Topics in the November 2010 Exam Paper for CHEM1612

Click on the links for resources on each topic.

2010-N-2:

- Chemical Equilibrium
- Acids and Bases
- Chemical Kinetics
- Introduction to Chemical Energetics

2010-N-3:

- Introduction to Chemical Energetics
- Chemical Equilibrium

2010-N-4:

- Gas Laws
- Solutions

2010-N-5:

- Chemical Equilibrium

2010-N-6:

- Chemical Equilibrium
- Complexes

2010-N-7:

- Acids and Bases
- Solutions

2010-N-8:

- Acids and Bases

2010-N-9:

- Radiochemistry

2010-N-10:

- Redox Reactions and Introduction to Electrochemistry
- Radiochemistry

2010-N-11:

- Redox Reactions and Introduction to Electrochemistry

2010-N-12:

- Complexes

2010-N-13:

- Chemical Kinetics

2010-N-14:

- Solubility

- Complexes

- Explain the following terms or concepts. **Marks 3**

a) Lewis base

A Lewis base is a species that donates an electron pair.

b) Le Châtelier's principle

When a chemical system in a state of equilibrium is disturbed, it reattains equilibrium by undergoing a net reaction that reduces the effect of the disturbance.

c) Heterogeneous catalysis

The acceleration of a reaction by the addition of a substance (the catalyst) which is in a different phase state from the reactants. Typically the catalyst is a solid which interacts with liquid or gaseous reactants and products. The solid's surface provides a different reaction pathway and increases the rate at which the reaction attains equilibrium.

- A bar of hot iron with a mass of 1.000 kg and a temperature of 100.00 °C is plunged into an insulated tank of water. The mass of water was 2.000 kg and its initial temperature was 25.00 °C. What will the temperature of the resulting system be when it has stabilised? (The specific heat capacities of water and iron are 4.184 J g^{-1} K^{-1} and 0.4498 J g^{-1} K^{-1}, respectively.) **3**

The heat lost by the iron is equal to the heat gained by the water.

The heat change is related to the temperature change through $q = mC\Delta T$ where m is the mass of the substance and C is its specific heat capacity.

For the water,

$$q = m_{H_2O} C_{H_2O} \Delta T_{H_2O} = (2.000 \times 10^3 \text{ g}) \times (4.184 \text{ J g}^{-1} \text{ K}^{-1}) \times ((T_f - 25.00) \text{ K})$$
$$= (8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 25.00) \text{ K})$$

For the iron,

$$q = m_{Fe} C_{Fe} \Delta T_{Fe} = (1.000 \times 10^3 \text{ g}) \times (0.4498 \text{ J g}^{-1}) \times ((T_f - 100.00) \text{ K})$$
$$= (0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 100.00) \text{ K})$$

Hence, as $q_{water} = - q_{iron}$:

$$(8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 25.00) \text{ K}) = -(0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 100.00) \text{ K})$$

$$T_f = 28.83 \text{ °C}$$

Answer: **28.83 °C**

Marks

- Calculate $\Delta G°$ for the reaction: $2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$ **2**

  Data: $4NO(g) \rightarrow 2N_2O(g) + O_2(g)$ $\Delta G° = -139.56$ kJ mol^{-1}

  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta G° = -69.70$ kJ mol^{-1}

Using $\Delta_r G° = \sum \Delta_f G°$(products) – $\sum \Delta_f G°$(reactants), the free energy changes in the 3 reactions are, respectively:

(1) $\Delta_r G° = 4\Delta_f G°(NO_2(g)) - 2\Delta_f G°(N_2O(g))$

(2) $\Delta_r G° = 2\Delta_f G°(N_2O(g)) - 4\Delta_f G°(NO(g)) = -139.56$ kJ mol^{-1}

(3) $\Delta_r G° = 2\Delta_f G°(NO_2(g)) - 2\Delta_f G°(NO(g)) = -69.70$ kJ mol^{-1}

Taking 2 × (3) – (2) gives:

$2 \times [2\Delta_f G°(NO_2(g)) - 2\Delta_f G°(NO(g))] - [2\Delta_f G°(N_2O(g)) - 4\Delta_f G°(NO(g))]$
$= (2 \times [-69.70] - [-139.56])$ kJ mol^{-1}

$4\Delta_f G°(NO_2(g)) - 2\Delta_f G°(N_2O(g)) = +0.16$ kJ mol^{-1}

From above, this is equal to the $\Delta_r G°$ for reaction (1) as required.

Answer: **+0.16 kJ mol^{-1}**

- Good wine will turn to vinegar if it is left exposed to air because the alcohol is oxidised to acetic acid. The equation for the reaction is: **2**

$$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$$

Calculate $\Delta S°$ for this reaction in J K^{-1} mol^{-1}.

Data:

	$S°$ (J K^{-1} mol^{-1})		$S°$ (J K^{-1} mol^{-1})
$C_2H_5OH(l)$	161	$CH_3COOH(l)$	160.
$O_2(g)$	205.0	$H_2O(l)$	69.96

Using $\Delta_r S° = \sum S°$(products) – $\sum \Delta S°$(reactants),

$\Delta_r S° = [S°(CH_3COOH(l) + S°(H_2O(l)] - [S°(CH_3CH_2OH(l) + S°(O_2)]$
$= ([160. + 69.96] - [161 + 205.0])$ J K^{-1} mol^{-1}
$= -136$ J K^{-1} mol^{-1}

Answer: **-136 J K^{-1} mol^{-1}**

Marks

- A cylinder fitted with a piston contains 5.00 L of a gas at a pressure of 4.0×10^5 Pa. The entire apparatus is maintained at a constant temperature of 25 °C. The piston is released and the gas expands against a pressure of 1.0×10^5 Pa. Assuming ideal gas behaviour, calculate the final volume occupied by the gas. **3**

As the number of moles and the temperature is constant, the initial and final pressures and volumes are related by:

$$V_1P_1 = V_2P_2$$

Hence,

$$V_2 = V_1P_1 / P_2 = (5.00\ \text{L}) \times (4.0 \times 10^5\ \text{Pa}) / (1.0 \times 10^5\ \text{Pa}) = 20.\ \text{L}$$

Answer: **20. L**

Calculate the amount of work done by the gas expansion.

The gas expands from 5.00 to 20. L: it expands by 15 L. As 1 m^3 = 1000 L, this corresponds to 15×10^{-3} m^3.

The work done by a gas expanding against an external pressure is given by:

$$w = -P_{ext}\,\Delta V = -(1.0 \times 10^5\ \text{Pa}) \times (15 \times 10^{-3}\ \text{m}^3) = -1.5 \times 10^3\ \text{J}$$

Answer: **-1.5×10^3 J**

- Isooctane, an important constituent of petrol, has a boiling point of 99.3 °C and an enthalpy of vaporisation of 37.7 kJ mol^{-1}. What is ΔS (in J K^{-1} mol^{-1}) for the vaporisation of isooctane? **2**

At the boiling point, the system is at equilibrium and so $\Delta G = 0$:

$$\Delta G = \Delta H - T\Delta S = 0 \quad \text{or} \quad \Delta S = \Delta H / T$$

As $T_{boiling}$ = (99.3 + 273.0) K = 372.3 K,

$$\Delta S = (+37.7 \times 10^3\ \text{J mol}^{-1}) / (373.2\ \text{K}) = +101\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Answer: **+101 J K^{-1} mol^{-1}**

Marks 5

- Consider the following reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

At 460 °C this reaction has a value of $K_c = 85.0$. Suppose 0.100 mol of SO_2, 0.0600 mol of NO_2, 0.0800 mol of NO and 0.120 mol of SO_3 are placed in a 10.0 L container at this temperature. What are the concentrations of all of the gases when the system reaches equilibrium?

The initial concentrations are:

$[SO_2(g)]$ = number of moles / volume = (0.100 mol) / (10.0 L) = 0.0100 M

$[NO_2(g)]$ = (0.0600 mol) / (10.0 L) = 0.00600 M

$[NO(g)]$ = (0.0800 mol) / (10.0 L) = 0.00800 M

$[SO_3(g)]$ = (0.120 mol) / (10.0 L) = 0.0120 M

The reaction quotient can be used to predict the direction that the reaction will shift:

$$Q = \frac{[NO(g)][SO_3(g)]}{[SO_2(g)][NO_2(g)]} = \frac{(0.0120)(0.00800)}{(0.0100)(0.00600)} = 1.6$$

As $Q < K$, the reaction will shift to the right – to increase the amount of products and decrease the amount of reactants. The reaction table is then:

	$SO_2(g)$	$NO_2(g)$	$\rightleftharpoons$	$NO(g)$	$SO_3(g)$
initial	**0.0100**	**0.00600**		**0.00800**	**0.0120**
change	**$-x$**	**$-x$**		**$+x$**	**$+x$**
equilibrium	**$0.0100 - x$**	**$0.00600 - x$**		**$0.00800 + x$**	**$0.0120 + x$**

Hence,

$$K = \frac{(0.00800+x)(0.0120+x)}{(0.0100-x)(0.00600-x)} = 85.0$$

$$85.0(x^2 - 0.01600x + 0.0000600) = x^2 + 0.02000x + 0.000096$$

$$84.0x^2 - 1.38x + 0.005004 = 0$$

Solving this quadratic equation gives $x = 0.0054$ and 0.011. The second root is not possible, as it leads to negative concentrations for the reactants.

Using $x = 0.0054$ M gives,

$[SO_2(g)]$ = (0.0100 – 0.0054) M = 0.00460 M

$[NO_2(g)]$ = (0.00600 – 0.0054) M = 0.000597 M

$[NO(g)]$ = (0.00800 + 0.0054) M = 0.0134 M

$[SO_3(g)]$ = (0.0120 + 0.0054) M = 0.0174 M

$[SO_2(g)]$ = **0.00460 M**	$[NO_2(g)]$ = **0.000597 M**
$[SO_3(g)]$ = **0.0174 M**	$[NO(g)]$ = **0.0134 M**

Marks

- Consider the ammonia synthesis reaction shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 6.0 \times 10^{-2} \text{ at } 500\ ^\circ C$$

ΔH° for this reaction is –92 kJ mol^{-1}. Calculate the value of K_c at 200 °C. **2**

Using the Van't Hoff equation,

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

with $K_1 = 6.0 \times 10^{-2}$ at $T_1 = (500 + 273)$ K = 773 K, the value of K_2 at $T_2 = (200 + 273)$ K = 473 K can be calculated:

$$\ln\left(\frac{K_2}{6.0 \times 10^{-2}}\right) = \frac{-(-92 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}\left(\frac{1}{(473\ K)} - \frac{1}{(773\ K)}\right)$$

$K_2 = 530$

Answer: **530**

- Explain why iron storage proteins are necessary for the transport of iron both intracellularly and extracellularly within the bloodstream at a pH of 7.4. **2**

The K_{sp} of $Fe(OH)_3$ is so low, that even at pH 7.4 there are sufficient OH^- ions present to precipitate the Fe^{3+} ions as $Fe(OH)_3$.

To avoid precipitation and to allow a higher concentration of Fe^{3+} to be circulated, Fe^{3+} is complexed by *transferrin* in the bloodstream and iron is stored within *ferritin* within the cell.

	Marks
• Explain the role played by the lungs and the kidneys in maintaining blood pH at a constant value of 7.4.	**4**

The most important buffer system in the blood is the hydrogencarbonate / carbonic acid system:

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$$

If the amount of H^+ exceeds the capacity of the buffering system (*e.g.* during vigorous exercise), the lungs can help by removing $CO_2(g)$. CO_2 is linked to the buffer system via

$$H_2CO_3(aq) \rightleftharpoons H_2O + CO_2(g)$$

Thus removal of $CO_2(g)$ will shift the HCO_3^-/H_2CO_3 equilibrium to the right, reducing H^+.

If the blood becomes too basic, the kidneys can help by excreting HCO_3^-. This will shift the buffer equilibrium to the left, producing more H^+.

• An aqueous solution with a volume of 10.0 mL contains 0.025 g of a purified protein of unknown molecular weight. The osmotic pressure of the solution was measured in an osmometer to be 0.0036 atm at 20.0 °C. Assuming ideal behaviour and no dissociation of the protein, estimate its molar mass.	**3**

The osmotic pressure is given by

$$\Pi = cRT$$

As 1 atm = 1.013×10^5 Pa, the osmotic pressure is

$$\Pi = (0.0036 \times 1.013 \times 10^5)\ \text{Pa} = 365\ \text{Pa}$$

Hence

$$c = \Pi / RT = (365\ \text{Pa}) / ((8.314\ \text{m}^3\ \text{Pa K}^{-1}\ \text{mol}^{-1}) \times (293\ \text{K})) = 0.15\ \text{mol m}^{-3}$$

As 1 m^3 = 1000 L, this corresponds to

$$c = 1.5 \times 10^{-4}\ \text{mol L}^{-1}$$

As 1 L contains 1.5×10^{-4} mol, the amount in 10.0 mL is:

$$\text{amount of protein} = (0.0100\ \text{L}) \times (1.5 \times 10^{-4}\ \text{mol L}^{-1}) = 1.5 \times 10^{-6}\ \text{mol}$$

As this amount has a mass of 0.025 g, the mass of 1 mol is:

$$\text{molar mass} = \text{mass} / \text{number of moles} = (0.025\ \text{g}) / (1.5 \times 10^{-6}\ \text{mol}) = 17000\ \text{g mol}^{-1}$$

Answer: **1.7×10^4 g mol^{-1}**

Marks 8

- Sketch the titration curve (pH against mL of added base) when 25.0 mL of 0.10 M hydrofluoric acid (HF) with a pK_a of 3.17 is titrated with 0.10 M NaOH.
  Calculate the pH at the following four points:
  (i) before any NaOH is added;
  (ii) when half of the HF has been neutralised;
  (iii) at the equivalence point; and
  (iv) 50% beyond the equivalence point, *i.e.* when 1.5 times the equivalence volume has been added.

(i) At this point, the solution contains only a weak acid.

As HF is a weak acid, $[H^+]$ must be calculated by considering the equilibrium:

	HF	⇌	F^-	H^+
initial	**0.10**		**0**	**0**
change	**$-x$**		**$+x$**	**$+x$**
final	**$0.10 - x$**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[F^-][H^+]}{[HF]} = \frac{x^2}{(0.10-x)}$$

As pK_a = 3.17, $K_a = 10^{-3.17}$. K_a is very small so $0.10 - x \sim 0.10$ and hence:

$$x^2 = 0.10 \times 10^{-3.17} \quad \text{or} \quad x = 0.00822\ \text{M} = [H^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H^+] = -\log_{10}[0.00822] = 2.09$$

(ii) At this point, half of the original HF has been converted to its conjugate base F^-. The pH can be calculated using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = 3.17 + \log\frac{[F^-]}{[HF]} = 3.17 + + \log(1) = 3.17$$

(iii) At this point, all of the original HF has been converted to F^-. The number of moles of HF originally present is:

$$\text{number of moles of HF} = \text{concentration} \times \text{volume}$$
$$= (0.10\ \text{mol L}^{-1}) \times (0.025\ \text{L}) = 0.0025\ \text{mol}$$

This is equal to the amount of F^- present at equivalence. As 25.0 mL of NaOH has been added at this point, the total volume is now (25.0 + 25.0) mL = 50.0 mL. The concentration of F^- is therefore:

$$[F^-] = \text{number of moles / volume} = (0.0025\ \text{mol}) / (0.050\ \text{L}) = 0.050\ \text{mol L}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

As F^- is a weak base. [OH^-] must be calculated using a reaction table.

	F^-	H_2O	⇌	HF	OH^-
initial	**0.050**	**large**		**0**	**0**
change	**$-y$**	**negligible**		**$+y$**	**$+y$**
final	**$0.050 - y$**	**large**		**y**	**y**

The equilibrium constant K_b is given by:

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{y^2}{(0.050 - y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 3.17 = 10.83$$

As $pK_b = 10.83$, $K_b = 10^{-10.83}$. K_b is very small so $0.050 - y \sim 0.050$ and hence:

$$y^2 = 0.050 \times 10^{-10.83} \text{ or } y = 8.59 \times 10^{-7} \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = \log_{10}[8.59 \times 10^{-7}] = 6.07$$

Finally, pH + pOH = 14.00 so

$$pH = 14.00 - 6.07 = 7.93$$

(iv) At this point, there is excess strong base present. Addition of 1.5 times the equivalence volume corresponds to addition of (1.5 × 25.0) mL = 37.5 mL. This volume of 0.10 M NaOH contains

$$\text{number of moles of NaOH} = \text{concentration} \times \text{volume}$$
$$= (0.10 \text{ mol L}^{-1}) \times (0.0375 \text{ L}) = 0.00375 \text{ mol}$$

From (iii), there was original 0.0025 mol of HF present so the excess of OH^- is:

$$\text{excess moles of } OH^- = (0.00375 - 0.0025) \text{ mol} = 0.00125 \text{ mol}$$

This is present in a total volume of (25.0 + 37.5) mL = 62.5 mL, so its concentration is:

$$[OH^-] = \text{number of moles / volume}$$
$$= (0.00125 \text{ mol}) / (0.0625 \text{ L}) = 0.020 \text{ mol L}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

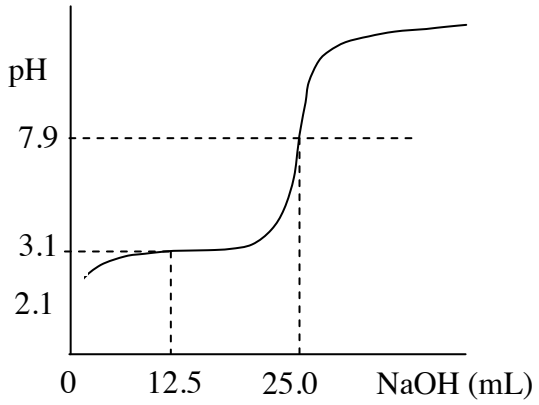
Hence,

pOH -= -log$_{10}$[OH$^-$] = -log$_{10}$(0.020) = 1.70

Lastly, pH = 14.00 – pOH:

pH = 14.00 – 1.70 = 12.30

Putting these 4 points together gives the titration curve:



	Marks
• The ^{14}C specific activity of a tooth found in an archaeological dig is 0.34 Bq. The ^{14}C specific activity in living organisms is 15.3 Bq. How old is the tooth?	4

The ^{14}C age is given by:

$$^{14}\text{C age} = 8033 \ln\frac{A_0}{A_t}$$

Hence,

$$^{14}\text{C age} = 8033 \ln\left(\frac{15.3}{0.34}\right) = 31000 \text{ years}$$

Answer: **31000 years**

Give two reasons why the accuracy of radiocarbon dating is more uncertain for older objects.

The very low activities of very old objects means that errors in measurement are proportionally more significant.

Small amounts of contamination from modern organic material may have a larger proportional effect on the activity of older samples.

• Why are positron emitters the best type of radioisotope to use for tomography?	2

Positrons immediately annihilate when they collide with their antiparticles (electrons) and produce 2 gamma rays that propagate in opposite directions.

These are easily detected and, with the aid of computers, allow determination of the line along which the source must have been.

Statistical repetition allows a 3-dimensional image to be generated.

- Explain the following terms or concepts. **Marks 3**

a) Lipid bilayer

A 2-dimensional self-assembled structure consisting of two layers of lipids with their non-polar (hydrophobic) tails pointing inwards and their polar (hydrophilic) heads at the interface with the solution.

b) Oxidation number

The charge an atom would have if all the electrons involved in covalent bonds were allocated to the more electronegative of the 2 atoms they are shared between.

c) Electrolysis

The process of forcing a non-spontaneous redox reaction to occur by providing sufficient energy in the form of an applied electrical potential.

- How many minutes would be required to obtain 10.0 g of liquid mercury by passing a constant current of 0.17 A through a solution containing $Hg_2(NO_3)_2(aq)$? **2**

The number of moles of Hg in 10.0 g is:

amount of mercury = mass / molar mass = (10.0 g) / (200.59 g mol^{-1})
= 0.0499 mol

The redox reaction is the 2 electron process below:

$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg$

Hence, for each mole of Hg, 1 mol of electrons is required so 0.0499 mol of electrons are required.

The number of moles of electrons passed by a current *I* in a time *t* is given by:

number of moles of electrons = *It* / *F*

The time required to pass 0.0499 mol of electrons using *I* = 0.17 A is therefore:

***t* = (0.0499 mol) × (96485 C mol^{-1}) / (0.17 A) = 28000 s = 470 mins**

Answer: **470 mins**

- Write balanced nuclear equations for the following reactions. **2**

Beta decay of nickel-66.

$^{66}_{28}Ni \rightarrow {}^{66}_{29}Cu + {}^{0}_{-1}e$

Electron capture of selenium-72

$^{72}_{34}Se + {}^{0}_{-1}e \rightarrow {}^{72}_{33}As$ + X-rays

Marks
3

- Calculate $\Delta G°$ for the following reaction:

$$3Cu(s) + Cr^{3+}(aq) \rightleftharpoons 3Cu^{+}(aq) + Cr(s)$$

The two electrode potentials are:

$Cu(s) \rightarrow Cu^{+}(aq) + e^{-}$ $\quad E_{ox}° = -0.53$ V

$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$ $\quad E_{red}° = -0.74$ V

The overall cell potential is therefore:

$$E° = E_{ox}° + E_{red}° = (-0.53\text{ V}) + (-0.74\text{ V}) = -1.27\text{ V}$$

Using $\Delta G° = -nFE°$ for this 3 electron transfer reaction:

$$\Delta G° = -(3 \times 96485\text{ C mol}^{-1}) \times (-1.27\text{ V}) = +368\text{ kJ mol}^{-1}$$

Answer: **+368 kJ mol^{-1}**

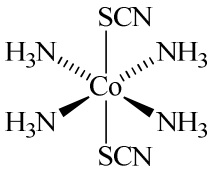
Is the reaction spontaneous under standard conditions? Give a reason for your answer.

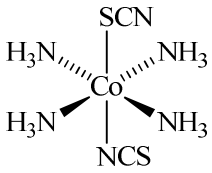
No. $\Delta G° > 0$ and it must be negative for a spontaneous reaction.
Equivalently, $E° < 1$ and it must be positive for a spontaneous reaction.

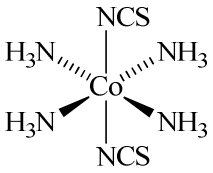
Marks 7

- Write out the full name in standard notation of $[Co(NH_3)_4(SCN)_2]Cl$ and draw all the possible isomers of the complex ion.

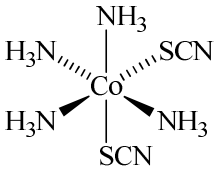
tetraamminedithiocyanatocobalt(III) chloride

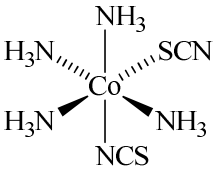


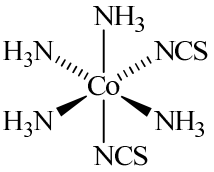




trans-isomers







cis-isomers

2 thiocyanato ligands

1 thiocyanato ligand &
1 isothiocyanato ligand

2 isothiocyanato ligands

Describe and contrast the nature of the chemical bonds:

(a) between N and H in NH_3;
(b) between Co and NH_3; and
(c) between $[Co(NH_3)_4(SCN)_2]$ and Cl in this compound.

N–H bonds are covalent in NH_3. These bonds are relatively short, strong and highly directional. They involve the sharing of electrons from both atoms involved in the bond.

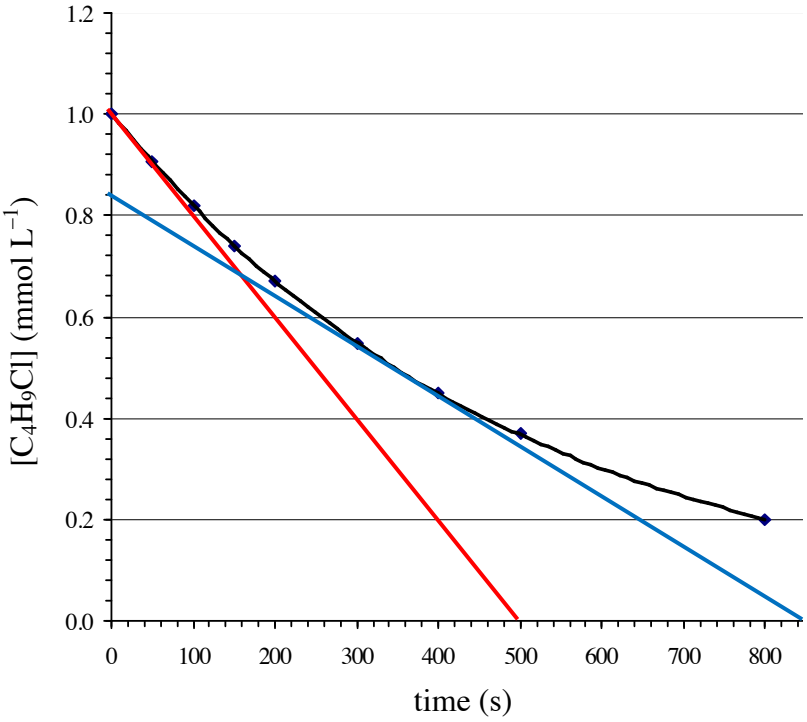
Co–:NH_3 coordination bonds are due to the donation of the lone pair of electrons on N to the Co^{3+}. These bonds are highly polar and are generally weaker, longer and less directional than covalent bonds.

$[Co(NH_3)_4(SCN)_2]^+$ and Cl^- are ionically bonded in the solid state due to Coulombic attraction between the oppositely charged ions. These bonds are strong but not directional (i.e. they occur between every pair of ions in the solid with a strength that decreases with their separation).

Marks 4

- The following chart shows the concentration of butyl chloride, C_4H_9Cl, as a function of time when it reacts with water according to the following equation:

$$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + H^+(aq) + Cl^-(aq)$$



Determine the instantaneous rate of reaction when $[C_4H_9Cl] = 1.0$ mmol L^{-1}.

The rate of the reaction at any point in time is given by:

$$\textbf{rate} = -\frac{\Delta[\mathbf{C_4H_9Cl}]}{\Delta \boldsymbol{t}}$$

The rate when $[C_4H_9Cl] = 1.0$ mmol L^{-1} is given by the gradient of the curve at this point. This is shown by the red line above. Hence,

$$\textbf{rate} \approx -\frac{(0.0-1.0)\ \textbf{mmol L}^{-1}}{(500.-0.)\textbf{s}} = \textbf{0.0020 mmol L}^{-1}\ \textbf{s}^{-1}$$

Answer: **2.0×10^{-3} mmol L^{-1} s^{-1}**

Determine the instantaneous rate of reaction when $[C_4H_9Cl] = 0.5$ mmol L^{-1}.

The rate when $[C_4H_9Cl] = 0.5$ mmol L^{-1} is given by the gradient of the curve at this point. This is shown by the blue line above. Hence,

$$\textbf{rate} \approx -\frac{(0.00-0.84)\ \textbf{mmol L}^{-1}}{(840.\ -0.)\textbf{s}} = \textbf{0.001 mmol L}^{-1}\ \textbf{s}^{-1}$$

Answer: **1.0×10^{-3} mmol L^{-1} s^{-1}**

THIS QUESTION CONTINUES ON THE NEXT PAGE

What is the order of the reaction with respect to C_4H_9Cl? **Marks 4**

From 2010-N-13, the rate of the reaction is:

rate = 2.0×10^{-3} mmol L^{-1} s^{-1} when $[C_4H_9Cl] = 1.0$ mmol L^{-1}

and

rate = 1.0×10^{-3} mmol L^{-1} s^{-1} when $[C_4H_9Cl] = 0.5$ mmol L^{-1}

Halving the concentration, halves the rate so the reaction is first order with respect to C_4H_9Cl.

Answer: **first order**

How long would be required for the concentration of C_4H_9Cl to reach 0.01 mmol L^{-1}?

From 2010-N-13, the time taken for the concentration to halve from its initial value of 1.0 mmol L^{-1} to 0.5 mmol L^{-1} is approximately 350 s. This is shown by the green dotted line on the figure in 2010-N-13.

The half life is ≈ 350 s. Hence, the rate constant is given by:

$$k = \ln(2) / t_{1/2} = \ln(2) / 350 \text{ s} = 0.0020 \text{ s}^{-1}$$

For a first order reaction, the concentration changes with time according to:

$$\ln[C_4H_9Cl] = \ln[C_4H_9Cl]_0 - kt$$

With $k = 0.0020$ s^{-1}, the time taken to reduce the concentration its starting value of $[C_4H_9Cl]_0 = 1.0$ mmol L^{-1} to $[C_4H_9Cl] = 0.01$ mmol L^{-1} can be found using:

$$\ln(0.01) = \ln(1.0) - 0.0020t \quad \text{so } t = 2300 \text{ s}$$

Answer: **2300 s**

- During lectures a demonstration was performed called the "One pot experiment". In this experiment, silver ions reacted with an alternating series of anions and ligands to form insoluble precipitates and soluble complexes. Explain how an insoluble precipitate can possibly be "dissolved" by the addition of ligands to the solution. **2**

The insoluble precipitate is actually in equilibrium with its ions, but the equilibrium lies heavily to the left.

e.g. $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

When a ligand is added, the $Ag^+(aq)$ ions form a complex and are removed from the above equilibrium.

e.g. $Ag^+(aq) + 2CN^-(aq) \rightarrow [Ag(CN)_2]^-(aq)$

Due to Le Chatelier's principle, more AgCl(s) must dissolve to try and re-establish the equilibrium and eventually all the "insoluble" precipitate will dissolve.