

**Topics in the November 2014 Exam Paper for CHEM1612**

Click on the links for resources on each topic.

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- [Complexes](#)
- [Chemical Equilibrium](#)
- [Chemical Kinetics](#)
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2014-N-13:

- [Redox Reactions and Introduction to Electrochemistry](#)

2014-N-14:

- Chemical Kinetics

<ul style="list-style-type: none"> <li>Explain the following terms or concepts.</li> </ul>	<b>Marks</b> <b>3</b>
<p>Lewis base</p> <p><b>A species that can form a bond by donating a lone pair of electrons, <i>e.g.</i> H<sub>2</sub>O.</b></p>	
<p>Le Châtelier's principle</p> <p><b>Used to predict the effect of a change in the conditions on a reaction at equilibrium, this principle predicts that a reaction shifts to counteract the change.</b></p>	
<p>Heterogeneous catalysis</p> <p><b>Catalysis that occurs with the reactants and catalyst are in different phases, such as a solid catalysing the reaction of gases.</b></p>	
<ul style="list-style-type: none"> <li>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 reached equilibrium? The specific heat capacities of water and iron are 4.184 J g<sup>-1</sup> K<sup>-1</sup> and 0.4498 J g<sup>-1</sup> K<sup>-1</sup>, respectively.</li> </ul>	<b>3</b>
<p><b>The heat lost by the iron is equal to the heat gained by the water.</b></p> <p><b>The heat change is related to the temperature change through <math>q = mC\Delta T</math> where <math>m</math> is the mass of the substance and <math>C</math> is its specific heat capacity.</b></p> <p><b>For the water,</b></p> $q = m_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} \Delta T_{\text{H}_2\text{O}} = (2.000 \times 10^3 \text{ g}) \times (4.184 \text{ J g}^{-1} \text{ K}^{-1}) \times ((T_f - 25.00) \text{ K})$ $= (8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 25.00) \text{ K})$ <p><b>For the iron,</b></p> $q = m_{\text{Fe}} C_{\text{Fe}} \Delta T_{\text{Fe}} = (1.000 \times 10^3 \text{ g}) \times (0.4498 \text{ J g}^{-1} \text{ K}^{-1}) \times ((T_f - 100.00) \text{ K})$ $= (0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 100.00) \text{ K})$ <p><b>Hence, as <math>q_{\text{water}} = -q_{\text{iron}}</math>:</b></p> $(8.368 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 25.00) \text{ K}) = -(0.4498 \times 10^3 \text{ J K}^{-1}) \times ((T_f - 100.00) \text{ K})$ $T_f = 28.83 \text{ °C}$	
<p>Answer: <b>28.83 °C</b></p>	

- A mass of 1.250 g of benzoic acid,  $C_7H_6O_2$ , underwent combustion in a bomb calorimeter. The heat of combustion of benzoic acid is  $-3226 \text{ kJ mol}^{-1}$ . What is the change in internal energy during this reaction?

**Marks**  
**4**

The molar mass of benzoic acid is:

$$\text{molar mass} = (7 \times 12.01 \text{ (C)}) + 6 \times 1.008 \text{ (H)} + 2 \times 16.00 \text{ (O)} \text{ g mol}^{-1} \\ = 122.12 \text{ g mol}^{-1}$$

The number of moles of benzoic acid in 1.250 g is therefore:

$$\text{number of moles} = \text{mass} / \text{molar mass} = 1.250 \text{ g} / 122.12 \text{ g mol}^{-1} \\ = 0.01024 \text{ mol}$$

As combustion of 1 mol leads to a heat change of  $-3226 \text{ kJ}$ , this quantity will generate an energy change of:

$$q = (0.01024 \text{ mol}) \times (-3226 \text{ kJ mol}^{-1}) = -33.02 \text{ kJ}$$

Answer: **-33.02 kJ**

If the heat capacity of the calorimeter is  $10.134 \text{ kJ K}^{-1}$ , calculate the temperature change that should have occurred in the apparatus.

The heat change,  $q$ , and temperature change,  $\Delta T$ , are related by the heat capacity,  $C$ :

$$q = C\Delta T$$

or

$$\Delta T = q / C = 33.02 \text{ kJ} / 10.134 \text{ kJ K}^{-1} = 3.258 \text{ K}$$

An exothermic reaction will lead to a temperature increase in the apparatus.

Answer: **+3.258 K**

- Phenylketonuria is an inherited disorder in which phenylacetic acid,  $C_6H_5CH_2COOH$ , (simplified here to HPAC) accumulates in the blood. A study of the acid shows that the pH of a 0.12 M HPAC solution is 2.60. What is the  $pK_a$  of phenylacetic acid?

**3**

As HPAC is a weak acid, the equilibrium for its dissociation can be studied using an 'ICE' table:

	HPAC	$\rightleftharpoons$	PAc <sup>-</sup>	H <sup>+</sup>
<b>initial</b>	<b>0.12</b>		<b>0</b>	<b>0</b>
<b>change</b>	<b>-x</b>		<b>+x</b>	<b>+x</b>
<b>final</b>	<b>0.12 - x</b>		<b>x</b>	<b>x</b>

**ANSWER CONTINUES ON THE NEXT PAGE**

By definition,  $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$  so  $[\text{H}^+(\text{aq})] = 10^{-2.60} \text{ M}$ . From the reaction table,  $x = [\text{H}^+(\text{aq})]_{\text{eq}}$  so:

$$[\text{HPAc}]_{\text{eq}} = 0.12 - x = (0.12 - 10^{-2.60}) \text{ M} = 0.12 \text{ M (to 2 s.f.)}$$

$$[\text{H}^+(\text{aq})]_{\text{eq}} = x = 10^{-2.60} \text{ M}$$

$$[\text{PAc}^-(\text{aq})]_{\text{eq}} = x = 10^{-2.60} \text{ M}$$

The equilibrium constant  $K_{\text{a}}$  is given by:

$$K_{\text{a}} = \frac{[\text{HPac}^-][\text{H}^+]}{[\text{HPAc}]} = \frac{(10^{-2.60})(10^{-2.60})}{(0.12)} = 5.26 \times 10^{-5}$$

By definition,  $\text{p}K_{\text{a}} = -\log_{10}K_{\text{a}}$  so:

$$\text{p}K_{\text{a}} = -\log_{10}(5.26 \times 10^{-5}) = 4.28$$

Answer: **4.28**

- The freezing point of a sample of seawater is measured as  $-2.15\text{ }^{\circ}\text{C}$  at 1 atm pressure. Assuming that the concentrations of other solutes are negligible, determine the molality (in  $\text{mol kg}^{-1}$ ) of NaCl in this sample. The molal freezing point depression constant for  $\text{H}_2\text{O}$  is  $1.86\text{ }^{\circ}\text{C kg mol}^{-1}$ .

**Marks**  
**3**

The freezing point depression,  $\Delta T_f$ , is given by,

$$\Delta T_f = K_f m$$

where  $K_f$  is the molal freezing point depression and  $m$  is the molality. The molality is the number of moles of ions dissolved in a kilogram of solvent.

If  $\Delta T_f = 2.15\text{ }^{\circ}\text{C}$  and  $K_f = 1.86\text{ }^{\circ}\text{C m}^{-1}$ :

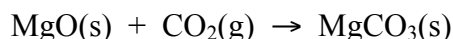
$$m_{\text{ions}} = \Delta T_f / K_f = (2.15\text{ }^{\circ}\text{C}) / (1.86\text{ }^{\circ}\text{C m}^{-1}) = 1.156\text{ m}^{-1} = 1.156\text{ mol kg}^{-1}$$

A mole of NaCl dissolves to give two particles ( $\text{Na}^+$  and  $\text{Cl}^-$ ) so  $(1.156 / 2)\text{ mol} = 0.578\text{ mol}$  of NaCl per kilogram of water is needed:

$$m_{\text{NaCl}} = 0.578\text{ mol kg}^{-1}$$

Answer: **0.578 mol kg<sup>-1</sup>**

- What is the value of the enthalpy change for the following reaction?



Data:	Compound	MgO(s)	CO <sub>2</sub> (g)	MgCO <sub>3</sub> (s)
	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-602	-394	-1096

Using  $\Delta H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$ , the enthalpy change is:

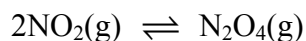
$$\begin{aligned} \Delta H^\circ &= \Delta_f H^\circ (\text{MgCO}_3(\text{s})) - [\Delta_f H^\circ (\text{MgO}(\text{s})) + \Delta_f H^\circ (\text{CO}_2(\text{g}))] \\ &= (-1096 - [-394 - 602])\text{ kJ mol}^{-1} = -100.\text{ kJ mol}^{-1} \end{aligned}$$

Answer: **-100. kJ mol<sup>-1</sup>**

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**1**

- Consider the following reaction and associated thermochemical data?



Data:	Compound	$\text{NO}_2(\text{g})$	$\text{N}_2\text{O}_4(\text{g})$
	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	33	9
	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	240	304

What is the expression for the equilibrium constant,  $K_c$ , for this reaction?

$$K_c = \frac{[\text{N}_2\text{O}_4(\text{g})]}{[\text{NO}_2(\text{g})]^2}$$

What are the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction?

Using  $\Delta H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$ , the enthalpy change is:

$$\begin{aligned} \Delta H^\circ &= 2\Delta_f H^\circ (\text{products}) - \Delta_f H^\circ (\text{reactants}) \\ &= (9 - 2 \times 33) \text{ kJ mol}^{-1} = -57 \text{ kJ mol}^{-1} \end{aligned}$$

Using  $\Delta S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$ , the entropy change is:

$$\begin{aligned} \Delta S^\circ &= 2S^\circ (\text{products}) - S^\circ (\text{reactants}) \\ &= (304 - 2 \times 240) \text{ J K}^{-1} \text{mol}^{-1} = -176 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

$$\Delta H^\circ = -57 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -176 \text{ J K}^{-1} \text{mol}^{-1}$$

What is the value of  $\Delta G^\circ$  for the reaction at 298 K?

Using  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ :

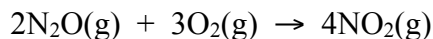
$$\begin{aligned} \Delta G^\circ &= (-57 \times 10^3 \text{ J mol}^{-1}) - (298 \text{ K})(-176 \text{ J K}^{-1} \text{mol}^{-1}) \\ &= -5000 \text{ J mol}^{-1} = -5 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta G^\circ = -5 \text{ kJ mol}^{-1}$$

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**Marks**  
**3**

- Consider the following reaction:



Calculate  $\Delta G^\circ$  for this reaction given the following data.



**Marks**  
**3**

Using  $\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$ , the free energy changes in the 3 reactions are, respectively:

$$\Delta_r G^\circ(1) = 4\Delta_f G^\circ(\text{NO}_2(\text{g})) - 2\Delta_f G^\circ(\text{N}_2\text{O}(\text{g}))$$

$$\Delta_r G^\circ(2) = 2\Delta_f G^\circ(\text{N}_2\text{O}(\text{g})) - 4\Delta_f G^\circ(\text{NO}(\text{g})) = -139.56 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ(3) = 2\Delta_f G^\circ(\text{NO}_2(\text{g})) - 2\Delta_f G^\circ(\text{NO}(\text{g})) = -69.70 \text{ kJ mol}^{-1}$$

Mathematically, the combination  $2\Delta_r G^\circ(3) - \Delta_r G^\circ(2)$  leads to  $\Delta_r G^\circ(1)$ :

$$2\Delta_r G^\circ(3) = 4\Delta_f G^\circ(\text{NO}_2(\text{g})) - 4\Delta_f G^\circ(\text{NO}(\text{g}))$$

$$\Delta_r G^\circ(2) = 2\Delta_f G^\circ(\text{N}_2\text{O}(\text{g})) - 4\Delta_f G^\circ(\text{NO}(\text{g}))$$

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$$2\Delta_r G^\circ(3) - \Delta_r G^\circ(2) = 4\Delta_f G^\circ(\text{NO}_2(\text{g})) - 2\Delta_f G^\circ(\text{N}_2\text{O}(\text{g})) = \Delta_r G^\circ(1)$$


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$$\begin{aligned} \Delta_r G^\circ(1) &= 2\Delta_r G^\circ(3) - \Delta_r G^\circ(2) = [(2 \times -69.70) - (-139.56)] \text{ kJ mol}^{-1} \\ &= 0.16 \text{ kJ mol}^{-1} \end{aligned}$$

Answer: **0.16 kJ mol<sup>-1</sup>**

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**



- A sample of hydrofluoric acid (0.10 M, 25.0 mL) is titrated with 0.10 M NaOH. The  $pK_a$  of hydrofluoric acid, HF, is 3.17. Calculate the pH at the following four points.

before any NaOH is added

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	$\rightleftharpoons$	F <sup>-</sup>	H <sup>+</sup>
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:

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

$$pH = 2.09$$

when half of the HF has been neutralised

At this point, half of the original HF has been converted to its conjugate base F<sup>-</sup>. The pH can be calculated using the Henderson-Hasselbalch equation:

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

$$pH = 3.17$$

at the equivalence point

At this point, all of the original HF has been converted to F<sup>-</sup>. The number of moles of HF originally present is:

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

This is equal to the amount of F<sup>-</sup> 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<sup>-</sup> is therefore:

ANSWER CONTINUES ON THE NEXT PAGE

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

	$F^-$	$H_2O$	$\rightleftharpoons$	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

$$pH = 14.00 - 6.07 = 7.93$$

pH = 7.93
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after the addition of 37.5 mL of NaOH

This volume of 0.10 M NaOH contains

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

From above, 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  $(25.0 + 37.5) \text{ mL} = 62.5 \text{ mL}$ , so its concentration is:

ANSWER CONTINUES ON THE NEXT PAGE

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

Hence,

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(0.020) = 1.70$$

Lastly,  $\text{pH} = 14.00 - \text{pOH}$ :

$$\text{pH} = 14.00 - 1.70 = 12.30$$

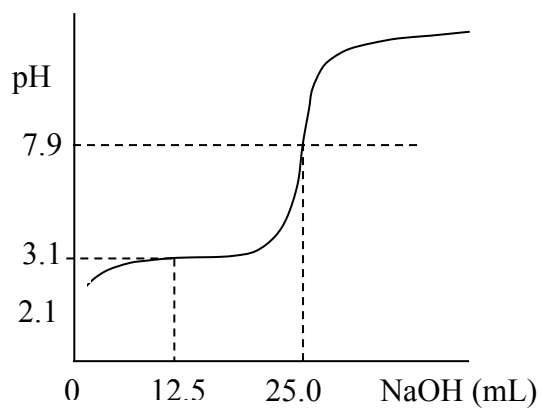
$$\text{pH} = 12.30$$

**THIS QUESTION CONTINUES ON THE NEXT PAGE.**

Sketch the titration curve.

**Marks**  
**2**

**Putting the 4 points from 2014-N-7 together gives the titration curve:**



**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

- At 700 °C, hydrogen and iodine react according to the following equation.



If 0.250 mol of HI(g) is introduced into a 2.00 L flask at 700 °C, what will be the concentration of I<sub>2</sub>(g) at equilibrium?

**Marks**  
**4**

The initial concentration of HI(g) is  $0.250 / 2.00 \text{ mol L}^{-1} = 0.125 \text{ mol L}^{-1}$ .

	H <sub>2</sub> (g)	I <sub>2</sub> (g)	$\rightleftharpoons$	2HI(g)
<b>Initial</b>	<b>0</b>	<b>0</b>		<b>0.125</b>
<b>Change</b>	<b>+x</b>	<b>+x</b>		<b>-2x</b>
<b>Equilibrium</b>	<b>x</b>	<b>x</b>		<b>0.125 - 2x</b>

Thus,

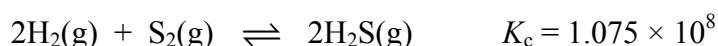
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.125-2x)^2}{(x)(x)} = \frac{(0.125-2x)^2}{x^2} = 49.0$$

$$(49.0)^{1/2} = \frac{(0.125-2x)}{x}$$

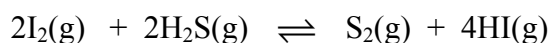
Rearranging gives  $x = [\text{I}_2(\text{g})] = 0.0139 \text{ M}$ .

Answer: **0.0139 M**

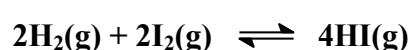
Hydrogen also reacts with sulfur at 700 °C:



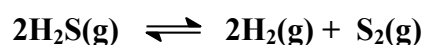
Determine  $K_c$  for the following overall equilibrium reaction at 700 °C.



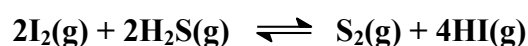
The overall reaction corresponds to the twice the first reaction combined with the reverse of the second reaction:



$$K_c(1) = (49.0)^2$$



$$K_c(2) = 1/(1.075 \times 10^8)$$



$$K_c(3) = K_c(1) \times K_c(2)$$

The 1<sup>st</sup> reaction is doubled so the original equilibrium constant is squared.

The 2<sup>nd</sup> reaction is reversed so the reciprocal of the equilibrium constant is used.

**ANSWER CONTINUES ON THE NEXT PAGE**

**The two reactions are then combined and the overall equilibrium constant is then the product:**

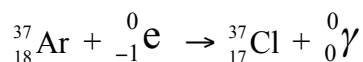
$$K_c(3) = K_c(1) \times K_c(2) = (49.0)^2 \times (1/(1.075 \times 10^8)) = 2.23 \times 10^{-5}$$

Answer:  $2.23 \times 10^{-5}$

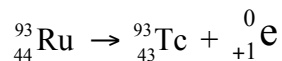
- Write balanced nuclear equations for the following changes.

**Marks**  
**4**

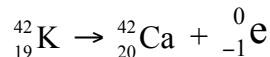
Electron capture by  $^{37}_{18}\text{Ar}$



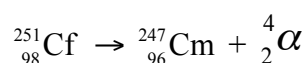
Positron emission by  $^{93}_{44}\text{Ru}$



Beta particle emission by  $^{42}_{19}\text{K}$



Alpha particle emission by  $^{251}_{98}\text{Cf}$



- Give the oxidation number of the indicated atom in the following compounds.

**2**

Compound	Atom	Oxidation number
$\text{HNO}_2$	N	<b>+III or +3</b>
$\text{NI}_3$	N	<b>-III or -3</b>
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$	Co	<b>+III or +3</b>
$\text{K}_3[\text{CrCl}_6]$	Cr	<b>+III or +3</b>

- Write down the formulas for the following compounds.

**2**

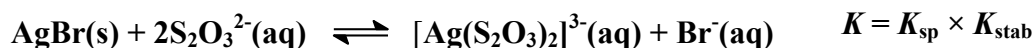
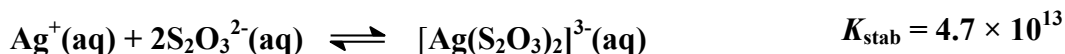
Compound	Formula
hexaaquacobalt(II) carbonate	<b><math>[\text{Co}(\text{OH}_2)_6]\text{CO}_3</math></b>
tetraamminecopper(II) sulfate	<b><math>[\text{Cu}(\text{NH}_3)_4]\text{SO}_4</math></b>
ammonium hexafluoridoferrate(III)	<b><math>(\text{NH}_4)_2[\text{FeF}_6]</math></b>
potassium hexacyanidomanganate(II)	<b><math>\text{K}_4[\text{Mn}(\text{CN})_6]</math></b>

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

- The  $K_{sp}$  of AgBr is  $5.0 \times 10^{-13}$ . The  $K_{stab}$  of  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  is  $4.7 \times 10^{13}$ . Calculate the value of the equilibrium constant for the dissolution of AgBr in  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

**Marks**  
**7**

The reactions corresponds to  $K_{sp}$  and  $K_{stab}$  can be added together to give the reaction for the dissolution of AgBr in  $\text{Na}_2\text{S}_2\text{O}_3$  solution:



The equilibrium constant for the overall reaction is the product of the equilibrium constants for the individual reactions:

$$K = K_{sp} \times K_{stab} = (5.0 \times 10^{-13}) \times (4.7 \times 10^{13}) = 24$$

Answer: **24**

Calculate the solubility of AgBr in 2.0 M  $\text{Na}_2\text{S}_2\text{O}_3$ .

The solubility can be calculated using a reaction table, assuming  $x$  mol dissolves:

	AgBr(s)	$2\text{S}_2\text{O}_3^{2-}(\text{aq})$	$\rightleftharpoons$	$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}(\text{aq})$	$\text{Br}^-(\text{aq})$
initial	excess	2.0		0	0
change	-x	-2x		+x	+x
final	excess	$2.0 - 2x$		x	x

$$K = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}(\text{aq})[\text{Br}^-(\text{aq})]}{[\text{S}_2\text{O}_3^{2-}(\text{aq})]^2}$$

$$= \frac{(x)(x)}{(2.0-2x)^2} = \frac{x^2}{(2.0-2x)^2} = 24$$

Taking square roots of both sides gives:

$$\frac{x}{(2.0-2x)} = (24)^{1/2} \quad x = 0.91 \text{ mol L}^{-1}$$

Answer: **0.91 mol L<sup>-1</sup>**

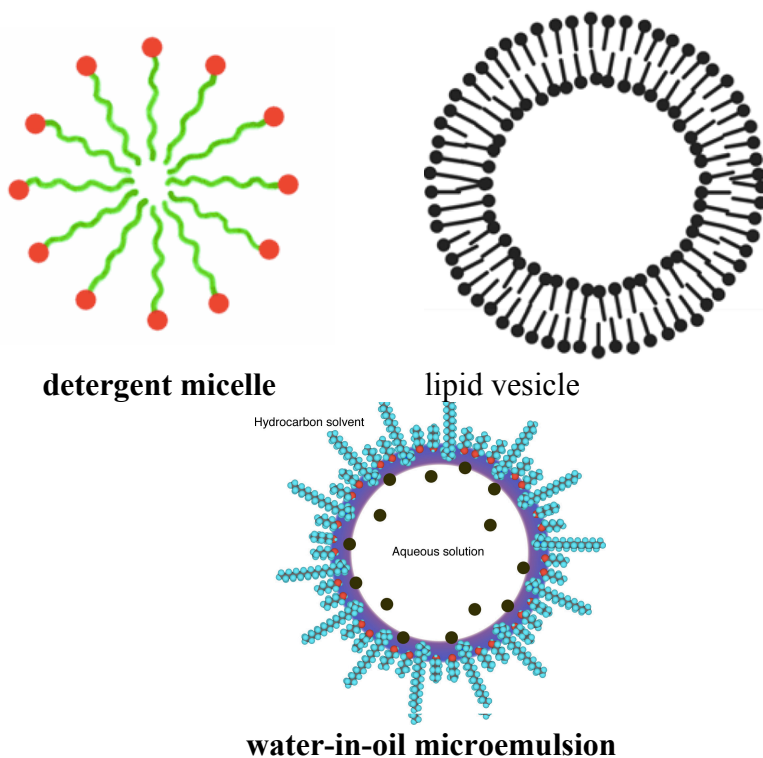
The  $K_{stab}$  for  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  is much greater than the  $K_{stab}$  for  $[\text{Ag}(\text{NH}_3)_2]^+$ . Explain why this is so.

**$\text{S}_2\text{O}_3^{2-}$  is a stronger ligand than  $\text{NH}_3$ , presumably because of its negative charge.**



- Draw sketches of a detergent micelle, a lipid vesicle and a water-in-oil microemulsion.

**Marks**  
**3**



- In the electrolytic production of Al, what mass of Al can be deposited in 2.00 hours by a current of 1.8 A?

**2**

**The number of moles of electrons passed in 2.00 hours by a current of 1.8 A is:**

$$\begin{aligned}\text{number of moles of electrons} &= It / F \\ &= (1.8 \text{ A})(2.00 \times 60.0 \times 60.0 \text{ s}) / 96485 \text{ C mol}^{-1} \\ &= 0.13 \text{ mol}\end{aligned}$$

**Aluminium is produced from  $\text{Al}_2\text{O}_3$  which contains  $\text{Al}^{3+}$ . 3 electrons are needed to produce each Al so 3 mol of electrons are needed to produce 1 mol of Al. This quantity of electrons will therefore deposit:**

$$\text{number of moles of Al} = 0.13 / 3 \text{ mol} = 0.045 \text{ mol}$$

**As Al has a molar mass of  $26.98 \text{ g mol}^{-1}$ , this quantity corresponds to:**

$$\begin{aligned}\text{mass of Al} &= \text{number of moles} \times \text{molar mass} \\ &= 0.045 \text{ mol} \times 26.98 \text{ g mol}^{-1} = 1.2 \text{ g}\end{aligned}$$

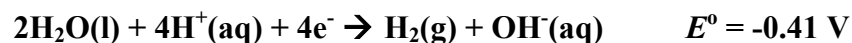
Answer: 1.2 g

**ANSWER CONTINUES ON THE NEXT PAGE**

- What products would you expect at the anode and the cathode on electrolysis of a 1 M aqueous solution of  $\text{NiI}_2$ ? Explain your answers.

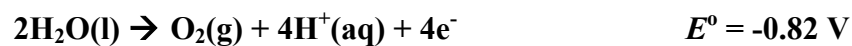
2

**At the cathode, there are two possible reduction reactions:**



**Reduction of  $\text{Ni}^{2+}(\text{aq})$  is easier, even without considering an overpotential for water.**

**At the anode, there are two possible oxidation reactions:**



**Both reactions will have an overpotential but oxidation of iodine is easier and this will probably occur.**

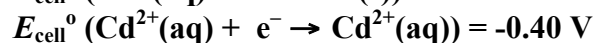
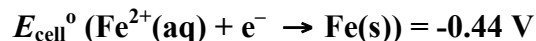
**Overall,  $\text{Ni}(\text{s})$  will be produced at the cathode and  $\text{I}_2(\text{g})$  will be produced at the anode.**

**Marks**  
**8**

- An electrochemical cell consists of 1.0 L half-cells of Fe/Fe<sup>2+</sup> and Cd/Cd<sup>2+</sup> with the following initial concentrations: [Fe<sup>2+</sup>] = 0.800 M, [Cd<sup>2+</sup>] = 0.200 M.

What is the initial  $E_{\text{cell}}$  at 25 °C?

From the reduction potential table,



The Fe<sup>2+</sup>/Fe half cell has the more negative reduction potential so it is the half cell that is turned around to act as the oxidation half cell:  $E_{\text{cell}}^{\circ} (\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{e}^{-}) = +0.44 \text{ V}$

In combination with the Cd<sup>2+</sup>/Cd reduction half cell, this gives an overall reaction and cell potential of:



For this reaction with [Fe<sup>2+</sup>(aq)] = 0.800 M and [Cd<sup>2+</sup>(aq)] = 0.200 M:

$$Q = \frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = \frac{0.800}{0.200}$$

For the 2e<sup>-</sup> reaction, the Nernst equation gives the cell potential as:

$$\begin{aligned} E_{\text{cell}} &= E^{\circ} - \frac{RT}{nF} \ln Q \\ &= (0.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{0.800}{0.200} = +0.02 \text{ V} \end{aligned}$$

Answer: +0.02 V

What is  $E_{\text{cell}}$  when [Cd<sup>2+</sup>] reaches 0.15 M?

[Cd<sup>2+</sup>(aq)] has decreased from 0.200 M to 0.15 M: a change of 0.05 M. [Fe<sup>2+</sup>(aq)] will increase by the same amount: [Fe<sup>2+</sup>(aq)] = (0.800 + 0.05) M = 0.85 M. Using the Nernst equation again gives:

$$\begin{aligned} E_{\text{cell}} &= E^{\circ} - \frac{RT}{nF} \ln Q \\ &= (0.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{0.85}{0.15} = +0.02 \text{ V} \end{aligned}$$

Answer: +0.02 V

ANSWER CONTINUES ON THE NEXT PAGE

What is  $[\text{Cd}^{2+}]$  when  $E_{\text{cell}}$  reaches 0.015 V?

$$E_{\text{cell}} = (0.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = +0.015 \text{ V}$$

so:

$$\frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = 7.0$$

If the change from the initial concentrations is  $x$ ,  $[\text{Cd}^{2+}(\text{aq})] = (0.200 - x) \text{ M}$  and  $[\text{Fe}^{2+}(\text{aq})] = (0.800 + x) \text{ M}$ :

$$\frac{0.800 - x}{0.200 + x} = 7.0 \quad x = -0.075 \text{ M}$$

So that  $[\text{Cd}^{2+}(\text{aq})] = (0.200 - 0.075) \text{ M} = 0.125 \text{ M}$ .

Answer: **0.125 M**

What are the equilibrium concentrations of both ions?

Using  $E^{\circ} = \frac{RT}{nF} \ln K = 0.04 \text{ V}$  gives  $K = 22.5$

so:

$$\frac{[\text{Fe}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]} = 22.5$$

If the change from the initial concentrations is  $x$ ,  $[\text{Cd}^{2+}(\text{aq})] = (0.200 - x) \text{ M}$  and  $[\text{Fe}^{2+}(\text{aq})] = (0.800 + x) \text{ M}$ :

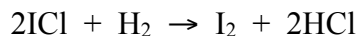
$$\frac{0.800 - x}{0.200 + x} = 22.5 \quad x = 0.158 \text{ M}$$

So that  $[\text{Cd}^{2+}(\text{aq})] = (0.200 - 0.158) \text{ M} = 0.042 \text{ M}$  and  $[\text{Fe}^{2+}(\text{aq})] = (0.800 + 0.158) \text{ M} = 0.958 \text{ M}$

$[\text{Cd}^{2+}] = 0.042 \text{ M}$

$[\text{Fe}^{2+}] = 0.958 \text{ M}$

- At a certain temperature the following data were collected for the reaction shown.



Experiment	Initial [ICl] (mol L <sup>-1</sup> )	Initial [H <sub>2</sub> ] (mol L <sup>-1</sup> )	Rate of formation of [I <sub>2</sub> ] (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.10	0.10	0.0015
2	0.20	0.10	0.0030
3	0.10	0.050	0.00075

Determine the rate law for the reaction.

Between experiments (1) and (2), [ICl] is doubled and [H<sub>2</sub>] is constant. This change leads to a doubling of the rate: the rate is proportional to [ICl].

Between experiments (1) and (3), [ICl] is constant and [H<sub>2</sub>] is halved. This change leads to a halving of the rate: the rate is proportional to [H<sub>2</sub>].

Overall:

$$\text{rate} = k[\text{ICl}][\text{H}_2]$$

What is the value of the rate constant?

Using experiment (1), rate = 0.0015 mol L<sup>-1</sup> s<sup>-1</sup>, [ICl] = 0.10 mol L<sup>-1</sup> and [H<sub>2</sub>] = 0.10 mol L<sup>-1</sup>:

$$\text{rate} = k[\text{ICl}][\text{H}_2] = k(0.10 \text{ mol L}^{-1})(0.10 \text{ mol L}^{-1}) = 0.0015 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$k = (0.0015 \text{ mol L}^{-1} \text{ s}^{-1}) / (0.10 \text{ mol L}^{-1})(0.10 \text{ mol L}^{-1}) = 0.15 \text{ L mol}^{-1} \text{ s}^{-1}$$

Answer: 0.15 L mol<sup>-1</sup> s<sup>-1</sup>

**Marks**  
**4**

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