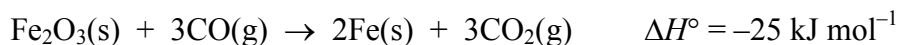
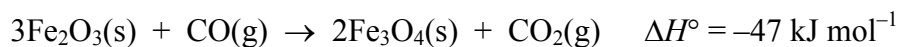


Marks
5

- Carbon monoxide is commonly used in the reduction of iron ore to iron metal. Iron ore is mostly haematite, Fe_2O_3 , in which case the complete reduction reaction is:

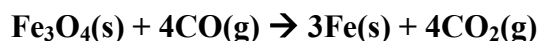


Incomplete reduction, however, results in the formation of magnetite, Fe_3O_4 :

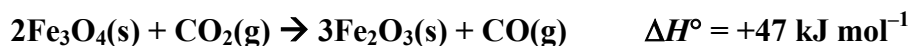


Use these heats of reaction to calculate the enthalpy change when one mole of magnetite is reduced to iron metal using carbon monoxide.

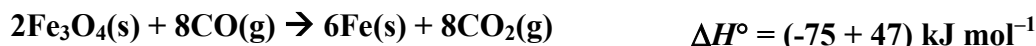
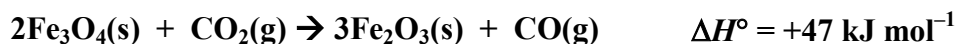
The required reaction is:



The second reaction in the question is reversed so that it leads to loss of $\text{Fe}_3\text{O}_4(\text{s})$:



This reaction is then added to $3 \times$ the first reaction:



The chemical reaction is exactly twice that required, so for one mole of $\text{Fe}_3\text{O}_4(\text{s})$, the $\Delta H^\circ = (-75 + 47) / 2 \text{ kJ mol}^{-1} = -14 \text{ kJ mol}^{-1}$.

Alternatively, using the data in the next part of the question,

$$\Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - \sum n\Delta_fH^\circ(\text{reactants}),$$

$$\Delta_{\text{rxn}}H^\circ = [4\Delta_fH^\circ(\text{CO}_2(\text{g}))] - [\Delta_fH^\circ(\text{Fe}_3\text{O}_4(\text{s})) + 4\Delta_fH^\circ(\text{CO}(\text{g}))]$$

$\Delta_fH^\circ(\text{Fe}(\text{s})) = 0$ as it is an element in its standard state.

Hence using the data in the table below:

$$\Delta_{\text{rxn}}H^\circ = ([4 \times -394] - [-1118 + 4 \times -111]) \text{ kJ mol}^{-1} = -14 \text{ kJ mol}^{-1}$$

Answer: $\Delta_{\text{rxn}}H^\circ = -14 \text{ kJ mol}^{-1}$

ANSWER CONTINUES ON THE NEXT PAGE

Another iron oxide that can be formed as an intermediate during reduction is FeO. Use the following table of thermochemical data to show whether the formation of FeO from Fe₃O₄ is spontaneous or not at 25 °C.

	$\Delta_f H^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
FeO	-272	61
Fe ₃ O ₄	-1118	146
CO	-111	198
CO ₂	-394	214

For the reaction,



$$\begin{aligned}\Delta_{\text{rxn}}H^\circ &= \sum m\Delta_f H^\circ(\text{products}) - \sum n\Delta_f H^\circ(\text{reactants}) \\ &= ([3 \times -272 - 394] - [-1118 - 111]) \text{ kJ mol}^{-1} = +19 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_{\text{rxn}}S^\circ &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \\ &= ([3 \times 61 + 214] - [146 + 198]) \text{ J K}^{-1} \text{ mol}^{-1} = +53 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Thus,

$$\begin{aligned}\Delta_{\text{rxn}}G^\circ &= \Delta_{\text{rxn}}H^\circ - T\Delta_{\text{rxn}}S^\circ \\ &= (+19 \times 10^3 \text{ J mol}^{-1}) - (298 \text{ K})(53 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= +3200 \text{ J mol}^{-1} = +3.2 \text{ kJ mol}^{-1}\end{aligned}$$

As $\Delta_{\text{rxn}}G^\circ > 0$, the reaction is not spontaneous.

Marks
4

- A 150.0 g block of iron metal is cooled by placing it in an insulated container with a 50.0 g block of ice at 0.0 °C. The ice melts, and when the system comes to equilibrium the temperature of the water is 78.0 °C. What was the original temperature (in °C) of the iron?

Data: The specific heat capacity of liquid water is $4.184 \text{ J K}^{-1} \text{ g}^{-1}$.
The specific heat capacity of solid iron is $0.450 \text{ J K}^{-1} \text{ g}^{-1}$.
The molar enthalpy of fusion of ice (water) is $6.007 \text{ kJ mol}^{-1}$.

The heat from the iron is used to melt the ice and to warm the water from 0.0 °C to 78.0 °C.

**The molar mass of H₂O is $(2 \times 1.008 \text{ (H)} + 16.00 \text{ (O)}) \text{ g mol}^{-1} = 18.02 \text{ g mol}^{-1}$.
Hence 50.0 g of ice corresponds to:**

$$\text{number of moles} = \text{mass} / \text{molar mass} = (50.0 \text{ g}) / (18.02 \text{ g mol}^{-1}) = 2.775 \text{ mol.}$$

Hence the heat used to melt ice is:

$$q_1 = 6.007 \text{ kJ mol}^{-1} \times 2.775 \text{ mol} = 16.67 \text{ kJ} = 16670 \text{ J}$$

The heat used to warm 50.0 g water by 78.0 °C is:

$$q_2 = m \times C \times \Delta T = (50.0 \text{ g}) \times (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (78.0 \text{ K}) = 16320 \text{ J}$$

Overall, the heat transferred from the iron is:

$$q = q_1 + q_2 = 16670 \text{ J} + 16320 \text{ J} = 32990 \text{ J}$$

This heat is lost from 150.0 g of iron leading to it cooling by ΔT :

$$q = m \times C \times \Delta T = (150.0 \text{ g}) \times (0.450 \text{ J K}^{-1} \text{ g}^{-1}) \times \Delta T = 32990 \text{ J}$$

$$\Delta T = 489 \text{ K} = 489 \text{ °C}$$

As the final temperature of the iron is 78.0 °C, its original temperature was $(78.0 + 489) \text{ °C} = 567 \text{ °C}$.

Answer: **567 °C**

Marks
5

- 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, and that the salt does not significantly change the density of the water from 1.00 kg L^{-1} , determine the concentration (in mol L^{-1}) of NaCl in this sample. (The molal freezing point depression constant for H_2O is $1.86\text{ }^{\circ}\text{C m}^{-1}$)

The freezing point depression, ΔT_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 particles dissolved in a kilogram of solvent.

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

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

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

As the density of the solution is 1.00 kg L^{-1} , a kilogram of solution has a volume of one litre. Hence:

$$\text{concentration required} = 0.578\text{ mol L}^{-1}$$

Answer: 0.578 mol L^{-1}

In principle, it would be possible to desalinate this water by pumping it into a cylindrical tower, and allowing gravity to push pure water through a semipermeable membrane at the bottom. At $25\text{ }^{\circ}\text{C}$, how high would the tower need to be for this to work? (The density of liquid Hg at $25\text{ }^{\circ}\text{C}$ is 13.53 g cm^{-3} .)

The osmotic pressure, Π , is given by $\Pi = cRT$ where c is the concentration of the particles. From above, $c = (2 \times 0.578)\text{ mol L}^{-1}$ and so:

$$\Pi = (2 \times 0.578\text{ mol L}^{-1}) \times (0.08206\text{ atm L mol}^{-1}\text{ K}^{-1}) \times (298\text{ K}) = 28.3\text{ atm}$$

As $1\text{ atm} = 760\text{ mmHg}$, this corresponds to $(28.3 \times 760)\text{ mmHg} = 21500\text{ mmHg}$.

Considering the relative densities of water and Hg, the height of water required to exert this pressure would be:

$$21500\text{ mmHg} = (21500 \times \frac{13.53}{1.000})\text{ mmH}_2\text{O} = 291000\text{ mmH}_2\text{O} \text{ or } 291\text{ mH}_2\text{O}.$$

The tower would need to be 291 m in height.

Answer: 291 m

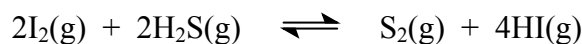
- At 700 °C, hydrogen and iodine react according to the following equation.



Hydrogen also reacts with sulfur at 700 °C:



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



Marks
5

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



The 1st reaction is doubled so the original equilibrium constant is squared.

The 2nd reaction is reversed so the reciprocal of the equilibrium constant is used.

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

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

$$K_c = 2.23 \times 10^{-5}$$

What is the standard free energy change at 700 °C for this overall equilibrium reaction?

The equilibrium constant in terms of pressures is first converted into the equilibrium constant in terms of pressures using $K_p = K_c(RT)^{\Delta n}$. The reaction involves the conversion of 4 mol of gas to 5 mol of gas so $\Delta n = +1$ and:

$$K_p = K_c(RT)^{\Delta n} = (2.23 \times 10^{-5}) \times (0.08206 \times 973)^1 = 0.00178$$

Note that as K_c is in terms of concentration units of mol L⁻¹, $R = 0.08206$ atm L mol⁻¹ K⁻¹ has been used.

As $\Delta G^\circ = -RT \ln K_p$:

$$\Delta G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (973 \text{ K}) \times \ln(0.00178) = +51.2 \text{ kJ mol}^{-1}$$

$$\text{Answer: } +51.2 \text{ kJ mol}^{-1}$$

THIS QUESTION CONTINUES ON THE NEXT PAGE.

If 0.250 mol of HI(g) is introduced into a 2.00 L flask at 700 °C, what will be the concentration of I₂(g) at equilibrium?

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

	H ₂ (g)	I ₂ (g)	\rightleftharpoons	2HI(g)
Initial	0	0		0.125
Change	+x	+x		-2x
Equilibrium	x	x		0.125 - 2x

Thus,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.125-2x)^2}{(x)(x)} = \frac{(0.125-2x)^2}{x^2} = 49.0 \text{ (from 2008-N-5)}$$

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

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

Answer: **0.0139 M**

If 0.274 g of H₂S were now introduced into the same flask, what would be the concentration of S₂(g) at equilibrium?

The molar mass of H₂S is $(2 \times 1.008 \text{ (H)} + 32.06 \text{ (S)}) = 34.08 \text{ g mol}^{-1}$. Hence, 0.274 g of H₂S corresponds to:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} \\ &= (0.274 \text{ g}) / (34.08 \text{ g mol}^{-1}) = 8.04 \times 10^{-3} \text{ mol} \end{aligned}$$

The initial concentration of H₂S is thus $8.04 \times 10^{-3} \text{ mol} / 2.00 \text{ M} = 4.02 \times 10^{-3} \text{ M}$.

From above, $[\text{I}_2(\text{g})] = 0.0139 \text{ M}$ and $[\text{HI}(\text{g})] = (0.125 - 2 \times 0.0139) \text{ M} = 0.00972 \text{ M}$.

Using the overall equilibrium reaction derived in 2008-N-5:

	2I ₂ (g)	2H ₂ S(g)	\rightleftharpoons	S ₂ (g)	4HI(g)
Initial	0.0139	0.00402		0	0.00972
Change	-2x	-2x		+x	+2x
Equilibrium	0.0139 - 2x	0.00402 - 2x		x	0.00972 + 4x

ANSWER CONTINUES ON THE NEXT PAGE

Thus,

$$K_c = \frac{[\text{S}_2][\text{HI}]^4}{[\text{I}_2]^2[\text{I}_2]^2} = \frac{(x)(0.00972+4x)^4}{(0.0139-2x)^2(0.00402-2x)^2}$$
$$\sim \frac{(x)(0.00972)^4}{(0.0139)^2(0.00402)^2} = 2.23 \times 10^{-5} \text{ (from 2008-N-5)}$$

where the small x approximation has been used as K_c is so small. This gives:

$$x = [\text{S}_2(\text{g})] = 7.82 \times 10^{-10} \text{ M}$$

Answer: $7.82 \times 10^{-10} \text{ M}$

- Calculate the pH of a 0.10 mol L^{-1} solution of HF. (The $\text{p}K_a$ of HF is 3.17.)

Marks
6

HF is a weak acid so the equilibrium concentrations need to be calculated using a reaction table:

	HF	\rightleftharpoons	$\text{H}^+(\text{aq})$	$\text{F}^-(\text{aq})$
Initial	0.10		0	0
Change	-x		+x	+x
Equilibrium	$0.10 - x$		x	x

As $\text{p}K_a = -\log_{10}K_a$, at equilibrium,

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{F}^-(\text{aq})]}{[\text{HF}(\text{aq})]} = \frac{(x)(x)}{(0.10-x)} = \frac{x^2}{(0.10-x)} = 10^{-3.17}$$

As K_a is so small, x will be tiny and $0.10 - x \sim 0.10$ and so

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

As $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$,

$$\text{pH} = -\log_{10}(0.00822) = 2.09$$

Answer: **2.09**

What mass of NaF needs to be added to 100.0 mL of the above solution to make a buffer with a pH of 3.00?

Using the Henderson-Hasselbalch equation for the pH of the buffer:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

To make a buffer with $\text{pH} = 3.00$ and $[\text{acid}] = [\text{HF}] = 0.10 \text{ M}$:

$$3.00 = 3.17 + \log\left(\frac{[\text{F}^-]}{0.10}\right) \text{ or } \log\left(\frac{[\text{F}^-]}{0.10}\right) = -0.17$$

Hence,

$$[\text{F}^-] = 0.10 \times 10^{-0.17} = 0.068 \text{ M}$$

The number of moles in 100.0 mL is thus 0.0068 mol. As NaF will dissolve to give one F^- per formula unit, this is also the number of moles of NaF required.

ANSWER CONTINUES ON THE NEXT PAGE

The formula mass of NaF is $(22.99 \text{ (Na)} + 19.00 \text{ (F)}) \text{ g mol}^{-1} = 41.99 \text{ g mol}^{-1}$. The mass of NaF required is thus:

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{formula mass} \\ &= (0.0068 \text{ mol}) \times (41.99 \text{ g mol}^{-1}) = 0.28 \text{ g} \end{aligned}$$

Answer: **0.28 g**

Explain why HCl is a much stronger acid than HF.

Cl is a much larger atom than F and is less electronegative. The H–Cl bond is therefore much longer and weaker than the H–F bond. The H–Cl bond is therefore easier to break and it is the stronger acid.

HF is actually a weak acid. F is smaller and more electronegative than O, so the H–F bond is stronger than the O–H bond. There is consequently little dissociation of HF when it is dissolved in water.

Marks
5

- Cisplatin, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, is a particularly effective chemotherapy agent against certain types of cancer. Calculate the concentration of $\text{Pt}^{2+}(\text{aq})$ ions in solution when 0.075 mol of cisplatin is dissolved in 1.00 L of a 1.00 M solution of NH_3 .
 K_{stab} of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] = 3.4 \times 10^{12}$.

The initial concentration of cisplatin when 0.075 mol is dissolved in 1.00 L is 0.075 M.

As K_{stab} refers to the formation of the complex, the reaction table is:

	$\text{Pt}^{2+}(\text{aq})$	$2\text{Cl}^-(\text{aq})$	$2\text{NH}_3(\text{aq})$	\rightleftharpoons	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
Initial	0	0	1.00		0.075
Change	+x	+2x	+2x		-x
Equilibrium	x	2x	1.00 + 2x		0.075 - x

Hence:

$$K_{\text{stab}} = \frac{[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]}{[\text{Pt}^{2+}][\text{Cl}^-]^2[\text{NH}_3]^2} = \frac{(0.075-x)}{(x)(2x)^2(1.00+2x)^2} = 3.4 \times 10^{12}$$

As K_{stab} is so large, x will be very, very small and so $(1.00 + 2x) \sim 1.00$ and $(0.075 - x) \sim 0.075$. With this:

$$K_{\text{stab}} \sim \frac{(0.075)}{(x)(2x)^2(1.00)^2} = \frac{(0.075)}{(4x)^3} = 3.4 \times 10^{12}$$

$$x = [\text{Pt}^{2+}(\text{aq})] = 1.8 \times 10^{-5} \text{ M}$$

Answer: $1.8 \times 10^{-5} \text{ M}$

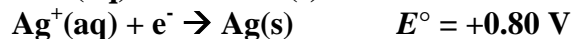
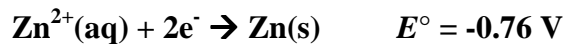
What changes would occur to the values of K_{stab} for cisplatin and the concentration of $\text{Pt}^{2+}(\text{aq})$ ions if solid KCl were dissolved in the above solution?

K_{stab}	increase	<u>no change</u>	decrease
$[\text{Pt}^{2+}(\text{aq})]$	increase	no change	<u>decrease</u>

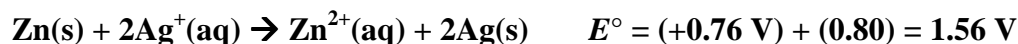
- K_{stab} is the stability constant – it is a constant at any given temperature.
- From Le Chatelier's principle, if $[\text{Cl}^-(\text{aq})]$ is increased then the equilibrium will shift to the right and so $[\text{Pt}^{2+}(\text{aq})]$ will decrease.

- A galvanic cell is made of a Zn^{2+}/Zn half cell with $[\text{Zn}^{2+}] = 2.0 \text{ M}$ and an Ag^+/Ag half cell with $[\text{Ag}^+] = 0.050 \text{ M}$. Calculate the electromotive force of the cell at 25°C .

The standard reduction reactions and potentials for the two half cells are:



The least positive (Zn^{2+}/Zn) couple is reversed giving the overall reaction:



As non-standard concentrations are used, the cell potential is calculated using the Nernst equation. The reaction involves the transfer of 2e^- so with $n = 2$ this becomes:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Ag}^+(\text{aq})]^2} \right)$$

$$= (+1.56 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \left(\frac{2.0}{0.050^2} \right) = +1.47 \text{ V}$$

Answer: +1.47 V

Calculate the equilibrium constant of the reaction at 25°C .

The equilibrium constant is related to the standard cell potential:

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

Hence,

$$\ln K = E^\circ \times \frac{nF}{RT} = (1.56 \text{ V}) \times \frac{(2 \times 96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 121.5$$

$$K = 5.9 \times 10^{52}$$

Answer: $K = 5.9 \times 10^{52}$

Calculate the standard Gibbs free energy of the reaction at 25°C .

Using $\Delta G^\circ = nFE^\circ$:

$$\Delta G^\circ = -(2 \times 96485 \text{ C mol}^{-1}) \times (+1.56 \text{ V}) = -301 \text{ kJ mol}^{-1}$$

Answer: -301 kJ mol^{-1}

Indicate whether the reaction is spontaneous or not. Give a reason for your answer.

As $E > 0$, $\Delta G^\circ < 0$ and K is very large: the reaction is spontaneous.

Express the overall reaction in the shorthand voltaic cell notation.

$\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) (2.0 \text{ M}) \parallel \text{Ag}^+(\text{aq}) (0.050 \text{ M}) \mid \text{Ag(s)}$

<ul style="list-style-type: none">Outline the rules that determine nuclear stability.	Marks 3
<p>The ratio of neutrons to protons (N/Z) is approximately 1 for low atomic numbers ($Z \leq 20$), but it slowly rises to about 1.5 as Z increases.</p> <p>All elements with $Z > 83$ are unstable.</p> <p>Atoms with even numbers of N and Z tend to be more stable than those with odd numbers. There are some particularly stable nuclei where the number of neutrons and or protons = 2, 8, 20, 28, 50, 82 and 126.</p>	
<ul style="list-style-type: none">Explain why surface effects are important in colloidal systems.	2
<p>The small size of the colloidal particles means that they have a very large total surface area.</p> <p>The colloid can be stabilised by steric and/or electrostatic effects. If surface interactions are unfavourable, they are minimised by flocculation and coagulation.</p>	

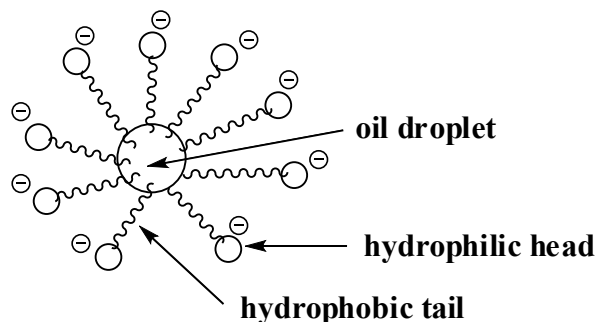
- Explain how soap acts to remove oil.

Marks
2

Soap molecules consist of a long hydrophobic tail and a charged hydrophilic head.

The molecules are able to form micelles (see diagram below) in which the tails interact with the oil particles and the heads interact with the water.

In this way, the oil is dissolved in the water and can be removed.



- A melt of NaCl is electrolysed for 35 minutes with a current of 3.50 A. Calculate the mass of sodium and volume of chlorine at 40 °C and 1.00 atm that are formed.

4

The number of moles of electrons delivered by a current, I , of 3.50 A in 35 minutes is:

$$\text{number of moles of electrons} = \frac{It}{F} = \frac{(3.50 \text{ A})(35 \times 60 \text{ s})}{(96485 \text{ C mol}^{-1})} = 0.076 \text{ mol}$$

The overall electrolysis reaction, $\text{NaCl(l)} \rightarrow \text{Na(s)} + \frac{1}{2}\text{Cl}_2\text{(g)}$, corresponds to reduction of Na^+ and oxidation of Cl^- :



As one mole of electrons would produce one mole of Na and half a mole of Cl_2 :

$$\text{number of moles of Na} = 0.076 \text{ mol}$$

$$\text{number of moles of Cl}_2 = \frac{1}{2} \times 0.076 \text{ mol} = 0.038 \text{ mol}$$

The mass of Na produced is therefore:

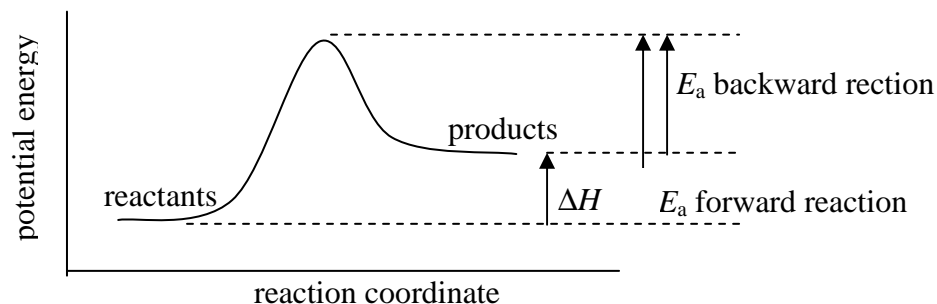
$$\begin{aligned} \text{mass of Na} &= \text{number of moles} \times \text{atomic mass} \\ &= (0.076 \text{ mol}) \times (22.99 \text{ g mol}^{-1}) = 1.8 \text{ g} \end{aligned}$$

Using the ideal gas law, $PV = nRT$, the volume of Cl_2 produced is:

$$V = \frac{nRT}{P} = \frac{(0.038 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(313 \text{ K})}{(1.00 \text{ atm})} = 0.98 \text{ L}$$

Marks
4

- Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reaction, and the enthalpy of reaction.



As the reaction is endothermic, the energy of the products is higher than that of the reactants.

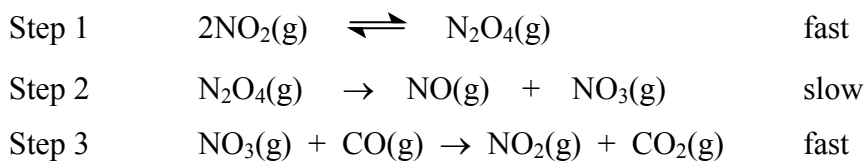
Would you expect the forward or the reverse reaction to be faster? Why?

The backward reaction would be faster as it has a lower activation energy.

This is a consequence of the reaction being endothermic. As the products have higher energy than the reactants and the same transition state is involved in both the forward and backward reactions, the activation energy for the backward reaction is larger than that for the forward reaction.

Marks
4

- Consider the reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
The experimentally determined rate equation is: $\text{Rate} = k[\text{NO}_2(\text{g})]^2$
Show the rate expression is consistent with the following mechanism:



Step 2 is rate determining step and this will determine the rate of the reaction. The subsequent step can be ignored in working out the rate.

Step 2 involves the decomposition of N_2O_4 and depends only on its concentration:

$$\text{rate} = k_2[\text{N}_2\text{O}_4(\text{g})]$$

As this involves the concentration of a reaction intermediate, it is not experimentally testable. The rate law should only involve the concentration of reactants, as their concentrations can be controlled.

As step 2 is slow, step 1 will be able to reach rapid equilibrium.

The forward reaction involves two NO_2 molecules reacting so has a rate:

$$\text{rate of forward reaction} = k_1[\text{NO}_2(\text{g})]^2$$

The backward reaction involves the decomposition of N_2O_4 and so depends only on its concentration:

$$\text{rate of backward reaction} = k_{-1}[\text{N}_2\text{O}_4(\text{g})]$$

If step 1 is at equilibrium then the rate of the forward and backward reactions will be equal:

$$k_1[\text{NO}_2(\text{g})]^2 = k_{-1}[\text{N}_2\text{O}_4(\text{g})] \text{ or } [\text{N}_2\text{O}_4(\text{g})] = \frac{k_1}{k_{-1}} [\text{NO}_2(\text{g})]^2 = K_{\text{eq}}[\text{NO}_2(\text{g})]^2$$

Using this expression for $[\text{N}_2\text{O}_4(\text{g})]$ gives:

$$\text{rate} = k_2[\text{N}_2\text{O}_4(\text{g})] = \frac{k_1 k_2}{k_{-1}} [\text{NO}_2(\text{g})]^2 \text{ or } \text{rate} = k_2 K_{\text{eq}} [\text{NO}_2(\text{g})]^2$$

This is consistent with the experiment rate law with $k = \frac{k_1 k_2}{k_{-1}} = k_2 K_{\text{eq}}$.

ANSWER CONTINUES ON THE NEXT PAGE

- The rate constant of a particular reaction quadruples when the temperature is increased from 30 °C to 50 °C. Calculate the activation energy, E_a , for this reaction.

The temperature dependence of the rate constant is given by the Arrhenius equation, $k = A\exp(-E_a/RT)$. Taking the natural logarithm of this gives:

$$\ln k = \ln A - \frac{E_a}{RT}$$

The rate constant at one temperature is thus related to that at another temperature by:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

If the rate constant quadruples then $\frac{k_2}{k_1} = 4$. With $T_2 = 323$ K and $T_1 = 303$ K:

$$\ln(4) = \frac{E_a}{R} \left(\frac{1}{323} - \frac{1}{303}\right)$$

$$E_a = +56.4 \text{ kJ mol}^{-1}$$

$$E_a = +56.4 \text{ kJ mol}^{-1}$$

Marks
8

- An Ag electrode immersed in a saturated aqueous solution of AgBr has a reduction potential of 0.437 V at 25 °C with respect to the standard hydrogen electrode. Calculate the solubility product of AgBr at 25 °C.

The standard potential for the reduction $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$, $E^\circ = +0.80 \text{ V}$.

The aqueous solution of AgBr will have $[\text{Ag}^+(\text{aq})]$ equal to the solubility of AgBr. This solution has a non-standard concentration of $\text{Ag}^+(\text{aq})$ and its potential is given by the Nernst equation with $n = 1$ for this reduction:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{F} \ln \left(\frac{1}{[\text{Ag}^+(\text{aq})]} \right)$$

$$E = (+0.80 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(1 \times 96485 \text{ C mol}^{-1})} \ln \left(\frac{1}{[\text{Ag}^+(\text{aq})]} \right) = +0.437 \text{ V}$$

This gives $[\text{Ag}^+(\text{aq})] = 7.25 \times 10^{-7}$.

As dissolution of AgBr(s) leads to equal amounts of $\text{Ag}^+(\text{aq})$ and $\text{Br}^-(\text{aq})$, this is also equal to $[\text{Br}^-(\text{aq})]$. Thus:

$$K_{\text{sp}} = [\text{Ag}^+(\text{aq})][\text{Br}^-(\text{aq})] = (7.25 \times 10^{-7})^2 = 5.3 \times 10^{-13}$$

Answer: $K_{\text{sp}} = 5.3 \times 10^{-13}$

A Pd electrode immersed in an aqueous solution containing 0.01 Pd(NO₃)₂ M and 1.00 M NaCl has a reduction potential of -0.860 V at 25 °C with respect to the Ag electrode above. Calculate the stability constant of the complex ion, $[\text{PdCl}_4]^{2-}$, at 25 °C.

The standard potential for the reduction $\text{Pd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pd}(\text{s})$, $E^\circ = +0.92 \text{ V}$.

The reduction potential of the Pd cell is -0.860 V with respect to the Ag electrode, which has a potential of +0.437 V. Thus,

$$E = (-0.860 + 0.437 \text{ V}) = -0.423 \text{ V}.$$

The aqueous solution will have a non-standard concentration of $\text{Pd}^{2+}(\text{aq})$ and its potential is given by the Nernst equation with $n = 2$ for this reduction:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{2F} \ln \left(\frac{1}{[\text{Pd}^{2+}(\text{aq})]} \right)$$

$$E = (+0.92 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \left(\frac{1}{[\text{Pd}^{2+}(\text{aq})]} \right) = -0.423 \text{ V}$$

This gives $[\text{Pd}^{2+}(\text{aq})] = 3.7 \times 10^{-46}$.

ANSWER CONTINUES ON THE NEXT PAGE

For the formation of $[\text{PdCl}_4]^{2-}(\text{aq})$, the reaction table is:

	$\text{Pd}^{2+}(\text{aq})$	$4\text{Cl}^{-}(\text{aq})$	\rightleftharpoons	$[\text{PdCl}_4]^{2-}$
Initial	0.01	1.00		0
Equilibrium	3.7×10^{-46}	0.96		0.01

As $[\text{Pd}^{2+}(\text{aq})]_{\text{eq}}$ is so small, *essentially* all of the initially present Pd^{2+} reacts with 4Cl^{-} to make $[\text{PdCl}_4]^{2-}$ so $[\text{Cl}^{-}]_{\text{eq}} = 1.00 - 4 \times 0.01 \text{ M} = 0.96 \text{ M}$ and $[\text{PdCl}_4]^{2-} = 0.01 \text{ M}$.

Hence:

$$K_{\text{stab}} = \frac{[\text{PdCl}_4^{2-}]}{[\text{Pd}^{2+}][\text{Cl}^{-}]^4} = \frac{0.01}{(3.7 \times 10^{-46})(0.96)^4} = 3 \times 10^{43}$$

Answer: 3×10^{43}