Topics in the November 2009 Exam Paper for CHEM1612

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- Introduction to Chemical Energetics

2009-N-3:

- Solutions
- Gas Laws

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- Acids and Bases

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2009-N-6:

- Introduction to Chemical Energetics
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2009-N-11:

- Introduction to Colloids and Surface Chemistry
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- Introduction to Colloids and Surface Chemistry
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- Redox Reactions and Introduction to Electrochemistry

2009-N-16:

- Chemical Equilibrium
- Redox Reactions and Introduction to Electrochemistry
- Complexes

Marks 4

- Nitroglycerine, $C_3H_5(NO_3)_3$, decomposes to form N_2, O_2, CO_2 and H_2O according to the following equation.

$$4C_3H_5(NO_3)_3(l) \rightarrow 6N_2(g) + O_2(g) + 12CO_2(g) + 10H_2O(g)$$

If 15.6 kJ of energy is evolved by the decomposition of 2.50 g of nitroglycerine at 1 atm and 25 °C, calculate the enthalpy change, $\Delta H°$, for the decomposition of 1.00 mol of this compound under standard conditions.

The molar mass of $C_3H_5(NO_3)_3$ is:

$$(3 \times 12.01\ (C) + 5 \times 1.008\ (H) + 3 \times 14.01\ (N) + 9 \times 16.00\ (O))\ g\ mol^{-1}$$

$$= 227.1\ g\ mol^{-1}$$

2.50 g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{2.50\ g}{227.1\ g\ mol^{-1}} = 0.0110\ mol$$

As this amount leads to 15.6 kJ being evolved, the enthalpy change for the decomposition of 1.00 mol is:

$$\Delta H° = 15.6\ kJ / 0.0110\ mol = –1420\ kJ\ mol^{-1}$$

Answer: **$–1420\ kJ\ mol^{-1}$**

Hence calculate the enthalpy of formation of nitroglycerine under standard conditions.

Data:

	$\Delta_f H°$ (kJ mol^{-1})
$H_2O(g)$	–242
$CO_2(g)$	–394

The balanced reaction above is for the decomposition of 4 mol of nitroglycerine. Hence, $\Delta_{rxn}H° = 4 \times -1420\ kJ\ mol^{-1} = -5670\ kJ\ mol^{-1}$.

Using $\Delta_{rxn}H° = \Sigma m\Delta_f H°(\text{products}) - \Sigma n\Delta_f H°(\text{reactants})$, the enthalpy change for the above reaction is:

$$\Delta_{rxn}H° = [12\Delta_f H°(CO_2(g)) + 10\Delta_f H°(H_2O(g))] - [4\Delta_f H°(C_3H_5(NO_3)_3(l))]$$

Hence:

$$-5670\ kJ\ mol^{-1} = [(12 \times -394 + 10 \times -242)\ kJ\ mol^{-1}] - [4\Delta_f H°(C_3H_5(NO_3)_3(l))]$$

$$\Delta_f H°(C_3H_5(NO_3)_3(l)) = –370.\ kJ\ mol^{-1}$$

Answer: **$–370.\ kJ\ mol^{-1}$**

Marks

4

- Assuming ideal behaviour, calculate the mass of $MgCl_2\cdot6H_2O$ that should be dissolved in 1.0 L of water at 37 °C to obtain a solution with an osmotic pressure of 6.0 atm, the same as that of cell cytoplasm.

The molar mass of $MgCl_2\cdot6H_2O$ is:

$$(24.31\ (\text{Mg}) + 2 \times 35.45\ (\text{Cl}) + 12 \times 1.008\ (\text{H}) + 6 \times 16.00\ (\text{O}))\ \text{g mol}^{-1}$$

$$= 203.3\ \text{g mol}^{-1}$$

An osmotic pressure of 6.0 atm corresponds to (6.0 × 101.3) kPa = 607.8 kPa.

The osmotic pressure, Π, is given by $\Pi = cRT$. Hence, the concentration, c, required is:

$$c = \Pi / RT = (607.8 \times 10^3\ \text{Pa}) / (8.314\ \text{m}^3\ \text{Pa K}^{-1}\ \text{mol}^{-1} \times ((37 + 273)\ \text{K}))$$

$$= 0.236\ \text{M}$$

$MgCl_2\cdot6H_2O$ dissolves to give $Mg^{2+} + 2Cl^-$: three particles per mole. Hence, the number of moles of $MgCl_2\cdot6H_2O$ required to give this concentration of particles in 1.0 L is:

number of moles = 0.236 / 3 mol = 0.0786 mol

Hence, the mass of $MgCl_2\cdot6H_2O$ required is:

mass = number of moles × molar mass = 0.0786 mol × 203.3 g mol^{-1} = 16 g

Answer: **16 g**

2

- The average speed of a gaseous neon atom at 300 K is 609 m s^{-1}. What is the average speed of a helium atom at the same temperature?

As $E_{\text{kinetic}} = \frac{1}{2} mv^2$:

$$E_{\text{kinetic}}\ (\text{helium}) = \tfrac{1}{2} m_{\text{He}} v_{\text{He}}^2$$

$$E_{\text{kinetic}}\ (\text{neon}) = \tfrac{1}{2} m_{\text{Ne}} v_{\text{Ne}}^2$$

The average kinetic energy of each gas is the same, at the same temperature, in the ideal gas model:

$$\tfrac{1}{2} m_{\text{He}} v_{\text{He}}^2 = \tfrac{1}{2} m_{\text{Ne}} v_{\text{Ne}}^2$$

$$v_{\text{He}}^2 = (m_{\text{Ne}} / m_{\text{He}}) \times v_{\text{Ne}}^2$$

The ratio of the atomic masses is the same as the ratio of the molar masses and so:

$$v_{\text{He}}^2 = (20.18 / 4.003) \times (609\ \text{m s}^{-1})^2$$

$$v_{\text{He}} = 1370\ \text{m s}^{-1}$$

Answer: **1370 m s^{-1}**

Marks

- Tris(hydroxymethyl)aminomethane is commonly used to make buffer solutions. It has a base ionisation constant of 1.26 × 10^{-6}. What is the pH of a 0.05 M aqueous solution of this compound?

3

The base ionization constant refers to the reaction below for which the reaction table is:

	tris	**+ H_2O**	$\rightleftharpoons$	**$trisH^+$**	**OH^-**
Initial	**0.05**			**0**	**0**
Change	**$-x$**			**$+x$**	**$+x$**
Equilibrium	**$0.05 - x$**			**x**	**x**

As pK_b = -log$_{10}$$K_b$, at equilibrium,

$$K_b = \frac{[\mathrm{trisH^+}][\mathrm{OH^-}]}{[\mathrm{tris}]} = \frac{(x)(x)}{(0.05-x)} = \frac{x^2}{(0.05-x)} = 1.26 \times 10^{-6}$$

As K_b is so small, x will be tiny and $0.05 - x \sim 0.05$ and so

$x^2 = 1.26 \times 10^{-6} \times 0.05$ or $x = [OH^-] = 2.5 \times 10^{-4}$ M

Hence, pOH = -log$_{10}$[OH^-] = -log$_{10}$(2.5×10^{-4}) = 3.60 and so:

pH = 14.00 – pOH = 10.4

Answer: **10.4**

- The ionisation constant of water, K_w, at 37 °C is 2.42 × 10^{-14}. What is the pH for a neutral solution at 37 °C?

1

By definition, $K_w = [H^+(aq)][OH^-(aq)]$. Water ionizes to produce equal amounts of H^+(aq) and OH^-(aq). Let $[H^+(aq)] = [OH^-(aq)] = y$:

$K_w = (y)(y) = y^2 = 2.42 \times 10^{-14}$

$y = 1.56\times 10^{-7}$ M = [H^+(aq)]

pH = -log$_{10}$[H^+(aq)] = -log$_{10}$(1.56×10^{-7}) = 6.81

Answer: **6.81**

Marks
3

- Consider the following reaction.

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K_p = 0.090 \text{ at } 298 \text{ K}$$

Calculate $\Delta G°$ (in J mol^{-1}) for this reaction.

Using $\Delta G° = -RT\ln K_p$:

$$\mathbf{\Delta G° = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.090) = 5.97 \times 10^3 \text{ J mol}^{-1}}$$

$\Delta G°$ = **5.97 kJ mol^{-1}**

Calculate ΔG (in J mol^{-1}) at 25 °C when $p(H_2O)$ = 18 mmHg, $p(Cl_2O)$ = 2.0 mmHg and $p(HOCl)$ = 0.10 mmHg.

The reaction quotient, Q, for this reaction is given by:

$$Q = \frac{(p_{HOCl})^2}{(p_{H_2O})(p_{Cl_2O})} = \frac{(0.10)^2}{(18) \times (2.0)} = 0.00028$$

Hence:

$$\Delta G = \Delta G° + RT\ln Q$$

$$= (5.97 \times 10^3 \text{ J mol}^{-1}) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.00028)$$

$$= -14.3 \times 10^3 \text{ J mol}^{-1}$$

Answer: **-14.3 kJ mol^{-1}**

Marks

Explain the following terms or concepts.

3

a) Lewis acid

A Lewis acid is a species that can accept an electron pair.

This includes both the H^+ and species such as BF_3 and Fe^{2+}:

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

$$Fe^{2+} + 6H_2O \rightleftharpoons [Fe(OH_2)_6]^{2+}$$

b) 3rd Law of Thermodynamics

The entropy of a perfect crystal is 0 at 0 K.

c) Brownian motion

The random motion of particles in a liquid that increase with increasing temperature.

- $\Delta_{vap}H°$ = 34.0 kJ mol^{-1} for benzene, which has a boiling point of 80.1 °C. What is the entropy change for the vaporisation of benzene in J K^{-1} mol^{-1}?

2

At the boiling point, $\Delta_{vap}G° = 0$ J mol^{-1}. As $\Delta_{vap}G° = \Delta_{vap}H° - T\Delta_{vap}S°$:

$$0 \text{ J mol}^{-1} = (34.0 \times 10^3 \text{ J mol}^{-1}) - ((80.1 + 273)) \text{ K}) \times \Delta_{vap}S°$$

$$\Delta_{vap}S° = +96.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer: **+96.3 J K^{-1} mol^{-1}**

Marks
4

- The general formula for a nickel(II) chloride compound complexed with ammonia is $[Ni(NH_3)_x]Cl_2$. A 0.59 g sample of the salt was dissolved in water and the ammonia from it was titrated with 153 mL of 0.100 M HCl. What is the value of the coefficient x?

The molar mass of $[Ni(NH_3)_x]Cl_2$ is:

$$(58.69\ (Ni) + x\ (14.01\ (N) + 3 \times 1.008\ (H)) + 2 \times 35.45\ (Cl))\ g\ mol^{-1}$$

$$= (129.59 + 17.034x)\ g\ mol^{-1}$$

A 0.59 g sample therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{0.59}{(129.59 + 17.034x)}\ \text{mol} \qquad (1)$$

The number of moles in 153 mL of 0.100 M HCl is:

$$\text{number of moles} = \text{concentration} \times \text{volume}$$

$$= 0.100\ mol\ L^{-1} \times 0.153\ L = 0.0153\ mol$$

Ammonia reacts with HCl according to the reaction $NH_3 + HCl \rightleftharpoons NH_4Cl$ and so this is equal to the number of moles of NH_3 present. Each mol of $[Ni(NH_3)_x]Cl_2$ contains x mol of NH_3 so the number of moles of $[Ni(NH_3)_x]Cl_2$ is:

$$\text{number of moles} = 0.0153 / x\ \text{mol} \qquad (2)$$

The value of x is calculated by equating (1) and (2). This is easiest to achieve by trial and error.

x	(1) / mol	(2) / mol
1	0.0040	0.015
2	0.0036	0.0077
3	0.0033	0.0051
4	0.0030	0.0038
5	0.0027	0.0031
6	0.0026	0.0026
7	0.0024	0.0022

The best agreement is for $x = 6$ - a common coordination number for Ni(II).

Answer: **6**

Marks

- Will AgCl precipitate if solutions of 25.0 mL of 2.0×10^{-5} M KCl and 75.0 mL of 1×10^{-5} M $AgNO_3$ are added to one another? Show your reasoning.
  K_{sp} for AgCl = 1.8×10^{-10} at 25 °C.

2

After mixing the solution has a volume of (25.0 + 75.0) mL = 100.0 mL. Using $c_1V_1 = c_2V_2$, this leads to Ag^+ and Cl^- concentrations of:

$$[Ag^+(aq)] = (75.0 / 100.0) \times 1 \times 10^{-5}\ M = 7.5 \times 10^{-6}\ M$$

$$[Cl^-(aq)] = (25.0 / 100.0) \times 2.0 \times 10^{-5}\ M = 5 \times 10^{-5}\ M$$

AgCl(s) dissolves to give $Ag^+(aq) + Cl^-(aq)$ with the ionic product, Q_{sp}:

$$Q_{sp} = [Ag^+(aq)][Cl^-(aq)] = (7.5 \times 10^{-6}) \times (5 \times 10^{-5}) = 4 \times 10^{-11}$$

As $Q_{sp} << K_{sp}$, there will be no precipitate.

Answer: **No precipitate forms**

- A mass of 1.250 g of benzoic acid ($C_7H_6O_2$) underwent combustion in a bomb calorimeter. If the heat capacity of the calorimeter was 10.134 kJ K^{-1} and the heat of combustion of benzoic acid is –3226 kJ mol^{-1}, what is the change in internal energy during this reaction?

4

The molar mass of benzoic acid is:

$$(7 \times 12.01\ (C) + 6 \times 1.008\ (H) + 2 \times 16.00\ (O))\ g\ mol^{-1} = 122.1\ g\ mol^{-1}$$

A mass of 1.250 g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.250\ g}{122.1\ g\ mol^{-1}} = 0.0102\ mol$$

As 3226 kJ are released per mole, the change in internal change for this amount is:

$$\Delta U = (-3226\ kJ\ mol^{-1}) \times (0.0102\ mol) = -33.02\ kJ$$

Answer: **–33.02 kJ**

Calculate the temperature change that should have occurred in the apparatus.

In a constant volume apparatus like a calorimeter, the change in internal energy is equal to the heat change, q_V. Using $q = C_p\Delta T$, the temperature change is:

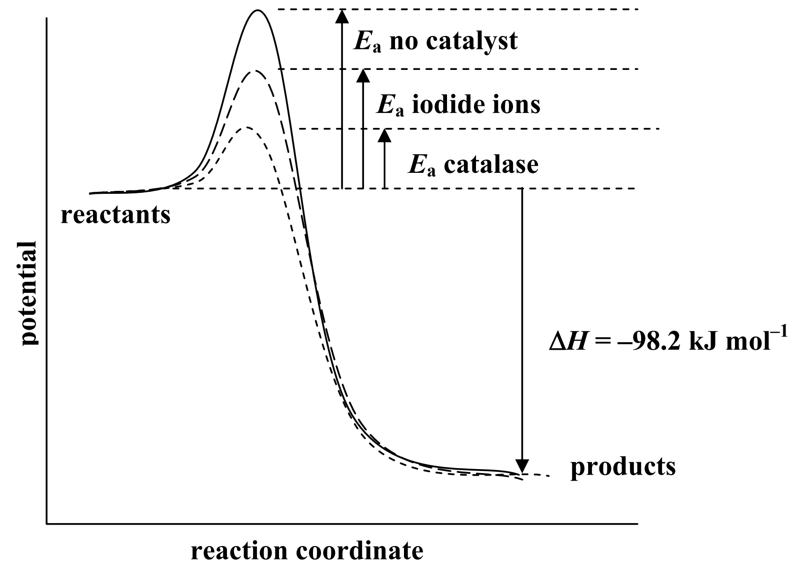
$$\Delta T = (33.02\ kJ) / (10.134\ kJ\ K^{-1}) = 3.528\ K$$

As the combustion reaction evolves heat, the temperature *increases*.

Answer: **+3.258 K**

Marks
6

- The disproportionation of hydrogen peroxide into oxygen and water has an enthalpy of reaction of –98.2 kJ mol^{-1} and an activation barrier of 75 kJ mol^{-1}. Iodide ions act as a catalyst for this reaction, with an activation barrier of 56 kJ mol^{-1}. The enzyme, catalase, is also a catalyst for this reaction, and this pathway has an activation barrier of 23 kJ mol^{-1}. Draw a labelled potential energy diagram for this process both without and with each of the catalysts.



Calculate the factor by which the reaction speeds up due to the presence of each of these two catalysts at a temperature of 37 °C. Assume that the pre-exponential Arrhenius factor remains constant.

Using the Arrhenius equation, $k = A\exp(-E_a / RT)$. Assuming that A is constant, the ratio of the rate constant for the reaction, at the temperature T = (37 + 273) K = 310 K, by a mechanism with activation energy $E_a(1)$ and by a mechanism with activation energy $E_a(2)$ is given by:

$$\frac{k(1)}{k(2)} = \frac{\exp(-\frac{E_a(1)}{RT})}{\exp(-\frac{E_a(1)}{RT})}$$

(i) iodide catalysis:

$$\frac{k(1)}{k(2)} = \frac{\exp(-\frac{56\times10^3}{8.314\times310})}{\exp(-\frac{75\times10^3}{8.314\times310})} = 1.6\times10^3$$

(ii) enzyme catalysis:

$$\frac{k(1)}{k(2)} = \frac{\exp(-\frac{23\times10^3}{8.314\times310})}{\exp(-\frac{75\times10^3}{8.314\times310})} = 5.8\times10^8$$

Marks

- A medical procedure requires 15.0 mg of ^{111}In. What mass of isotope would be required to be able to use it exactly 4 days later? The half life of ^{111}In is 2.80 days. **2**

With a half life, $t_{1/2}$ = 2.80 days, the activity coefficient, λ, is:

$\lambda = \ln 2/t_{1/2} = (\ln 2/2.80)\ \text{days}^{-1} = 0.248\ \text{days}^{-1}$

The amount of isotope at time t is related to the initial amount using $\ln(N_0/N_t) = \lambda t$. With N_t = 15.0 mg left after t = 4 days, the initial mass required is therefore:

$\ln(N_0/N_t) = \lambda t$

$\ln(N_0 / 15.0) = (0.248\ \text{days}^{-1}) \times (4\ \text{days})$

$N_0 = 40.4$ mg

Answer: **40.4 mg**

- Write balanced nuclear equations for the following reactions. **3**

Positron decay of potassium-40.

$$^{40}_{19}\text{K} \rightarrow {}^{40}_{18}\text{Ar} + {}^{0}_{+1}\text{e}$$

Electron capture by gallium-67.

$$^{67}_{31}\text{Ga} + {}^{0}_{-1}\text{e} \rightarrow {}^{67}_{30}\text{Zn}$$

Alpha decay of dysprosium-151.

$$^{151}_{66}\text{Dy} \rightarrow {}^{147}_{64}\text{Gd} + {}^{4}_{2}\text{He}$$

- Briefly explain the apparent contradiction between the following statements. **1**

“Alpha particles are easily stopped by the skin.”
“The alpha-emitter, radon, is thought to be a significant cause of cancer.”

Radon is a gas, so can be inhaled. The alpha particles are therefore generated in the lungs and can cause direct damage without needing to penetrate the skin.

Marks

- Give 2 examples of changes of conditions that might cause a colloidal dispersion to coagulate. In each case, explain why coagulation occurs.

4

Heating and stirring: increase the frequency and velocity of collisions that are necessary for coagulation to occur.

Addition of an electrolyte: neutralises the surface charges, thus removing the electrostatic repulsion between colloidal particles.

Changing the pH: can flatten / desorb electrosteric stabilisers

- A saturated solution of lithium carbonate in pure water at 20 °C contains 1.33 g of solute per 100.0 mL of solution. Calculate the aqueous solubility product of lithium carbonate at this temperature.

4

The molar mass of Li_2CO_3 is (2 × 6.941 (Li) + 12.01 (C) + 3 × 16.00 (O)) g mol^{-1} = 73.892 g mol^{-1}. A mass of 1.33 g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.33\text{ g}}{73.892\text{ g mol}^{-1}} = 0.0180\text{ mol}$$

The reaction table for the dissolution of Li_2CO_3 is:

	Li_2CO_3	$\rightleftharpoons$	$2Li^+(aq)$	$CO_3^{2-}(aq)$
Initial	0.0180		0	0
Change	$-x$		$+2x$	$+x$
Equilibrium	-		0.0360	0.0180

These number of moles of $Li^+(aq)$ and $CO_3^{2-}(aq)$ in 100.0 mL. In a litre, the concentrations are therefore $[Li^+(aq)]$ = 0.360 M and $[CO_3^{2-}(aq)]$ = 0.180 M. The solubility product is therefore:

$$K_{sp} = [Li^+(aq)]^2[CO_3^{2-}(aq)] = (0.360)^2(0.180) = 0.0233$$

K_{sp} = **0.0233**

When the temperature of the same solution is raised to 40 °C, the solubility is reduced to 1.17 g per 100.0 mL of solution. What conclusions can be drawn about the sign of the standard enthalpy of dissolution of lithium carbonate?

Increasing the temperature leads to less dissolution: the equilibrium has shifted towards reactants (to the left). According to Le Chatelier's principle, this is consistent with an exothermic reaction: $\Delta H < 0$.

- A mixture of NaCl (5.0 g) and $AgNO_3$ (5.0 g) was added to 1.0 L of water. What are the concentrations of Ag^+(aq), Cl^-(aq) and Na^+(aq) ions in solution after equilibrium has been established? $K_{sp}(AgCl) = 1.8 \times 10^{-10}$.

Marks
3

The molar masses of the two salts are:

$$M_{NaCl} = (22.99\ (Na) + 35.45\ (Cl))\ g\ mol^{-1} = 58.44\ g\ mol^{-1}$$

$$M_{AgNO_3} = (107.87\ (Ag) + 14.01\ (N) + 3 \times 16.00)\ g\ mol^{-1} = 169.88\ g\ mol^{-1}$$

The number of moles of salt added to the solution are therefore:

$$\text{number of moles of NaCl} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.0}{58.44\ \text{g mol}^{-1}} = 0.0855\ \text{mol}$$

$$\text{number of moles of } AgNO_3 = \frac{5.0}{169.88\ \text{g mol}^{-1}} = 0.0294\ \text{mol}$$

As 1.0 L of water is present, the initial concentrations of the ions are $[Na^+(aq)]$ = 0.086 M, $[Cl^-(aq)]$ = 0.086 M and $[Ag^+(aq)]$ = 0.029 mol. The Na^+(aq) will form any precipitate with the ions present: $[Na^+(aq)]$ = 0.086 M.

The ionic product for the precipitation of AgCl(s) is given by:

$$Q_{sp} = [Ag^+(aq)][Cl^-(aq)] = (0.029)(0.086) = 0.0025$$

As $Q_{sp} >> K_{sp}$, precipitation of AgCl(s) will occur. As $[Ag^+(aq)] < [Cl^-(aq)]$, the silver ion concentration is limiting and so:

$$[Cl^-(aq)] = (0.086 – 0.029)\ M = 0.056\ M$$

As AgCl(s) is present, $[Ag^+(aq)]$ is given by the solubility product:

$$K_{sp} = [Ag^+(aq)][Cl^-(aq)] = 1.8 \times 10^{-10}$$

$$[Ag^+(aq)] = (1.8 \times 10^{-10}) / (0.056)\ M = 3.2 \times 10^{-9}\ M$$

$[Ag^+(aq)]$ = **3.2×10^{-9} M**	$[Cl^-(aq)]$ = **0.056 M**	$[Na^+(aq)]$ = **0.086 M**

Marks

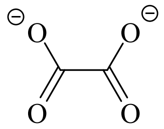
- Can methane act as a ligand? Explain your answer.

2

No. Ligands are, by definition, electron pair donors and so require at least one lone pair of electrons that can be donated to a metal ion to form a covalent bond. Methane, CH_4, has no lone pairs.

- Fe(II) generally forms octahedral complexes. How many different complex ions can be formed when $Fe(NO_3)_2$ is dissolved in an aqueous solution of sodium oxalate? The structure of the oxalate ligand is shown below.

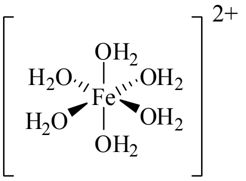
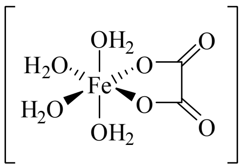
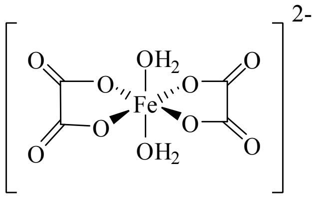
4

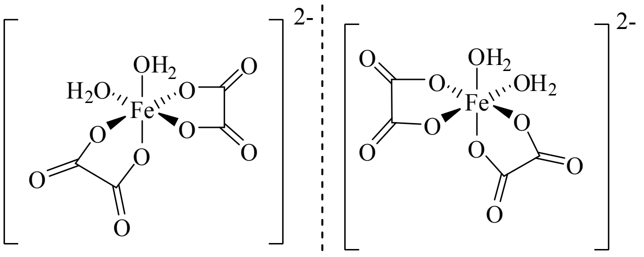


7 complex ions are possible – see below.

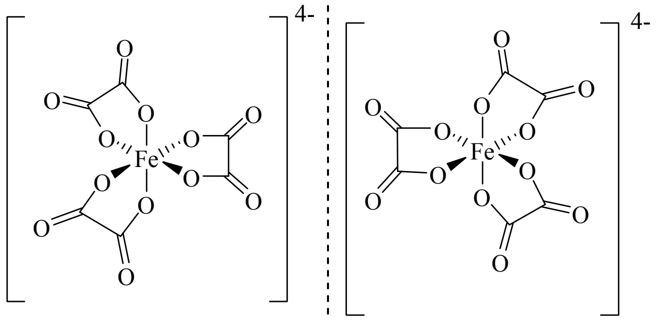
Answer: **7**

Draw diagrams of any 3 of these complexes, including at least one that is chiral.



chiral



chiral

Marks

- Explain how the self-assembly of phospholipids can be utilised in a drug delivery system. **2**

A lipid bilayer will self assemble to form vesicles, which contain solvent that is physically separated from the outer solvent. If the drug is present in the trapped solvent it must stay contained there until the vesicle is broken up where the drug is required.

- A proposed kinetic model for the reaction of NO(g) with Br_2(g) to form NOBr(g) is as follows. **3**

Step 1 $$NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

Step 2 $$N_2O_2(g) + Br_2(g) \xrightarrow{k_2} 2NOBr(g)$$

If Step 2 is assumed to be very slow compared to the equilibrium of Step 1, derive the overall rate equation you would expect to see for this mechanism.

If step 1 is at equilibrium, with equilibrium constant, *K*:

$$K = [N_2O_2(g)]/[NO(g)]^2$$

$$[N_2O_2(g)] = K\,[NO(g)]^2$$

Step 2 involves the bimolecular reaction of a N_2O_2 molecule with a Br_2 molecule. The rate of this step is therefore:

$$\text{rate} = k_2[N_2O_2(g)][Br_2(g)]$$

Using the expression for $[N_2O_2(g)]$ from the equilibrium step gives:

$$\text{rate} = k_2K[NO(g)]^2[Br_2(g)] = k[NO(g)]^2[Br_2(g)] \text{ where } k = k_2K$$

Marks

3

- The standard reduction potential of phosphorous acid to hypophosphorous acid is −0.499 V, with the following half-reaction:

$$H_3PO_3(aq) + 2H^+(aq) + 2e^- \rightarrow H_3PO_2(aq) + H_2O(l)$$

What would the reduction potential be for this half reaction at a temperature of 25 °C in an aqueous solution with pH of 2.3 and concentrations of $[H_3PO_3(aq)] = 0.37$ M and $[H_3PO_2(aq)] = 0.00025$ M?

As pH = $-\log_{10}[H^+(aq)]$, $[H^+(aq)] = 10^{-2.3}$ M. With $[H_3PO_3(aq)] = 0.37$ M and $[H_3PO_2(aq)] = 0.00025$ M, the reaction quotient, *Q*, is given by:

$$Q = \frac{[H_3PO_2(aq)]}{[H_3PO_2(aq)][H^+(aq)]^2} = \frac{(0.00025)}{(0.37)(10^{-2.3})^2} = 27$$

The reduction potential for this 2 electron reduction is given by the Nernst equation:

$$E = E° - \frac{RT}{nF}\ln Q = (-0.499 - \frac{(8.314 \times (25+273)}{2 \times 96485} \times \ln(27))\text{ V} = -0.541\text{ V}$$

Answer: **-0.541 V**

2

- A number of bacteria can reduce the nitrate ion in the presence of sulfur. A simplified unbalanced redox reaction can be written as:

$$S(s) + NO_3^-(aq) \rightarrow SO_2(g) + NO(g)$$

Balance this redox equation for acidic conditions.

$3S(s) + 4H^+(aq) + 4NO_3^-(aq) \rightarrow 3SO_2(g) + 4NO(g) + 2H_2O(l)$

Marks

- What is the value of the equilibrium constant for the following reaction at 298 K? **3**

$$2Fe^{3+}(aq) + 3Sn(s) \rightarrow 2Fe(s) + 3Sn^{2+}(aq)$$

Relevant electrode potentials can be found on the data page.

The relevant reduction potentials are:

$\mathbf{Fe^{3+}(aq) + 3e^- \rightarrow Fe(s) \quad E° = -0.04\ V}$

$\mathbf{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E° = -0.14\ V}$

As the Sn^{2+} / Sn couple is the more negative, it is reversed giving:

$\mathbf{E° = (-0.04 + 0.14)\ V = 0.10\ V}$

The equilibrium constant, *K*, is related to the standard reduction potential using:

$\mathbf{E° = (RT/nF) \times \ln K}$

$\mathbf{\ln K = nFE°/RT = (6 \times 96485 \times 0.10) / (8.314 \times 298) = 23.37}$

$\mathbf{K = e^{23.37} = 1.4 \times 10^{10}}$

Answer: $\mathbf{1.4 \times 10^{10}}$

- Complete the following table. **4**

Formula	Systematic name
$[CrCl(NH_3)_5]Cl_2$	**pentaamminechloridochromium(III) chloride**
$\mathbf{[PtBr_2(CO)_4](NO_2)_2}$	dibromidotetracarbonylplatinum(IV) nitrite
$K_3[CrF_6]$	**potassium hexafluoridochromate(III)**
$(NH_4)_3[CuF_5(OH_2)]$	**ammonium aquapentafluoridocuprate(II)**

- State two chemical factors that contribute to the bioavailability of a heavy metal in the human body. **2**

The solubility of the metal ion in the body and the transport properties of the ion.