

Topics in the June 2010 Exam Paper for CHEM1903

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2010-J-3:

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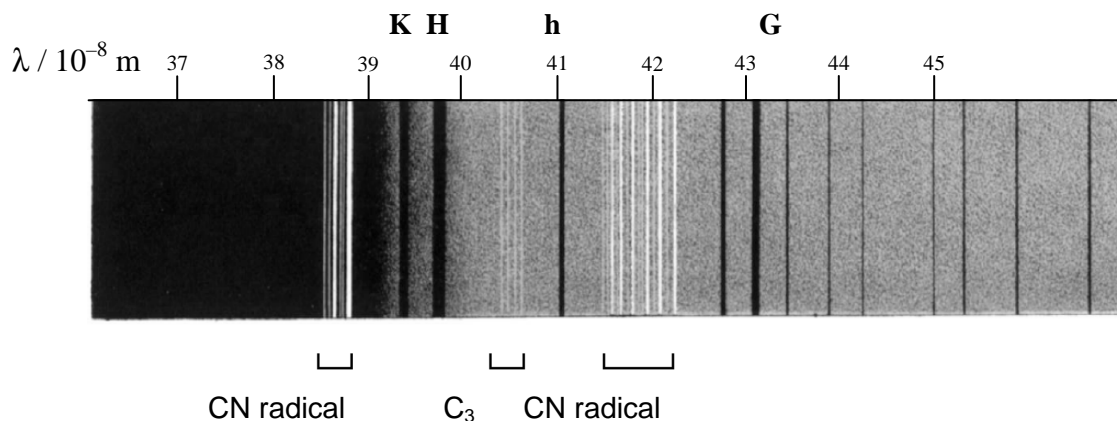
2010-J-11:

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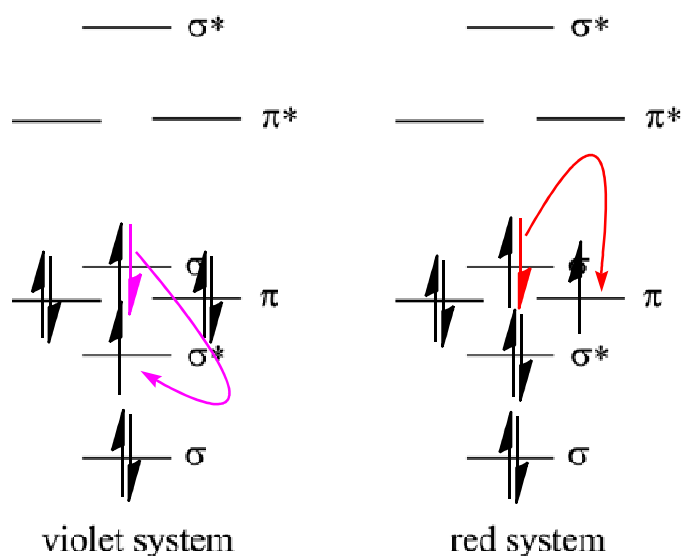
- [Electrochemistry](#)
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- The “Great Comet of 1881” was discovered by Tebbutt from his observatory at Windsor, NSW. Observations by Huggins of the comet’s emission spectrum (pictured) revealed the presence of what was later determined to be the CN radical.



This emission system of CN is known as the “violet system”, and results from a radical returning to the ground state as an electron makes a transition from a σ orbital to a σ^* orbital. The “red system” of CN results from a radical returning to the ground state as an electron makes a transition from a σ orbital to a π orbital.

On the diagram below, indicate the orbital occupancy, using arrow notation, of the upper electronic states of the “violet” and “red” systems of CN. Also indicate how the excited electron relaxes when the radical emits light (use a curved arrow).



Explain in terms of bond order why the upper state of the violet system exhibits a shorter bond length (1.15 Å) than the ground state (1.17 Å).

The bond order is an indication of the bond strength and bond length. A higher bond order leads to a strong and shorter bond. It can be calculated as:

$$\text{bond order} = \frac{1}{2} (\text{number of bonding electrons} - \text{number of antibonding electrons})$$

The upper state in the violet system has 8 bonding electrons ($2 \times \sigma$, $4 \times \sigma^*$ and $2 \times \sigma$) and 1 antibonding electron ($1 \times \sigma^*$):

$$\text{bond order} = \frac{1}{2} (8 - 1) = 7/2$$

The upper state in the red system has 7 bonding electrons ($2 \times \sigma$, $3 \times \sigma^*$ and $2 \times \sigma$) and 2 antibonding electron ($2 \times \sigma^*$):

$$\text{bond order} = \frac{1}{2} (7 - 2) = 5/2$$

The upper state in the violet system has a higher bond order and this is consistent with it having a shorter bond (i.e. it has more bonding and fewer antibonding electrons).

Also indicated in Huggin's spectrum are the Fraunhofer absorption features labelled K, H and G, which arise from calcium. Explain the appearance of these features. (Hint: they would also appear in the spectrum of moonlight.)

Blackbody emission from the sun is absorbed by Ca in the sun's atmosphere. the solar spectrum is then reflected by the comet.

The Fraunhofer feature labelled 'h' is due to atomic hydrogen. What is the electronic transition responsible for this absorption feature? (Hint: one of the energy levels involved is $n = 2$.)

The feature occurs at 41 nm. This corresponds to an energy of:

$$E = (hc/\lambda) = (6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}) / (41 \times 10^{-8} \text{ m}) = 4.85 \times 10^{-19} \text{ J}$$

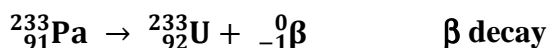
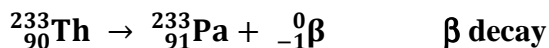
The energy of a level in hydrogen is given by $E_n = -E_R(1/n^2)$. The transition energy is the difference in the energies of the two levels involved:

$$\Delta E = \frac{-E_R}{n_f^2} - \frac{-E_R}{n_i^2} = E_R \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right] \text{ where } E_R \text{ is the Rydberg constant.}$$

As $n_i = 2$,

$$\Delta E = (2.18 \times 10^{-18} \text{ J}) \left[\frac{1}{2^2} - \frac{1}{n_f^2} \right] = 4.85 \times 10^{-19} \text{ J} \text{ which gives } n_f = 6.$$

- Thorium is a naturally occurring metal estimated to be about three to four times more abundant than uranium in the Earth's crust. Naturally occurring thorium is composed mainly of one isotope, ^{232}Th , and is an alternative fuel for nuclear energy production. ^{232}Th can absorb slow neutrons to produce ^{233}U via the intermediates ^{233}Th and ^{233}Pa . Write balanced nuclear equations to describe this sequential process.



When struck by a neutron, an atom of ^{233}U can undergo α -decay generating 200. MeV of energy. What initial mass of thorium ^{232}Th would be required to provide 6×10^{18} J, Australia's energy needs for one year?

As $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$,

$$200. \text{ MeV} = (200 \times 10^6 \times 1.602 \times 10^{-19}) \text{ J} = 3.20 \times 10^{-11} \text{ J}.$$

This is the amount of energy produced by 1 decay event so the number needed to generate 6×10^{18} J is:

$$\text{number of decay events} = (6 \times 10^{18}) / (3.20 \times 10^{-11}) = 1.87 \times 10^{29}$$

From the equations above, decay of one $^{232}_{90}\text{Th}$ produces one $^{233}_{92}\text{U}$ so this is also equal to the number of $^{232}_{90}\text{Th}$ atoms required. This corresponds to:

$$\text{number of moles of } ^{232}_{90}\text{Th} = (1.87 \times 10^{29}) / (6.022 \times 10^{23}) = 311000 \text{ mol}.$$

Hence, the mass required is:

$$\text{mass of } ^{232}_{90}\text{Th} = (232 \text{ g mol}^{-1}) \times (311000 \text{ mol}) = 7 \times 10^7 \text{ g} = 70 \text{ tonne}$$

Answer: **70 tonne**

^{232}Th also undergoes a $(n,2n)$ reaction to form ^{231}Th , which subsequently decays to ^{231}Pa . This side reaction is a major contributor to the long term radiotoxicity of spent nuclear fuel. Calculate the activity (in Bq) of 1.0 g of each of these isotopes.

Data:	Isotope	^{232}Th	^{231}Th	^{231}Pa
	half life	1.405×10^{10} years	25.5 hours	3.27×10^4 years

For an isotope with molar mass M , the number of nuclei in 1.0 g is given by;

$$\text{number of nuclei} = N = \frac{N_A}{M}$$

As the activity, A , is given by $A = \frac{\ln 2}{t_{1/2}} \times N$, the activity of 1.0 g is given by;

$$A = \frac{\ln 2}{t_{1/2}} \times \frac{N_A}{M}$$

ANSWER CONTINUES ON THE NEXT PAGE

^{232}Th :

$$A = \frac{\ln 2}{(1.405 \times 10^{10} \times 365.25 \times 24 \times 60 \times 60) \text{ s}} \times \left(\frac{6.022 \times 10^{23}}{232} \right) \text{ particles}$$

$$= 4.1 \times 10^3 \text{ Bq}$$

 ^{231}Th :

$$A = \frac{\ln 2}{(25.5 \times 60 \times 60) \text{ s}} \times \left(\frac{6.022 \times 10^{23}}{231} \right) \text{ particles}$$

$$= 2.0 \times 10^{16} \text{ Bq}$$

 ^{231}Pa :

$$A = \frac{\ln 2}{(3.27 \times 10^4 \times 365.25 \times 24 \times 60 \times 60) \text{ s}} \times \left(\frac{6.022 \times 10^{23}}{231} \right) \text{ particles}$$

$$= 1.8 \times 10^9 \text{ Bq}$$

 ^{232}Th : $4.1 \times 10^3 \text{ Bq}$ **^{231}Th: $2.0 \times 10^{16} \text{ Bq}$** **$^{231}\text{Pa}$: $1.8 \times 10^9 \text{ Bq}$**

How long does it take 1.0 g of ^{231}Th to decay to the same activity as 1.0 g of ^{232}Th ?

Marks
3

The half life of ^{231}Th is *very* short compared to that of ^{232}Th . All of the ^{231}Th will decay to ^{231}Pa in the time it takes for the ^{231}Th decay. Thus, the activity of 1.0 g of ^{231}Th will actually correspond to the activity of ^{231}Pa .

From 2010-J-4, the activity of 1.0 g of ^{232}Th is 4.1×10^3 Bq and the activity of 1.0 g of ^{231}Pa is 1.8×10^9 Bq. The time, t , it takes for the activity of ^{231}Pa to fall from 1.8×10^9 (A_0) to 4.1×10^3 Bq (A_t) needs to be calculated.

The number of nuclei varies with time according to $\ln(N_0/N_t) = \lambda t$. As activity is directly proportional to the number of nuclei, this can be rewritten in terms of activities:

$$\ln(A_0/A_t) = \lambda t = (\ln 2/t_{1/2}) \times t$$

Thus,

$$\ln(1.8 \times 10^9 / 4.1 \times 10^3) = \ln 2 / (3.27 \times 10^4 \times 365.25 \times 60 \times 60 \text{ s}) \times t$$

$$t = 1.93 \times 10^{13} \text{ s} = 6.1 \times 10^5 \text{ years}$$

Answer: 6.1×10^5 years

- Rationalise the order of the boiling points of the following liquids in terms of their intermolecular forces.

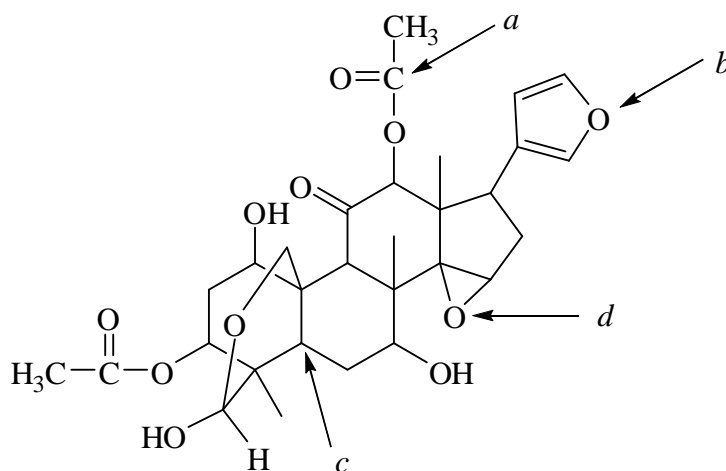
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liquid	F ₂	HCl	HBr	HI	Cl ₂	HF	Br ₂	I ₂
b.p. (° C)	-188	-85	-67	-35	-34	20	59	184

The boiling point reflects the strength of the intermolecular forces between the molecules in the liquid. Strong intermolecular forces leads to high boiling points.

- For the halogens, the boiling points increase in the order $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$. The only intermolecular force operating is dispersion. This depends on the polarizability of the electron clouds. Down the group, the electron clouds gets more diffuse and are less tightly held onto: the polarizability grows and hence the strength of the dispersion forces increase too.
- For the hydrogen halides, the boiling points increase in the order $\text{HCl} < \text{HBr} < \text{HI}$ for the same reason.
- The dispersion forces are stronger for the halogens than for the hydrogen halides as the former have more electrons. Note that this is more important for these molecules than the presence of dipole – dipole interactions in the hydrogen halides.
- The exception to the observations (b) and (c) is HF which has a higher boiling point than both HCl and F₂. The very high electronegativity of F leads to the presence of substantial partial charges on H and F in HF and this leads to strong hydrogen bonding between HF molecules.

- Toosendanin (pictured) is an ingredient from traditional Chinese medicine and is effective as an antitubercular agent both *in vitro* and *in vivo*. The compound can prevent death in animals suffering from botulism and help restore normal activity. It may also help to treat *Botox* overdoses in humans.



Complete the table concerning the atoms *a*, *b* and *c* indicated by the arrows.

Selected atom	Number of σ -bonds associated with the selected atom	Geometry of σ -bonds about the selected atom
<i>a</i>	3	trigonal planar
<i>b</i>	2	bent (V shaped)
<i>c</i>	4	tetrahedral

Comment on the actual bond angle exhibited by atom *d* as compared to electronically similar atoms elsewhere in the molecule. Is this *epoxide* group likely more or less reactive than an ether? Explain.

As the oxygen atom *d* makes 2 bonds and has 2 lone pairs, its electron pairs would naturally adopt a tetrahedral arrangement to minimize repulsion. The bond angle would then be expected to be close to 109° , as would the bond angles for the ether groups in the molecule.

The geometrical constraint of the 3-membered epoxide ring means that the angle is forced to be close to 60° . The electron pairs in the two C-O bonds are thus forced to be close to one another, introducing considerable repulsion or *strain*.

The epoxide group is thus likely to be considerably more reactive than the ether groups and the reactivity is likely to be such that opening of the ring is achieved.

Marks
3

- Calcium chloride (1.14 g) is completely dissolved in 100.0 mL of water at 27.00 °C in a 'coffee cup' calorimeter. The temperature of the water after dissolution is 28.97 °C. Calculate the standard enthalpy of solution of CaCl₂ (in kJ mol⁻¹). The density of water at 27.0 °C is 0.997 g mL⁻¹ and its heat capacity is 4.184 J K⁻¹ g⁻¹. Ignore the heat capacity of the CaCl₂.

The mass of 100.0 mL of water is:

$$\text{mass} = \text{density} \times \text{volume} = (0.997 \text{ g mL}^{-1}) \times (100.0 \text{ mL}) = 99.7 \text{ g}$$

Using $q = mC\Delta T$, the temperature increase of $(28.97 - 27.00) \text{ }^\circ\text{C} = 1.97 \text{ }^\circ\text{C} = 1.97 \text{ K}$ comes from a heat change

$$q = (99.7 \text{ g}) \times (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (1.97 \text{ K}) = 822 \text{ J}$$

This is the heat change for 1.14 g. The molar mass of CaCl₂ is $(40.08 + 2 \times 35.45) \text{ g mol}^{-1} = 110.98 \text{ g mol}^{-1}$. Hence, 1.14 g corresponds to

$$\text{number of moles} = \text{mass/molar mass} = (1.14 \text{ g}) / (110.98 \text{ g mol}^{-1}) = 0.0103 \text{ mol.}$$

The enthalpy of solution is therefore

$$\Delta_{\text{solution}}H^\circ = - (822 \text{ J}) / (0.0103 \text{ mol}) = -80.0 \text{ kJ mol}^{-1}$$

Note the negative sign: the enthalpy of solution is *exothermic* as the temperature of the water *increases*.

Answer: **-80.0 kJ mol⁻¹**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

- Ethanol is produced industrially by reacting ethylene with water according to the following equation.



Equal masses of solid ethylene and water ice are introduced to a 1.00 L flask at 100 K. The flask is evacuated of air, sealed and heated to 600 K. When equilibrium is reached, the flask contains 0.098 mol of ethylene gas and the total pressure is 26.5 atm. What mass of ethylene was introduced to the flask originally?

The molar mass of H_2O is $(16.00 + 2 \times 1.008) \text{ g mol}^{-1} = 18.016 \text{ g mol}^{-1}$. The molar mass of C_2H_4 is $(2 \times 12.01 + 4 \times 1.008) \text{ g mol}^{-1} = 28.052 \text{ g mol}^{-1}$.

If the mass of ethylene and water initially present = x g, then the number of moles of each initially present are:

$$\text{number of moles of } \text{H}_2\text{O} = n_{\text{H}_2\text{O},\text{initial}} = \text{mass} / \text{molar mass} = x/18.016 \text{ mol}$$

$$\text{number of moles of } \text{C}_2\text{H}_4 = n_{\text{C}_2\text{H}_4,\text{initial}} = x/28.052 \text{ mol}$$

As 0.098 mol of C_2H_4 are present at equilibrium, the amount that has reacted is given by

$$\Delta n_{\text{C}_2\text{H}_4} = n_{\text{C}_2\text{H}_4,\text{initial}} - 0.098 \text{ mol}$$

From the stoichiometry of the reaction, this is also equal to the *decrease* in the number of moles of H_2O and the *increase* in the number of moles of $\text{C}_2\text{H}_5\text{OH}$:

$$n_{\text{C}_2\text{H}_4,\text{equilibrium}} = 0.098 \text{ mol}$$

$$n_{\text{H}_2\text{O},\text{equilibrium}} = n_{\text{H}_2\text{O},\text{initial}} - \Delta n_{\text{C}_2\text{H}_4} = n_{\text{H}_2\text{O},\text{initial}} - n_{\text{C}_2\text{H}_4,\text{initial}} + 0.098 \text{ mol}$$

$$n_{\text{C}_2\text{H}_5\text{OH},\text{equilibrium}} = 0 + \Delta n_{\text{C}_2\text{H}_4} = n_{\text{C}_2\text{H}_4} - 0.098 \text{ mol}$$

The final pressure at 600. K of 26.5 atm is due to ethylene, water gas and ethanol. Using the ideal gas law, the total number of moles, n , is given by

$$n_{\text{total}} = PV/RT = (26.5 \text{ atm} \times 1.00 \text{ L}) / (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 600. \text{ K})$$

$$= 0.538 \text{ mol}$$

$$= n_{\text{C}_2\text{H}_4,\text{equilibrium}} + n_{\text{H}_2\text{O},\text{equilibrium}} + n_{\text{C}_2\text{H}_5\text{OH},\text{equilibrium}}$$

$$= (0.098 \text{ mol}) + (n_{\text{H}_2\text{O},\text{initial}} - n_{\text{C}_2\text{H}_4,\text{initial}} + 0.098 \text{ mol}) + (n_{\text{C}_2\text{H}_4} - 0.098 \text{ mol})$$

$$= (0.098 + \frac{x}{18.016} - \frac{x}{28.052} + 0.098 + \frac{x}{28.052} - 0.098) \text{ mol}$$

$$= (0.098 + \frac{x}{18.016}) \text{ mol}$$

Hence, $x = 7.93$ g.

Answer: 7.93 g

The same experiment is carried out in another flask, but with different initial masses of ethylene and ice. At equilibrium, this flask contains 5.81×10^{-3} mol of H_2O , 1.21×10^{-2} mol of C_2H_4 , and 6.33×10^{-1} mol of ethanol. Calculate the concentration equilibrium constant, K_c , at 600 K.

As the volume of the flask is 1.00 L, the equilibrium concentrations are:

$$[\text{H}_2\text{O}(\text{g})] = 5.81 \times 10^{-3} \text{ mol} / 1.00 \text{ L} = 5.81 \times 10^{-3} \text{ L}$$

$$[\text{C}_2\text{H}_4(\text{g})] = 1.21 \times 10^{-2} \text{ mol} / 1.00 \text{ L} = 1.21 \times 10^{-2} \text{ L}$$

$$[\text{C}_2\text{H}_5\text{OH}(\text{g})] = 6.33 \times 10^{-1} \text{ mol} / 1.00 \text{ L} = 6.33 \times 10^{-1} \text{ L}$$

Hence, the equilibrium constant in terms of concentrations, K_c , is:

$$K_c = \frac{[\text{C}_2\text{H}_5\text{OH}(\text{g})]}{[\text{H}_2\text{O}(\text{g})][\text{C}_2\text{H}_4(\text{g})]} = \frac{(6.33 \times 10^{-1})}{(5.81 \times 10^{-3})(1.21 \times 10^{-2})} = 9.00 \times 10^3$$

Answer: 9.00×10^3

Calculate the partial pressure equilibrium constant, K_p , at 600. K.

The reaction involves 2 mol of gaseous reactant \rightarrow 1 mol of gaseous product so the change in the number of moles of gas = $\Delta n = -1$.

Hence,

$$K_p = K_c(RT)^{\Delta n} = (9.00 \times 10^3) \times (0.08206 \times 600. \text{ K})^{-1} = 183$$

Answer: **183**

What is the standard entropy change ΔS° (in $\text{J K}^{-1} \text{ mol}^{-1}$) for the forward reaction at 600 K?

Using $\Delta G^\circ = -RT \ln K_p$,

$$\Delta G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600. \text{ K}) \times \ln(183) = -2.60 \times 10^4 \text{ J mol}^{-1}$$

From 2010-J-8, $\Delta H^\circ = -47.8 \text{ kJ mol}^{-1}$. Hence, using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$:

$$\begin{aligned} \Delta S^\circ &= (\Delta H^\circ - \Delta G^\circ) / T = [(-47.8 \times 10^3 \text{ J mol}^{-1}) - (-2.60 \times 10^4 \text{ J mol}^{-1})] / (600. \text{ K}) \\ &= -36.3 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Answer: **-36.3 J K⁻¹ mol⁻¹**

How will the yield of ethanol be affected by the following changes?

The volume of the flask is increased.

The yield will decrease as the reaction will shift to the left to increase the number of moles of gas.

The temperature is increased.

The yield will decrease as the reaction is exothermic.

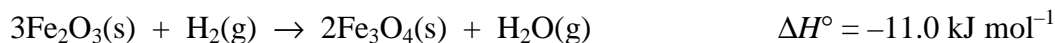
The walls of the flask are cooled so that only liquid water condenses out.

The yield will decrease as this will decrease the concentration of water.

A catalyst is added.

The yield will be unchanged as a catalyst does not affect the position of equilibrium.

- Iron oxide that has been exposed to the atmosphere for any length of time will generally contain a mixture of magnetite, Fe_2O_3 , and haematite, Fe_3O_4 . This mixture can be converted to pure Fe_3O_4 by heating it under an excess of flowing hydrogen gas:



If 0.364 kJ of heat is liberated during the conversion of a 7.18 g sample of iron oxide (consisting only of magnetite and haematite) to pure Fe_3O_4 , what was the initial mass percentage of haematite in the sample?

From the chemical equation, 1 mol of H_2 liberates 11.0 kJ of heat. Hence, the number of moles of H_2 that must be reacting to produce 0.0364 kJ of heat is:

$$\text{number of moles of } \text{H}_2 = (0.0364 / 11.0) \text{ mol} = 0.00331 \text{ mol}$$

From the chemical equation, 1 mol of H_2 reacts with 3 mol of Fe_2O_3 and so:

$$\text{number of moles of } \text{Fe}_2\text{O}_3 = (3 \times 0.00331) \text{ mol} = 0.00993 \text{ mol}$$

The molar mass of Fe_2O_3 is $(2 \times 55.85 + 3 \times 16.00) \text{ g mol}^{-1} = 159.7 \text{ g mol}^{-1}$. Hence, this amount of Fe_2O_3 corresponds to:

$$\begin{aligned} \text{mass of } \text{Fe}_2\text{O}_3 &= \text{number of moles} \times \text{molar mass} \\ &= (0.00993 \text{ mol}) \times (159.7 \text{ g mol}^{-1}) = 1.59 \text{ g} \end{aligned}$$

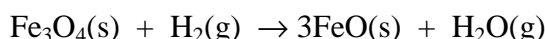
The mass percentage of Fe_2O_3 in the initial 7.18 g sample is therefore:

$$\text{mass percentage of } \text{Fe}_2\text{O}_3 = (1.59 / 7.18) \times 100\% = 22.1 \%$$

The mass percentage of haematite is therefore $(100.0 - 22.1)\% = 77.9\%$.

Answer: **77.9%**

Fe_3O_4 can be further reduced to FeO under flowing hydrogen.



Based on the following table of thermodynamic data, what is the minimum temperature at which this would be a spontaneous reaction?

	Fe	$\text{FeO}(\text{s})$	$\text{Fe}_3\text{O}_4(\text{s})$	$\text{H}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta_f H^\circ$ (kJ mol ⁻¹)		-272	-1118		-242
S° (J K ⁻¹ mol ⁻¹)	27	61	146	131	189

Using $\Delta_{\text{rxn}}H^\circ = \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$:

$$\begin{aligned} \Delta_{\text{rxn}}H^\circ &= [3\Delta_f H^\circ(\text{FeO}) + \Delta_f H^\circ(\text{H}_2\text{O}) - [\Delta_f H^\circ(\text{Fe}_3\text{O}_4)]] \\ &= [(3 \times -272) + (-242)] - [-1118] \text{ kJ mol}^{-1} = 60. \text{ kJ mol}^{-1} \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

Using $\Delta_{\text{rxn}}S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$:

$$\begin{aligned}\Delta_{\text{rxn}}S^\circ &= [3S^\circ(\text{FeO}) + S^\circ(\text{H}_2\text{O})] - [S^\circ(\text{Fe}_3\text{O}_4) + S^\circ(\text{H}_2)] \\ &= [(3 \times 61) + (189)] - [(146 + 131)] \text{ J K}^{-1} \text{ mol}^{-1} = 95 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

The reaction is spontaneous if $\Delta G^\circ < 0$. As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, this condition becomes:

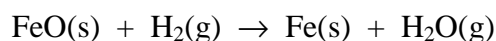
$$\Delta H^\circ - T\Delta S^\circ < 0$$

Hence:

$$\begin{aligned}(60. \times 10^3 \text{ J mol}^{-1}) - T \times (95 \text{ J K}^{-1} \text{ mol}^{-1}) &< 0 \\ T > (60. \times 10^3 \text{ J mol}^{-1}) / (95 \text{ J K}^{-1} \text{ mol}^{-1}) \\ T > 630 \text{ K}\end{aligned}$$

Answer: $T > 630 \text{ K}$

Would the resulting FeO be stable under those conditions, or would it be reduced further to Fe metal by the following reaction?



Explain, with calculations as appropriate.

Marks
5

For this reaction, using $\Delta_{\text{rxn}}H^\circ = \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$:

$$\begin{aligned}\Delta_{\text{rxn}}H^\circ &= [\Delta_f H^\circ(\text{H}_2\text{O})] - [\Delta_f H^\circ(\text{FeO})] \\ &= ([-242] - [-272]) \text{ kJ mol}^{-1} = 30. \text{ kJ mol}^{-1}\end{aligned}$$

Using $\Delta_{\text{rxn}}S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$:

$$\begin{aligned}\Delta_{\text{rxn}}S^\circ &= [S^\circ(\text{Fe}) + S^\circ(\text{H}_2\text{O})] - [S^\circ(\text{FeO}) + S^\circ(\text{H}_2)] \\ &= ([27 + 189] - [61 + 131]) \text{ J K}^{-1} \text{ mol}^{-1} = 24 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

At 630 K,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (30. \times 10^3) - (630 \text{ K}) \times (24 \text{ J K}^{-1} \text{ mol}^{-1}) = 15000 \text{ J mol}^{-1}$$

As $\Delta G^\circ > 0$, the reaction is *not* spontaneous and FeO is stable.

Describe the nature of the bonding in (i) FeO(s), (ii) H₂(g) and (iii) Fe(s).

FeO(s)

Ionic bonding between the Fe²⁺ and O²⁻ ions. The ions are positioned regularly within a stable crystal lattice.

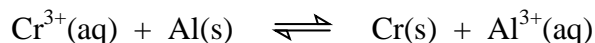
H₂(g)

Covalent bonding between the H atoms in the H₂ molecule. No bonding interactions between the H₂ molecules.

Fe(s)

Metallic bonding between the Fe atoms - the electrons are largely delocalised over many atoms.

- A voltaic cell is set up at 298 K based on the following reaction

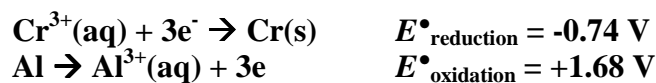


Express the overall reaction in voltaic cell notation.



Calculate the cell potential at 298 K when the concentration of $\text{Cr}^{3+}(\text{aq})$ is 0.213 M and the concentration of $\text{Al}^{3+}(\text{aq})$ is 0.078 M.

The two half cell reactions and standard potentials are:



Hence, the standard cell potential is:

$$E^\circ = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}} = (+1.68 - 0.74) \text{ V} = +0.94 \text{ V}$$

At the non-standard concentrations, the Nernst equation can be used to work out the potential for this 3-electron process:

$$\begin{aligned} E_{\text{cell}} &= E^\circ - \frac{RT}{nF} \ln Q \\ &= (+0.94 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(3)(96485 \text{ C mol}^{-1})} \ln \frac{(0.078)}{(0.213)} = +0.95 \text{ V} \end{aligned}$$

Answer: +0.95 V

Calculate the equilibrium constant at 298 K.

Using $E^\circ = \frac{RT}{nF} \ln K$,

$$+0.94 \text{ V} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(3)(96485 \text{ C mol}^{-1})} \ln K$$

$$K = 4.9 \times 10^{47}$$

Answer: 4.9×10^{47}

ANSWER CONTINUES ON THE NEXT PAGE

Marks
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- How long (in seconds) would it take for all the gold to be plated out of 55.0 mL of a $2.34 \times 10^{-3} \text{ mol L}^{-1}$ solution of $\text{Au}^{3+}(\text{aq})$, using a current of 0.75 A?

2

The number of moles of $\text{Au}^{3+}(\text{aq})$ to be reduced is:

$$\begin{aligned} \text{number of moles of Au}^{3+} &= \text{concentration} \times \text{volume} \\ &= (2.34 \times 10^{-3} \text{ mol L}^{-1}) \times (0.0550 \text{ L}) = 0.000129 \text{ mol} \end{aligned}$$

The reduction of each Au^{3+} ion requires 3 electrons so the number of moles of electrons required is:

$$\text{number of moles of electrons} = 3 \times 0.000129 \text{ mol} = 0.000386 \text{ mol}$$

A current I passing for a time t delivers It / F moles of electrons. Hence:

$$\begin{aligned} t &= \text{number of moles of electrons} \times (F / I) \\ &= (0.000386 \text{ mol}) \times (96485 \text{ C mol}^{-1}) / (0.75 \text{ C s}^{-1}) = 50. \text{ s} \end{aligned}$$

Answer: **50. s**

- The aluminium-air battery, in which aluminium metal is oxidised to Al^{3+} and O_2 is reduced to OH^- , is being considered as a power source in cars. Briefly compare the relative merits of such a battery with those of a fuel cell for such applications.

Fuel cells use $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ as the reactants.

Disadvantages: H_2 is highly flammable and a severe explosion hazard should the car be involved in a crash. It's likely cars would need to be heavier to prevent rupture of tanks. There are also handling difficulties as it's a gas.

Advantages: The only product of a fuel cell is water, so they are non-polluting. High efficiency.

Aluminium air battery uses $\text{Al}(\text{s})$ and O_2 as reactants.

Advantages: The fuel (Al) is not explosive and can easily be replaced when it is exhausted. Aluminium is very light metal and 3 electrons lost in its oxidation to Al^{3+} , so a lot of energy generated per g of fuel. Aluminium is very plentiful and cheap. Steady voltage as [Al] and [O_2] do not vary.

Disadvantages: The $\text{Al}(\text{OH})_3$ product needs to be recycled. Conversion back to Al metal involves large amounts of electricity and associated CO_2 output.