Topics in the November 2007 Exam Paper for CHEM1612

Click on the links for resources on each topic.

2007-N-2:

- Introduction to Chemical Energetics

2007-N-3:

- Chemical Equilibrium

2007-N-4:

- Chemical Equilibrium

2007-N-5:

- Solutions

2007-N-6:

- Introduction to Chemical Energetics
- Gas Laws
- Chemical Equilibrium

2007-N-7:

- Chemical Equilibrium

2007-N-8:

- Solubility
- Complexes

2007-N-9:

- Radiochemistry

2007-N-10:

- Redox Reactions and Introduction to Electrochemistry
- Acids and Bases

2007-N-11:

- Solubility
- Redox Reactions and Introduction to Electrochemistry

2007-N-12:

- Complexes
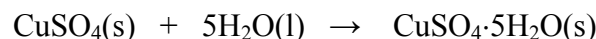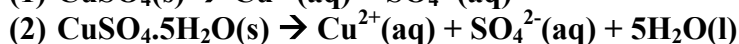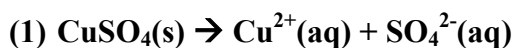- Introduction to Colloids and Surface Chemistry

2007-N-13:

- Chemical Kinetics

- Anhydrous copper(II) sulfate is a white powder that reacts with water to give blue crystals of copper(II) sulfate-5-water.

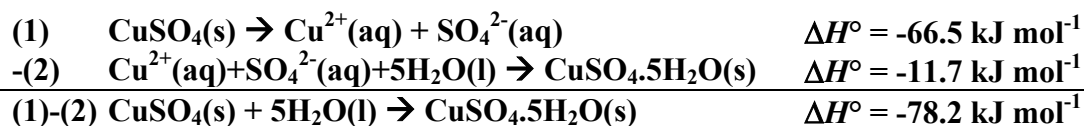$$CuSO_4(s) \ + \ 5H_2O(l) \ \rightarrow \ CuSO_4 \cdot 5H_2O(s)$$

Calculate the standard enthalpy change for this reaction from the heats of solution.

Compound	$\Delta H°_{solution}$ / kJ mol^{-1}
$CuSO_4(s)$	–66.5
$CuSO_4 \cdot 5H_2O(s)$	+11.7

The two reactions in the table correspond to:

(1) $CuSO_4(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$
(2) $CuSO_4.5H_2O(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + 5H_2O(l)$

Taking (1) – (2) gives the required reaction:

(1)	**$CuSO_4(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$**	**$\Delta H° = $ -66.5 kJ mol^{-1}**
-(2)	**$Cu^{2+}(aq)+SO_4^{2-}(aq)+5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$**	**$\Delta H° = $ -11.7 kJ mol^{-1}**
(1)-(2)	**$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$**	**$\Delta H° = $ -78.2 kJ mol^{-1}**

Answer: -78.2 kJ mol^{-1}

- Using the given data, calculate $\Delta H°$ for the reaction: $H(g) \ + \ Br(g) \ \rightarrow \ HBr(g)$ **2**

  Data: $H_2(g) \ \rightarrow \ 2H(g)$ $\Delta H° = +436$ kJ mol^{-1}

              $Br_2(g) \rightarrow \ 2Br(g)$ $\Delta H° = +193$ kJ mol^{-1}

              $H_2(g) \ + \ Br_2(g) \ \rightarrow \ 2HBr(g)$ $\Delta H° = -72$ kJ mol^{-1}
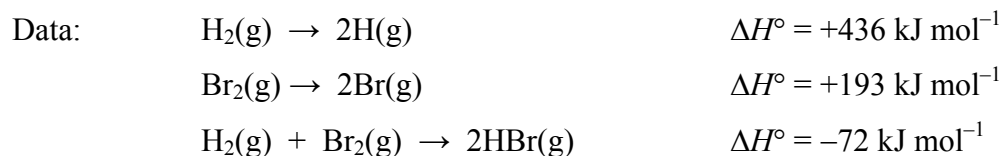
The reaction corresponds to the combination:

$H(g) \rightarrow \frac{1}{2} H_2(g)$	**$\Delta H° = -\frac{1}{2} \times (+436)$ kJ mol^{-1}**
$Br(g) \rightarrow \frac{1}{2} Br_2(g)$	**$\Delta H° = -\frac{1}{2} \times (+193)$ kJ mol^{-1}**
$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightarrow HBr(g)$	**$\Delta H° = +\frac{1}{2} \times (-72)$ kJ mol^{-1}**
$H(g) + Br(g) \rightarrow HBr(g)$	**$\Delta H° = (-218) + (-96.5) + (-36) = -350$ kJ mol^{-1}**
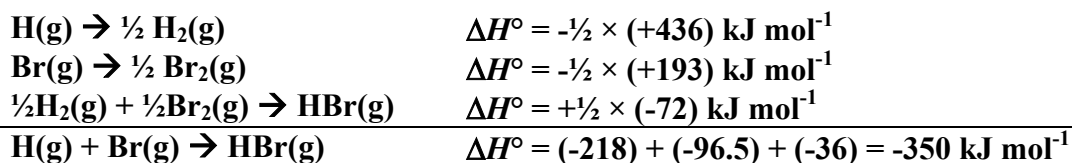
$\Delta H° = $ -350 kJ mol^{-1}

Marks
5

- Consider the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Delta H° = -198.4$ kJ mol^{-1} and $\Delta S° = -187.9$ J K^{-1} mol^{-1} at 25 °C.

Show that this reaction is spontaneous at 25 °C.

Using $\Delta G° = \Delta H° - T\Delta S°$,

  $\Delta G° = (-198.4\times10^3$ J mol^{-1}) $-$ ((25+273) K) $\times$(-187.9 J mol^{-1})
       = -142400 J mol^{-1} = -142.4 kJ mol^{-1}

As $\Delta G° < 0$, the reaction is spontaneous.

If the volume of the reaction system is increased at 25 °C, in which direction will the reaction move?

An increase in volume corresponds to a decrease in pressure. According to Le Chatelier's principle, the reaction will shift to increase the pressure. It does this by favouring the side with a *greater* number of gaseous molecules:

The reaction will shift to the left (3 moles of gas on the left, 2 moles of gas on the right).

Calculate the value of the equilibrium constant, *K*, at 25 °C.

Using $\Delta G° = -RT\ln K$,

  -142.2 $\times 10^3$ J mol^{-1} = -(8.314 J K^{-1} mol^{-1}) $\times$ ((25 + 273) K) $\times$ ln$K$

  $K = 9.170 \times 10^{24}$ (essentially complete conversion to products)

$K = 9.170 \times 10^{24}$ (no units)

Assuming $\Delta H°$ and $\Delta S°$ are independent of temperature, in which temperature range is the reaction non-spontaneous?

The reaction is non-spontaneous when $\Delta G° > 0$, or when $\Delta H° - T\Delta S° > 0$:

  (-198.4 $\times 10^3$ J mol^{-1}) $- T \times$ (-187.9 J mol^1) > 0

 **$T > \dfrac{-198.4 \times 10^3 \text{ J mol}^{-1}}{-187.9 \text{ J mol}^{-1}}$ so $T > 1055$ K**

Note that, as demonstrated above, the reaction is spontaneous at 298 K and, as the reaction is exothermic, it becomes less favourable as the temperature increases (Le Chatelier's principle).
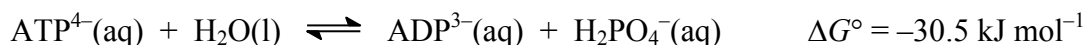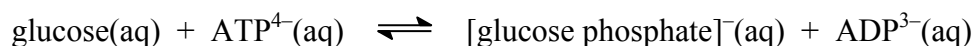
Answer: *T* > 1055 K

- The first step in the metabolism of glucose in biological systems is the addition of a phosphate group in a dehydration-condensation reaction:

$$glucose(aq) + H_2PO_4^-(aq) \rightleftharpoons [glucose\ phosphate]^-(aq) + H_2O(l)$$
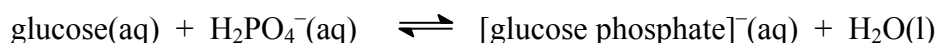
The free energy change associated with this reaction is $\Delta G° = 13.8$ kJ mol^{-1}. The reaction is driven forwards by harnessing the free energy associated with the hydrolysis of adenosine triphosphate, ATP^{4-}, to adenosine diphosphate, ADP^{3-}:

$$ATP^{4-}(aq) + H_2O(l) \rightleftharpoons ADP^{3-}(aq) + H_2PO_4^-(aq) \qquad \Delta G° = -30.5 \text{ kJ mol}^{-1}$$

The overall reaction is thus:

$$glucose(aq) + ATP^{4-}(aq) \rightleftharpoons [glucose\ phosphate]^-(aq) + ADP^{3-}(aq)$$

Calculate the equilibrium constant associated with this overall reaction at body temperature (37 °C).

The overall reaction is the sum of the two reactions:

	$\Delta G°$ (kJ mol^{-1})
glucose(aq) + H$_2$PO$_4^-$(aq) $\rightleftharpoons$ [glucose phosphate]$^-$(aq) + H$_2$O(l)	**13.8**
ATP^{4-}(aq) + H$_2$O(l) $\rightleftharpoons$ ADP^{3-}(aq) + H$_2$PO$_4^-$(aq)	**-30.5**
glucose(aq)+ATP^{4-}(aq) $\rightleftharpoons$ [glucose phosphate]$^-$(aq)+ADP^{3-}(aq)	**-16.7**

For the overall reaction, $\Delta G° = ((13.8) + (-30.5))$ kJ mol^{-1}= -16.7 kJ mol^{-1}. Using $\Delta G° = -RT\ln K$,

$$-16.7 \times 10^3 = -8.314 \times (37 + 273)\ln K \quad \text{or} \quad K = e^{6.48} = 652$$

Answer: $K = 652$ (no units)

This overall equilibrium reaction is investigated by adding 0.0100 mol of ATP^{4-} to a flask containing 175 mL of a 0.0500 M aqueous solution of glucose at 37 °C. What percentage of the ATP^{4-} will have been consumed when the system reaches equilibrium?

The initial concentration of ATP^{4-} is $\dfrac{n}{V} = \dfrac{0.0100\,\text{mol}}{0.175\,\text{L}} = 0.0571$ M. The reaction table is then:

	glucose(aq)	ATP^{4-}(aq)	$\rightleftharpoons$	[glucose phosphate]$^-$(aq)	ADP^{3-}(aq)
initial	**0.0500**	**0.0571**		**0**	**0**
change	**-x**	**-x**		**+x**	**+x**
equilibrium	**0.0500-x**	**0.0571-x**		**x**	**x**

At equilibrium,

$$K = \frac{[glucose\text{-}phosphate^-(aq)][ADP^{3-}(aq)]}{[glucose(aq)][ATP^{4-}(aq)]} = \frac{x^2}{(0.0500 - x)(0.0571 - x)} = 652$$

ANSWER CONTINUES ON THE NEXT PAGE

As the equilibrium constant is large so is x and this expression cannot be approximated. Instead, the full quadratic equation must be solved.

$x^2 = 652(0.0500-x)(0.0571-x)$ or

$651x^2 - 652(0.0500+0.0571) + (652 \times 0.0500 \times 0.0571) = 0$

The two roots are $x_1 = 0.0578$ M and $x_2 = 0.0495$ M. As x_1 gives a negative [glucose(aq)], it is not physically significant. As x is the concentration consumed, using x_2 gives:

percentage of ATP^{4-}(aq) consumed $= \dfrac{0.0495\,M}{0.0571\,M} \times 100\% = 87\%$

Answer: **87%**

Suggest two simple ways of further reducing the remaining percentage of ATP^{4-}.

The remaining ATP^{4-} can be reduced by **(i)** adding more glucose and **(ii)** reducing the temperature. Removal of either product would also drive the reaction to the right but would be very difficult to achieve in practice.

Marks
3

- Lysozyme is an enzyme that breaks down bacterial cell walls. A solution containing 0.150 g of this enzyme in 210 mL of solution has an osmotic pressure of 0.00125 atm at 25 °C. What is the molar mass of lysozyme?

The osmotic pressure, π, is given by $\pi = cRT$

Hence, if $\pi = 0.00125$ atm, the concentration at 25 °C is given by:

$$c = \frac{\pi}{RT} = \frac{0.00125\,\text{atm}}{(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times ((25+273)\,\text{K})} = 5.1 \times 10^{-5}\,\text{M}$$

As $c = \dfrac{n}{V}$, $n = cV = (5.1 \times 10^{-5}\,\text{mol L}^{-1}) \times (0.210\,\text{L}) = 1.1 \times 10^{-5}\,\text{mol}$

This amount corresponds to 0.150 g, so the molar mass, M, is:

$$M = \frac{m}{M} = \frac{0.150\,\text{g}}{1.1 \times 10^{-5}\,\text{mol}} = 1.40 \times 10^{4}\,\text{g mol}^{-1}$$

Answer: **1.40×10^{4} g mol^{-1}**

- What mass of ethylene glycol, $HOCH_2CH_2OH$, is required to lower the freezing point of 1.00 L of water to -10.0 °C? The freezing point depression constant of water is 1.86 °C kg mol^{-1}. Assume the density of water is 1.00 g mL^{-1} at 0 °C.

3

The freezing point depression, ΔT_f, is related to the molality, m, and the freezing point depression constant, K_f, by $\Delta T_f = K_f m$

Hence, $m = \dfrac{\Delta T_f}{K_f} = \dfrac{10.0\ ^\circ\text{C}}{1.86\ ^\circ\text{C kg mol}^{-1}} = 5.38\,\text{mol kg}^{-1}$

If the density of water is 1.00 g mL^{-1}, 1000 mL will have a mass of 1.00 kg.

As the molality is given $m = \dfrac{\text{amount of solute (mol)}}{\text{mass of solvent (kg)}}$, the amount of solute is:

amount of solute (mol) = molality (mol kg^{-1}) × mass of solvent (kg)
= 5.38 × 1.00 mol = 5.38 mol

The molar mass of $HOCH_2CH_2OH$ ($C_2H_6O_2$) is (2 × 12.01 (C)) + (6 × 1.008 (H)) + (2 × 16.00 (O)) = 62.068 g mol^{-1}. The mass of 5.38 mol is therefore:

mass (g) = molar mass (g mol^{-1}) × amount (mol) = 62.068 × 5.38 g = 334 g

Answer: **334 g**

Marks
3

- Acetylene, C_2H_2, is an important fuel in welding. It is produced in the laboratory when calcium carbide, CaC_2, reacts with water:

$$CaC_2(s) + 2H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(s)$$
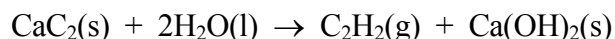
For a sample of C_2H_2 collected over water, the total gas pressure was 748 mmHg and the volume was 543 mL. At the gas temperature (23 °C), the vapour pressure of water is 21 mmHg. What mass of acetylene was collected?

The total pressure is the sum of the partial pressures due to $C_2H_2(g)$ and $H_2O(g)$:

$$p_{total} = 748 \text{ mmHg} = p_{H_2O} + p_{C_2H_2} = (21 \text{ mmHg}) + p_{C_2H_2}$$

$$p_{C_2H_2} = (748 - 21) = 727 \text{ mmHg}$$

As 760 mmHg corresponds to 1 atm, $p_{C_2H_2} = \dfrac{727}{760}$ atm = 0.957 atm. Using the ideal gas law, $pV = nRT$, the number of moles of C_2H_2 formed is:

$$n = \frac{pV}{RT} = \frac{(0.957\,\text{atm}) \times (0.543\,\text{L})}{(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times ((23 + 273)\,\text{K})} = 0.0214 \text{ mol}$$

The molar mass of C_2H_2 is (2 × 12.01 (C)) + (2 × 1.008 (H)) = 26.036 g mol⁻¹. This amount therefore corresponds to a mass of,

mass = number of moles × molar mass = 0.0214 mol × 26.036 g mol⁻¹
= 0.557 g

Answer: **0.557 g**

The solubility of acetylene in water at 22.0 °C is small. If the temperature were raised, would you expect this solubility to increase or decrease?

The solubility of gases in water decreases with temperature. The dissolution of a gas is entropically disfavoured and only occurs because it is exothermic. Like all exothermic process, the process becomes less favourable at higher temperatures (Le Chatelier's principle).

- Why is helium instead of nitrogen mixed with oxygen in deep sea diving? Explain the origin of any differences in relevant properties.

2

Increased pressure in lungs during deep sea diving causes an increased solubility of all gases in the blood. On ascending too quickly, these gases can bubble out of the blood. This is a serious problem with nitrogen as the bubbles can rupture blood vessels causing "the bends". The He atom is much smaller than the N_2 molecule, has a smaller electron cloud and is less polarisable. It therefore is less soluble in blood than nitrogen and is preferred as the above dangers are reduced.

**Marks
6**

- The isomerisation of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P) is a key step in the metabolism of glucose for energy.

$$G6P \; \rightleftharpoons \; F6P$$
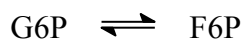
At 298 K, the equilibrium constant for the isomerisation is 0.510. Calculate the value of $\Delta G°$ at 298 K.

**$\Delta G° = -RT\ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.510)$
     $= +1670 \text{ J mol}^{-1} = +1.67 \text{ kJ mol}^{-1}$**

Answer: **+1.67 kJ mol⁻¹**

Calculate ΔG at 298 K when the [F6P] / [G6P] ratio = 10.

The reaction quotient, for the reaction, is $Q = \dfrac{[\text{F6P}]}{[\text{G6P}]} = 10$

Using $\Delta G = \Delta G° + RT\ln Q$,

**$\Delta G = (+1.67 \times 10^3 \text{ J mol}^{-1}) + (8.314 \times 298 \text{ J mol}^{-1}) \times \ln(10)$
     $= +7400 \text{ J mol}^{-1} = +7.4 \text{ kJ mol}^{-1}$**

Answer: **+7.4 kJ mol⁻¹**

In which direction will the reaction shift in order to establish equilibrium? Why?

As ΔG is positive, the forward reaction is non-spontaneous and the backward reaction is spontaneous. The reaction thus shift backwards, increasing [G6P] and reducing [F6P] until $Q = K$.

Sketch a graph of G_{sys} *versus* "extent of reaction", with a curve showing how G_{sys} varies as G6P is converted to F6P. Indicate the position on this curve corresponding to the point where [F6P] / [G6P] ratio = 10. Indicate on the graph that section of the curve where $Q > K$.
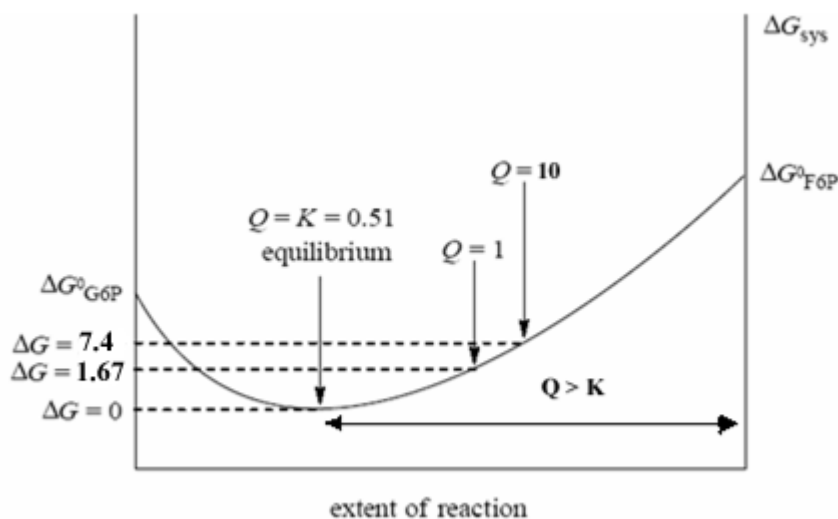
	Marks
• What is the molar solubility of $Cu(OH)_2$ at 25 °C given its $K_{sp} = 4.5 \times 10^{-21}$ M^3?	2

The solubility expression and product for Cu(OH)₂(s) are:

$$Cu(OH)_2 \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Cu^{2+}(aq)][OH^-(aq)]^2$$
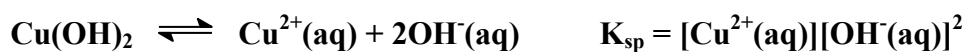
If the molar solubility is S, $[Cu^{2+}(aq)] = S$ and $[OH^-(aq)] = 2S$. Hence,

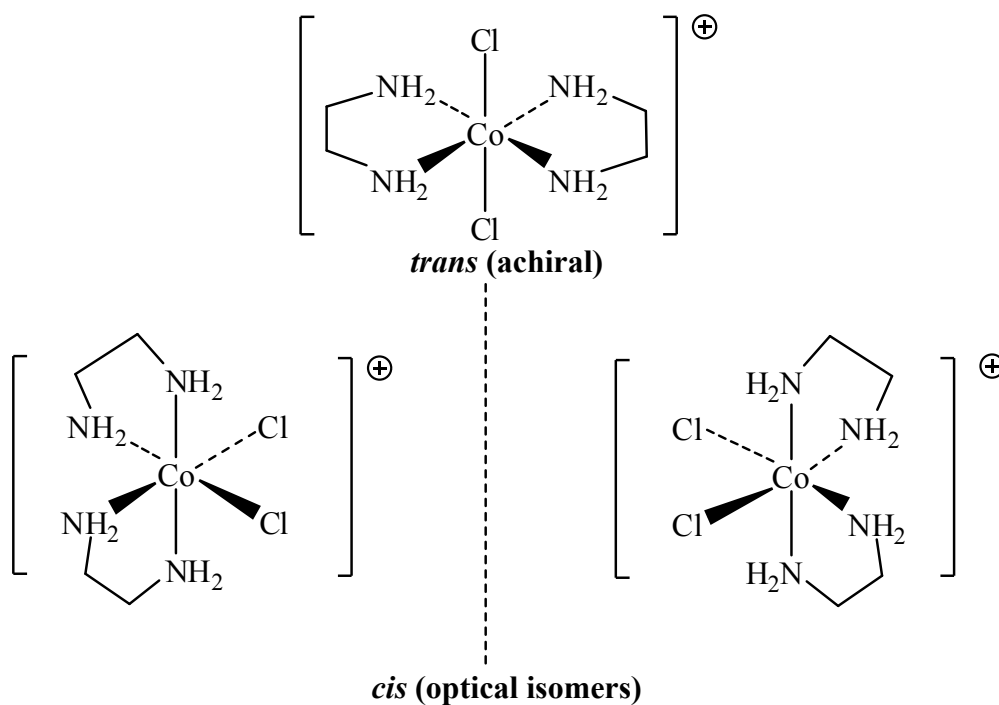$$K_{sp} = (S) \times (2S)^2 = 4S^3 = 4.5 \times 10^{-21}$$

$$S = 1.0 \times 10^{-7} \text{ M}$$

Answer: **1.0×10^{-7} M**
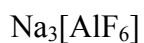
	Marks
• Draw all possible stereoisomers of the complex ion $[CoCl_2(en)_2]^+$. Label each as *cis* or *trans*. en = ethylenediamine = $NH_2CH_2CH_2NH_2$	3

trans (achiral)

cis (optical isomers)

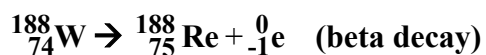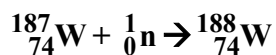|	Marks
• Name the following complexes.	2

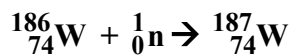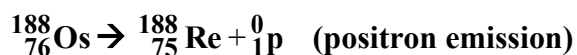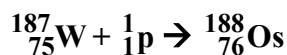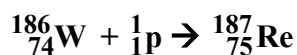| $Na_3[AlF_6]$	**sodium hexafluoroaluminate(III)**
$[CoBr(NH_3)_5]SO_4$	**pentaamminebromocobalt(III) sulfate**

**Marks
7**

- A cyclotron facility can produce beams of neutrons or protons. Theoretically, $^{188}_{75}\text{Re}$ can be produced by irradiation of $^{186}_{74}\text{W}$ with either particle followed by radioactive decay of the intermediate nuclide. Give the relevant equations to describe both sequences of reactions.

neutron bombardment

$$^{186}_{74}\text{W} + {}^{1}_{0}\text{n} \rightarrow {}^{187}_{74}\text{W}$$

$$^{187}_{74}\text{W} + {}^{1}_{0}\text{n} \rightarrow {}^{188}_{74}\text{W}$$

$$^{188}_{74}\text{W} \rightarrow {}^{188}_{75}\text{Re} + {}^{0}_{-1}\text{e} \quad \textbf{(beta decay)}$$

proton bombardment

$$^{186}_{74}\text{W} + {}^{1}_{1}\text{p} \rightarrow {}^{187}_{75}\text{Re}$$

$$^{187}_{75}\text{W} + {}^{1}_{1}\text{p} \rightarrow {}^{188}_{76}\text{Os}$$

$$^{188}_{76}\text{Os} \rightarrow {}^{188}_{75}\text{Re} + {}^{0}_{1}\text{p} \quad \textbf{(positron emission)}$$

In practice, only the sequence using neutron bombardment is used. Give one possible reason why proton bombardment is not used.

Energy required to add positively charged protons to nucleus is large.

Intermediate in proton bombardment ($^{188}_{76}\text{Os}$) is stable.

THE ANSWER CONTINUES ON THE NEXT PAGE

Rhenium-188 is used for the relief of cancer-induced bone pain and has a half life of 16.7 hours. What mass of $^{188}_{75}\text{Re}$ needs to be produced to allow shipment 24 hours later of a solution with a specific activity of 500 mCi?

The decay constant is related to the half life as $t_{1/2} = \dfrac{\ln 2}{\lambda}$. Thus,

$$\lambda = \frac{\ln 2}{(16.7 \times 60 \times 60\,\text{s})} = 1.15 \times 10^{-5}\,\text{s}^{-1}$$

As $A = \lambda N$, the activity of one mole is,

$$A_m = (1.15 \times 10^{-5}) \times (6.022 \times 10^{23})$$
$$= 6.94 \times 10^{18}\,\text{Bq mol}^{-1} = \frac{6.94 \times 10^{18}}{3.70 \times 10^{10}} = 1.88 \times 10^{8}\,\text{Ci mol}^{-1}$$

For ^{188}Re, the atomic mass = 188 and hence the activity per gram is,

$$A_g = \frac{1.88 \times 10^{8}}{188} = 1.00 \times 10^{6}\,\text{Ci g}^{-1}$$

As the number of nuclei is proportional to the activity, the activity decreases with time according to the equation,

$$\ln\left(\frac{A_0}{A_t}\right) = \lambda t$$

Hence, if A = 500 mCi after 24 hours,

$$\ln\left(\frac{A_0}{500 \times 10^{-3}}\right) = (1.15 \times 10^{-5}) \times (24 \times 60 \times 60)$$

$$A_0 = 1.35\,\text{Ci}$$

Hence,

$$\text{mass required} = \frac{\text{activity required}}{\text{activity per gram}} = \frac{A_0}{A_g} = \frac{1.35}{1.00 \times 10^{6}}$$
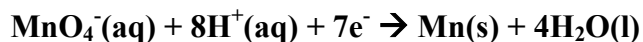$$= 1.35 \times 10^{-6}\,\text{g} = 1.35\,\mu\text{g}$$

Answer: **1.35 μg**

- How many minutes would be required to electroplate 25.0 g of manganese by passing a constant current of 4.8 A through a solution containing MnO_4^-?

**Marks
2**

25.0 g of manganese corresponds to

$$\text{number of moles} = \frac{\text{mass}}{\text{atomic mass}} = \frac{25.0\,\text{g}}{54.94\,\text{g}\,\text{mol}^{-1}} = 0.455\,\text{mol}$$

The reduction of MnO_4^- is a 7e$^-$ process:

$$MnO_4^-(aq) + 8H^+(aq) + 7e^- \rightarrow Mn(s) + 4H_2O(l)$$

Production of 0.455 mol of Mn(s) requires (7 × 0.455) = 3.19 mol of electrons.

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

$$\text{number of moles of electrons} = \frac{I \times t}{F}$$

$$3.19\,\text{mol} = \frac{(4.8\,\text{A}) \times t}{96485\,\text{C}\,\text{mol}^{-1}} \quad \text{so } t = 64000\,\text{s} = 1100\,\text{minutes}$$

Answer: **1100 minutes**

THE ANSWER CONTINUES ON THE NEXT PAGE

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the pK_a of iodic acid, HIO$_3$, is 0.79, how many moles of sodium iodate, NaIO$_3$, would need to be added to this solution to raise its pH to 2.00?

3

As pH = -log$_{10}$([H$_3$O$^+$(aq)],

  [H$_3$O$^+$(aq)]$_{initial}$ = 10$^{-1.22}$ = 0.0600 and [H$_3$O$^+$(aq)]$_{final}$ = 10$^{-2.00}$ = 0.0100

The reaction table is:

	IO$_3^-$(aq)	H$_3$O$^+$(aq)	⇌	HIO$_3$	H$_2$O
initial	x	0.0600		0	large
final	x − 0.0500	0.0100		0.0500	large

The solution contains a weak acid (HIO$_3$ and its conjugate base (IO$_3^-$). It is a buffer and can be treated using the Henderson-Hasselbalch equation,

$$pH = pK_a + \log_{10}\left(\frac{[base]}{[acid]}\right)$$

$$2.00 = 0.79 + \log_{10}\left(\frac{(x - 0.0500)}{0.0500}\right)$$

x = 0.865 M

This concentration is present in 300.0 mL of solution so the number of moles of IO$_3^-$ which has been added is,

  number of moles = concentration × volume = 0.865 × 0.3000 = 0.260 mol

Answer: **0.260 mol**

Marks
6

- The solubility product constant of AgCl is $K_{sp} = 1.8 \times 10^{-10}$ M². Using the relevant electrode potentials found on the data page, calculate the reduction potential at 298 K of a half-cell formed by:

(a) an Ag electrode immersed in a saturated solution of AgCl.

The standard electrode potential for $Ag^+(aq) + e^- \rightarrow Ag(s)$ is $E° = +0.80$ V. This refers to the potential with $[Ag^+(aq)] = 1$ M.

For the dissolution of $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, $K_{sp} = [Ag^+(aq)][Cl^-(aq)]$. As $[Ag^+(aq)] = [Cl^-(aq)]$,

$$[Ag^+(aq)] = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

Using the Nernst equation, the cell potential at 298 K (25 °C) is,

$$E = E° - \frac{0.0592}{n} \log Q$$

The $Ag^+(aq) + e^- \rightarrow Ag(s)$ half cell involves one electron and so $n = 1$. The reaction quotient is $\dfrac{1}{[Ag^+(aq)]}$. Hence,

$$E = (+0.80) - \frac{0.0592}{1} \log\left(\frac{1}{1.3 \times 10^{-5}}\right) = +0.52 \text{ V}$$

Answer: $E = +0.52$ V

(b) an Ag electrode immersed in a 0.5 M solution of KCl containing some AgCl precipitate.

$[Cl^-(aq)] = 0.5$ M and as $K_{sp} = [Ag^+(aq)][Cl^-(aq)]$,

$$[Ag^+(aq)] = \frac{K_{sp}}{[Cl^-(aq)]} = \frac{1.8 \times 10^{-10} \text{ M}^2}{0.5 \text{ M}} = 3.6 \times 10^{-10} \text{ M}$$

The electrode potential is now,

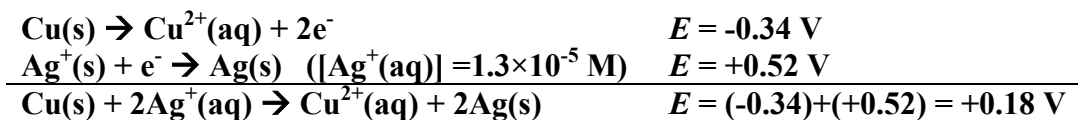$$E = (+0.80) - \frac{0.0592}{1} \log\left(\frac{1}{3.6 \times 10^{-10}}\right) = +0.24 \text{ V}$$

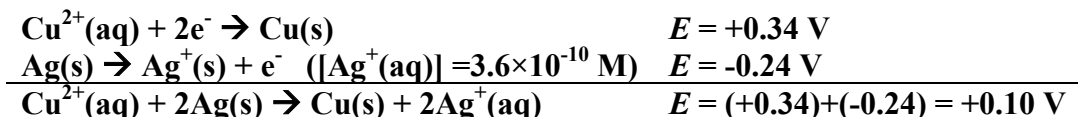Answer: $E° = +0.24$ V

ANSWER CONTINUES ON THE NEXT PAGE

Each of these half-cells is connected to a standard Cu^{2+}(1 M)/Cu(s) half-cell. In which half-cell, (a) or (b), will clear evidence of a reaction be seen? Describe the change(s) observed.

For the Cu^{2+} (1 M)/Cu(s) half cell, the reduction potential is $E° = +0.34$ V.

If the half cell is combined with half cell (a), the former has the least positive cell potential and is reversed:

|	
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	$E = -0.34$ V
$Ag^+(s) + e^- \rightarrow Ag(s)$ ([$Ag^+(aq)$] $=1.3×10^{-5}$ M)	$E = +0.52$ V
$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$	$E = (-0.34)+(+0.52) = +0.18$ V

If the half cell is combined with half cell (b), the latter has the least positive cell potential and is reversed:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E = +0.34$ V
$Ag(s) \rightarrow Ag^+(s) + e^-$ ([$Ag^+(aq)$] $=3.6×10^{-10}$ M)	$E = -0.24$ V
$Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$	$E = (+0.34)+(-0.24) = +0.10$ V

Although both reactions have $E > 0$ V and so are spontaneous, only the second reaction will give clear evidence of a reaction. The $Ag^+(aq)$ ions produced will react with the excess $Cl^-(aq)$ present to give a white precipitate of AgCl around the electrode

**Marks
3**

- Zinc sulfate (0.50 g) is dissolved in 1.0 L of a 1.0 M solution of KCN. Write the chemical equation for the formation of the complex ion $[Zn(CN)_4]^{2-}$.

$$Zn^{2+}(aq) + 4CN^-(aq) \;\rightleftharpoons\; [Zn(CN)_4]^{2-}(aq)$$
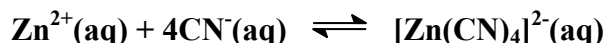
Calculate the concentration of Zn^{2+}(aq) in solution at equilibrium. Ignore any change in volume upon addition of the salt. K_{stab} of $[Zn(CN)_4]^{2-} = 4.2 \times 10^{19}$ M^{-4}.

The formula mass of $ZnSO_4$ is 65.39 (Zn) + 32.07 (S) + 4 × 16.00 (O) = 161.46.

0.50 g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{0.50\,\text{g}}{161.46\,\text{g mol}^{-1}} = 0.0031 \text{ mol}$$

As $K_{stab} = 4.2 \times 10^{19}$ and is *very* large, the reaction essentially goes to completion. The reaction requires a 4:1 ratio $CN^- : Zn^{2+}$(aq) ions and as 0.0031 mol of Zn^{2+} and 1.0 mol of CN^- are present, CN^- is in excess.

Let the tiny amount of uncomplexed Zn^{2+}(aq) and its concentration in 1.0 L be:

$$\text{amount of } Zn^{2+}(aq) = x \text{ mol and } [Zn^{2+}(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{x}{1.0} \text{ M}$$

The amount of $[Zn(CN)_4]^{2+}$(aq) formed is therefore:

$$\text{amount of } [Zn(CN)_4]^{2-}(aq) = (0.0031 - x) \sim 0.0031 \text{ mol as } x \text{ is so small.}$$

Hence,

$$[[Zn(CN)_4]^{2-+}(aq)] \sim \frac{0.0031}{1.0} = 0.0031 \text{ M}$$

Formation of 0.0031 mol of $[Zn(CN)_4]^{2-}$(aq) requires (4 × 0.0031) = 0.012 mol of cyanide, leaving:

$$\text{amount of } CN^- = (1.0 - 0.012) = 0.99 \text{ mol and } [CN^-(aq)] = \frac{0.99}{1.0} \text{ M}$$

Hence,

$$K_{stab} = \frac{[[Zn(CN)_4]^{2-}(aq)]}{[Zn^{2+}(aq)][CN^-(aq)]^4} = \frac{(0.0031)}{(x)(0.99)^4} = 4.2 \times 10^{19}$$

$$x = 7.7 \times 10^{-23} \text{ mol and so } [Zn^{2+}(aq)] = 7.7 \times 10^{-23} \text{ M}$$

Answer: **7.8×10^{-23}**

THE ANSWER CONTINUES ON THE NEXT PAGE

- Describe how the addition of an electrolyte can alter the state of a colloidal dispersion.

2

If the colloidal particle has a charge, a layer of oppositely charged ions will form on the surface (the Stern layer). In the region around the outside of the colloid, there is therefore a build-up of counter ions creating a double charge layer. The charge surrounding one colloid will repel the charge surrounding other particles and so coagulation is prevented.

Addition of an electrolyte leads to reduction in the net charge surrounding each colloid and prevents this electrostatic stabilization. As a result, the colloid particles tend to coagulate and the colloidal dispersion is lost.

Marks
5

- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$
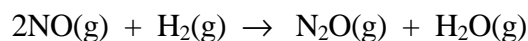
The following rate data were collected at 225 ^{o}C.

Experiment	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial rate ($d[NO]/dt$, M s^{-1})
1	6.4×10^{-3}	2.2×10^{-3}	2.6×10^{-5}
2	1.3×10^{-2}	2.2×10^{-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. Doubling $[NO]_0$ leads to the rate increasing by a factor of four. The rate is second-order with respect to NO.

Between experiments 1 and 3, $[NO]_0$ is constant. Doubling $[H_2]_0$ leads to the rate doubling. The rate is second-order with respect to H_2.

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

Calculate the value of the rate constant at 225 ^{o}C.

Using experiment 1, the rate is 2.6×10^{-5} M s^{-1} when $[NO]_0 = 6.4 \times 10^{-3}$ M and $[H_2]_0 = 2.2 \times 10^{-3}$. Hence,

2.6×10^{-5} M s^{-1} = $k(6.4 \times 10^{-3}$ M$)^2 \times (2.2 \times 10^{-3}$ M)
k = 290 M^{-2} s^{-1}

The units of k are found by requiring that the units in the rate law balance:

-d[NO]/dt = $k[NO]^2[H_2]$
M s^{-1} = (units of k) $\times$ (M)$^2 \times$ (M)
units of k = M^{-2} s^{-1}

Answer: **290 M^{-2} s^{-1}**

THE ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of N_2O when $[NO] = [H_2] = 6.6 \times 10^{-3}$ M.
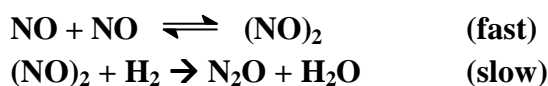
As $-d[NO]/dt = 290[NO]^2[H_2]$,

$-d[NO]/dt = (290 \text{ M}^{-2} \text{ s}^{-1}) \times (6.6 \times 10^{-3} \text{ M})^2 \times (6.6 \times 10^{-3} \text{ M}) = 8.3 \times 10^{-5} \text{ M s}^{-1}$

From the chemical equation, two NO are lost for every one N_2O that is made. Hence the rate of appearance of N_2O is half this value:

$-d[NO]/dt = \frac{1}{2} \times 8.3 \times 10^{-5} \text{ M s}^{-1} = 4.1 \times 10^{-5} \text{ M s}^{-1}$

Answer: **4.1×10^{-5} M s^{-1}**

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

$NO + NO \rightleftharpoons (NO)_2$ (fast)
$(NO)_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

The second step is rate determining as it is slow. For this elementary step, the rate law can be written down using the stoichiometry of the reaction equation:

$rate = k_2[(NO)_2][H_2]$

If the equilibrium in the first step is rapidly obtained then,

$K_{eq} = \dfrac{[(NO)_2]}{[NO]^2}$ or $[(NO)_2] = K_{eq}[NO]^2$

Substituting this back into the rate law for the rate determining step gives,

$rate = k_2[(NO)_2][H_2] = k_2 \times K_{eq}[NO]^2 \times [H_2] = k_{eff}[NO]^2[H_2]$

This rate law is consistent with the one determined experimentally and so the proposed mechanism is consistent.