ligands are easily replaced, allowing Pt(II) to bind to DNA and stop cell replication. It appears that the *cis*-geometry of the Pt-DNA bonds is important in this. The flat nature of the complex means it can approach the **DNA closer.**

• Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation. $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$

The following rate data were collected at 225 °C.

Experiment	[NO] ₀ (M)	$[H_2]_0(M)$	Initial rate (d[NO]/dt, M s ⁻¹)
1	6.4×10^{-3}	$2.2 imes 10^{-3}$	2.6×10^{-5}
2	1.3×10^{-2}	$2.2 imes 10^{-3}$	1.0×10^{-4}
3	6.4×10^{-3}	4.4×10^{-3}	5.1×10^{-5}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[H_2]_0$ is constant and $[NO]_0$ doubles. As the rate increases by a factor of $\frac{1.0 \times 10^{-4}}{2.6 \times 10^{-5}} = 3.8 \sim 4$, the rate is second order with respect to $[NO]_0$. Between experiments (1) and (3), $[H_2]_0$ doubles and $[NO]_0$ is constant. As the rate increases by a factor of $\frac{5.1 \times 10^{-5}}{2.6 \times 10^{-5}} = 2.0$, the rate is first order with respect to $[NO]_0$. Overall,

rate = $k[NO]^2[H_2]$

Calculate the value of the rate constant at 225 °C.

Using experiment (1),

2.6 × 10⁻⁵ M s⁻¹ =
$$k \times (6.4 \times 10^{-3} \text{ M})^2 \times (2.2 \times 10^{-3} \text{ M})$$

 $k = 2.9 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$

Answer:
$$k = 2.9 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$$

Calculate the rate of appearance of N₂O when [NO] = [H₂] = 6.6×10^{-3} M.

rate of disappearance of NO =
$$k[NO]^{2}[H_{2}]$$

= $(2.9 \times 10^{2} \text{ M}^{2} \text{ s}^{-1}) \times (6.6 \times 10^{-3} \text{ M})^{2} \times (6.6 \times 10^{-3} \text{ M})$
= $8.3 \times 10^{-5} \text{ M s}^{-1}$

The rate of appearance of N_2O is *half* this value as, from the chemical equation, NO is disappearing at twice the rate than N_2O is appearing.

Answer: $4.1 \times 10^{-5} \text{ M s}^{-1}$

ANSWER CONTINUES ON THE NEXT PAGE

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

Step 1: $2NO(g) \rightleftharpoons N_2O_2(g)$ This is a fast equilibrium and so $K = \frac{[N_2O_2(g)]}{[NO(g)]^2}$ or $[N_2O_2(g)] = K[NO(g)]^2$ Step 2: $N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ slow (*i.e.* rate determining) As this is rate determining, $rate = k_2[N_2O_2][H_2]$ As $[N_2O_2(g)] = K[NO(g)]^2$, this can be rewritten as, $rate = kK[NO]^2[H_2]$

This is consistent with the experimentally determined rate law with $k_{exp} = k_2 K$.

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Marks • The diagram below shows the structure of perovskite, a mineral made up of calcium (at each of the corners), oxygen (in the centre of each of the faces), and titanium (at the centre of the cube). The unit cell dimension (edge length, a) for perovskite is 0.38 nm.



What is the chemical formula of perovskite?

There are eight Ca²⁺ ions on the corners of the cube. These are each shared between eight unit cells: number of Ca^{2+} ions = $8 \times 1/8 = 1$.

There is a single, unshared Ti⁴⁺ ion at the cube centre.

There are six O^{2-} ions at the centres of the faces of the cube. These are each shared between two cubes: number of O^{2-} ions = 6 × 1/2 =3.

Overall, Ca^{2+} : Ti^{4+} : $O^{2-} = 1 : 1 : 3$. The formula is $CaTiO_3$.

Answer: CaTiO₃

What is the volume of the unit cell?

The length of the side of the cube = a = 0.38 nm. As V = a^3 ,

$$V = (0.38 \times 10^{-9} \text{ m})^3 = 5.5 \times 10^{-29} \text{ m}^3$$

Answer: $5.5 \times 10^{-29} \text{ m}^3$

What is the density of perovskite? Give your answer in $g \text{ cm}^{-3}$.

As the atomic mass is the mass of a mole, the mass of one atom is $\frac{M}{N_a}$. From above, each unit cell contains 1 Ca²⁺, 1 Ti⁴⁺ and 3 O²⁻. The mass of one cell is therefore:

mass of cell =
$$\frac{M_{Ca}}{N_a} + \frac{M_{Ti}}{N_a} + 3\frac{M_O}{N_a} = \frac{1}{N_a} (40.08 + 47.88 + 16.00) g$$

= $\frac{1}{N_a} \times 135.96 g = 2.258 \times 10^{-22} g$

As 1 cm = 0.01 m, 1 cm³ = $(0.01)^3$ m³ = 1 × 10⁻⁶ m³. From above, V = 5.5×10^{-29} m³ so,

volume =
$$5.5 \times 10^{-29} / 1 \times 10^{-6} \text{ cm}^3 = 5.5 \times 10^{-23} \text{ cm}^3$$
.

Hence,

density =
$$\frac{\text{mass (g)}}{\text{volume(cm^3)}} = \frac{2.258 \times 10^{-22} \text{ g}}{5.5 \times 10^{-23} \text{ cm}^3} = 4.1 \text{ g cm}^{-3}$$

Answer: **4.1 g cm**⁻³

ANSWER CONTINUES ON THE NEXT PAGE

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Answer: 4.1 g cm⁻³

 Write balanced ionic equations for the reactions that occur in each of the following. If no reaction occurs, write "NO REACTION".
 Excess 16 M ammonia solution is added to solid silver iodide.
 No reaction (See E19 of Lab Handbook)
 Excess 4 M ammonia solution is added to a 1 M magnesium sulfate solution.
 Mg²⁺(aq) + 2NH₃(aq) + 2H₂O → Mg(OH)₂(s) + 2NH₄⁺(aq)
 Excess 4 M hydrochloric acid is added to solid cadmium sulfide.
 No reaction (See E5 of Lab Handbook)
 Excess 4 M sodium hydroxide solution is added to 1 M zinc nitrate solution.

 $Zn^{2+}(aq) + 4OH^{-}(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$

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Marks • Compound X undergoes an addition reaction on treatment with hydrogen gas in the 6 presence of a palladium on carbon catalyst to form a mixture of cyclic alkanes. Х $H^{\prime\prime\prime}$ Clearly draw all possible products that can form from this reaction, taking care to represent the stereochemistry of the products clearly. Η ۰H Η Η achiral achiral Clearly label each isomer drawn above as either chiral or achiral (not chiral). Circle one of the isomers and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.







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