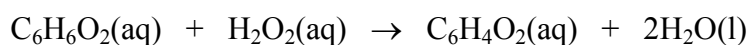
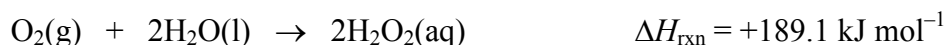
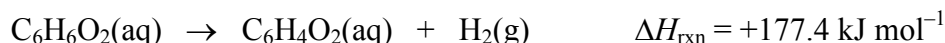


Marks
8

- The conversion of hydroquinone ($C_6H_6O_2(aq)$) to quinone ($C_6H_4O_2(aq)$) is involved in many important biochemical reactions. The bombardier beetle, for example, uses the explosive reaction between hydroquinone and hydrogen peroxide (as described by the equation below) as a defence mechanism.



From the following reaction data, calculate ΔH_{rxn} for the reaction between 1.00 mol of hydroquinone and 1.00 mol of hydrogen peroxide.



$O_2(aq)$ and $H_2O_2(aq)$ and this is related to reaction (1) and the reverse of reaction (2). As the former generates $H_2(g)$ and the latter $O_2(g)$ neither of which are present in the conversion reaction, they are combined with the reverse of reaction (3).

To ensure a balance equation, the combination is thus (1) – $\frac{1}{2}$ × (2) – (3):

				ΔH_{rxn}
(1)	$C_6H_6O_2$	\rightarrow	$C_6H_4O_2 + H_2$	177.4
- $\frac{1}{2}$ × (2)	H_2O_2	\rightarrow	$\frac{1}{2}O_2 + H_2O$	- $\frac{1}{2}$ x 1891.
- (3)	$H_2 + \frac{1}{2}O_2$	\rightarrow	H_2O	- 285.8
	$C_6H_6O_2 + H_2O_2$	\rightarrow	$C_6H_4O_2 + 2H_2O$	-203 kJ mol ⁻¹

$$\Delta H_{rxn} = -203 \text{ kJ mol}^{-1}$$

Use the answer you obtained above to calculate the heat liberated (in joules) in the oxidation of 3.86×10^{-4} mol of hydroquinone to quinone.

As 203 kJ are liberated by 1 mol, the heat change for 3.86×10^{-4} mol is:

$$q = (203 \text{ kJ mol}^{-1}) \times (3.86 \times 10^{-4} \text{ mol}) = 0.0784 \text{ kJ} = 78.4 \text{ J}$$

Answer: **78 J**

Calculate the temperature rise of 0.250 g of water for this quantity of heat. (The heat capacity of water, $C_p = 4.184 \text{ J K}^{-1} \text{ g}^{-1}$)

Using, $q = m \times C \times \Delta T$,

$$\Delta T = \frac{q}{m \times C} = \frac{(78.4 \text{ J})}{(0.250 \text{ g}) \times (4.184 \text{ J K}^{-1} \text{ g}^{-1})} = 74.9 \text{ K}$$

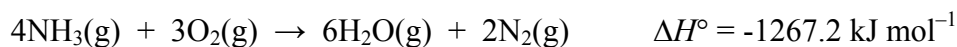
Answer: **74.9 K**

Marks
6

- The final step in the industrial production of urea, $\text{CO}(\text{NH}_2)_2$, is:



Using the following data, calculate the standard enthalpy of formation ΔH°_f of solid urea.



Using $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants})$, $\Delta_{\text{rxn}} H^\circ$ for the industrial production of urea is given by

$$\Delta_{\text{rxn}} H^\circ = [\Delta_f H^\circ (\text{H}_2\text{O}(\text{l})) + \Delta_f H^\circ (\text{CO}(\text{NH}_2)_2(\text{s}))] - [\Delta_f H^\circ (\text{CO}_2(\text{g})) + 2\Delta_f H^\circ (\text{NH}_3(\text{g}))]$$

$\Delta_f H^\circ (\text{NH}_3(\text{g}))$ is not known. $\text{NH}_3(\text{g})$ is produced in the reverse of reaction (1). Reaction (1) requires formation of $\text{H}_2\text{O}(\text{l})$ which is given by reaction (3). Combining these two reactions therefore allows $\Delta_f H^\circ (\text{NH}_3(\text{g}))$ to be calculated.



Therefore, $\Delta_f H^\circ (\text{NH}_3) = \frac{1}{4} (1267.2 - 3 \times 483.8) \text{ kJ mol}^{-1} = -46.05 \text{ kJ mol}^{-1}$.

Hence for the industrial production of urea,

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= [(0.5 \times -483.6) + \Delta_f H^\circ (\text{CO}(\text{NH}_2)_2(\text{s}))] - [(-393.5) + (2 \times -46.05)] \text{ kJ mol}^{-1} \\ &= -90.1 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, $\Delta_f H^\circ (\text{CO}(\text{NH}_2)_2(\text{s})) = 333.6 \text{ kJ mol}^{-1}$

$$\Delta H^\circ_f = -333.6 \text{ kJ mol}^{-1}$$

ANSWER CONTIUNES ON THE NEXT PAGE

The formation of urea in this process is only spontaneous above 821 °C. What is the value of the entropy change ΔS° (in $\text{J K}^{-1} \text{mol}^{-1}$) for the reaction?

For a reaction to be spontaneous requires $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0$.

At 821 °C, $\Delta H^\circ - T\Delta S^\circ = 0$ so

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{(-90.1 \times 10^3 \text{ J mol}^{-1})}{(821+273)\text{K}} = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Actually, the question is incorrect. Above this temperature, ΔG° is positive and the reaction is non-spontaneous. This can be verified by substituting a higher temperature into $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

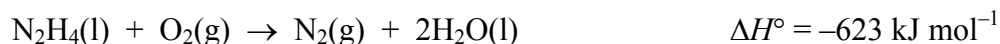
$$\Delta S^\circ = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Rationalise the sign of ΔS° in terms of the physical states of the reactants and products.

ΔS° is negative as 3 moles of gas react to give 1 mole of gas and 1 mole of solid. There is a decrease in randomness.

Marks
3

- The combustion of hydrazine, N_2H_4 , with oxygen is described by the following equation:



Given that ΔH°_f of $\text{H}_2\text{O}(\text{l})$ is -286 kJ mol^{-1} , find the standard enthalpy of formation of $\text{N}_2\text{H}_4(\text{l})$.

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

$$\Delta_{\text{rxn}} H^\circ = [\Delta_f H^\circ (\text{N}_2(\text{g})) + 2\Delta_f H^\circ (\text{H}_2\text{O}(\text{l}))] - [\Delta_f H^\circ (\text{N}_2\text{H}_4(\text{l})) + \Delta_f H^\circ (\text{O}_2(\text{g}))]$$

As $\Delta_f H^\circ = 0$ for an element in its standard state, this becomes:

$$\Delta_{\text{rxn}} H^\circ = [0 + (2 \times -286)] - [\Delta_f H^\circ (\text{N}_2\text{H}_4(\text{l})) + 0] = -623$$

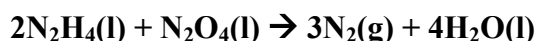
Hence,

$$\Delta_f H^\circ (\text{N}_2\text{H}_4(\text{l})) = +51 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_f = +51 \text{ kJ mol}^{-1}$$

The combustion of 1.00 mol of $\text{N}_2\text{H}_4(\text{l})$ can also be accomplished using $\text{N}_2\text{O}_4(\text{l})$ as the oxidant, whereupon 629 kJ of energy is released at standard temperature and pressure. What is the standard enthalpy of formation of $\text{N}_2\text{O}_4(\text{l})$?

The chemical equation for the combustion of $\text{N}_2\text{H}_4(\text{l})$ with $\text{N}_2\text{O}_4(\text{l})$ is:



As written, this reaction corresponds to burning two moles of $\text{N}_2\text{H}_4(\text{l})$ and hence $\Delta_{\text{rxn}} H^\circ = 2\Delta_{\text{comb}} H^\circ = 2 \times (-629 \text{ kJ mol}^{-1}) = -1258 \text{ kJ mol}^{-1}$. The negative sign indicates that energy is released during the reaction.

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

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= [3\Delta_f H^\circ (\text{N}_2(\text{g})) + 4\Delta_f H^\circ (\text{H}_2\text{O}(\text{l}))] - [2\Delta_f H^\circ (\text{N}_2\text{H}_4(\text{l})) + \Delta_f H^\circ (\text{N}_2\text{O}_4(\text{l}))] \\ &= [(3 \times 0) + (4 \times -286)] - [(2 \times +51) + \Delta_f H^\circ (\text{N}_2\text{O}_4(\text{l}))] = -1258 \end{aligned}$$

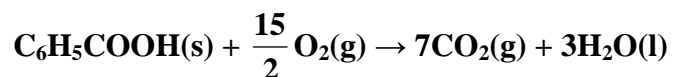
Hence,

$$\Delta_f H^\circ (\text{N}_2\text{O}_4(\text{l})) = +12 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_f = +12 \text{ kJ mol}^{-1}$$

Marks
6

- High-purity benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, ($\Delta H^\circ_{\text{comb}} = -3227 \text{ kJ mol}^{-1}$) is used to calibrate a bomb calorimeter that has a 1.000 L capacity. A 1.000 g sample of $\text{C}_6\text{H}_5\text{COOH}$ is placed in the bomb calorimeter, along with 750 mL of pure $\text{H}_2\text{O}(\text{l})$, and the remaining 250 mL cavity is filled with pure $\text{O}_2(\text{g})$ at 10.00 atm. The $\text{C}_6\text{H}_5\text{COOH}$ is ignited and completely burned, causing the temperature of the water and the bomb calorimeter to rise from 27.20 °C to 33.16 °C. Write the chemical equation corresponding to the standard enthalpy of combustion ($\Delta H^\circ_{\text{comb}}$) of $\text{C}_6\text{H}_5\text{COOH}$.



Given that $\text{H}_2\text{O}(\text{l})$ has a heat capacity of $4.184 \text{ J K}^{-1} \text{ g}^{-1}$ and a density of 0.997 g mL^{-1} , calculate the heat capacity of the bomb calorimeter itself (in units of J K^{-1}). Ignore the heat capacity of the gases and of $\text{C}_6\text{H}_5\text{COOH}$.

The molar mass of $\text{C}_6\text{H}_5\text{COOH}$ is $(7 \times 12.01 \text{ (C)}) + (6 \times 1.008 \text{ (H)}) + (2 \times 16.00 \text{ (O)}) = 122.118$. Therefore 1.000 g corresponds to:

$$\text{amount of } \text{C}_6\text{H}_5\text{COOH} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.000}{122.118} = 0.008189 \text{ mol}$$

As combustion of 1 mol gives out 3227 kJ of heat, this amount gives out:

$$q = 0.008189 \times 3227 = 26.42 \text{ kJ} = 26.43 \times 10^3 \text{ J}$$

This heat leads to a temperature increase of $(33.16 - 27.20) = 5.96 \text{ }^\circ\text{C}$ for the combination of the calorimeter and the water. As water has a density of 0.997 g mL^{-1} , 750 mL has a mass of $750 \times 0.997 \text{ g}$.

$$q = (mC_{\text{water}} + C_{\text{calorimeter}}) \times \Delta T$$

$$= ((750 \times 0.997 \times 4.184) + (C_{\text{calorimeter}})) \times 5.96 = 26.42 \times 10^3$$

$$C_{\text{calorimeter}} = 1305 \text{ J K}^{-1}$$

Answer: **1305 J K⁻¹**

ANSWER CONTINUES ON THE NEXT PAGE

If 30.0% of the CO₂ produced dissolves in the water, calculate the final total pressure (in atm) inside the 250 mL cavity of the bomb calorimeter. Assume oxygen is insoluble in water and ignore the vapour pressure of water.

Initially, 10.00 atm of oxygen is present in a volume of 250 mL and a temperature of 27.20 °C. Using the ideal gas equation, $PV = nRT$,

$$\text{initial } n_{\text{O}_2(\text{g})} = \frac{PV}{RT} = \frac{(10.00) \times (0.250)}{(0.08206) \times (273 + 27.20)} = 0.1015 \text{ mol}$$

From the chemical equation, $\frac{15}{2}$ mol of O₂ are required for the combustion of every mole of C₆H₅COOH. As 0.008189 mol of C₆H₅COOH is present,

$$\text{consumed } n_{\text{O}_2(\text{g})} = 0.008189 \times \frac{15}{2} = 0.06142 \text{ mol}$$

Therefore,

$$\text{final } n_{\text{O}_2(\text{g})} = 0.1015 - 0.06142 = 0.0400 \text{ mol}$$

From the chemical equation, 7 moles of CO₂ are produced for the combustion every mole of C₆H₅COOH. As 0.008189 mol of C₆H₅COOH is present,

$$\text{total } n_{\text{CO}_2} = 0.008189 \times 7 = 0.05732 \text{ mol}$$

As 30% of this dissolves,

$$n_{\text{CO}_2(\text{g})} = 0.70 \times 0.05732 = 0.04013 \text{ mol}$$

The total number of moles of O₂(g) and CO₂(g) is therefore 0.0400 + 0.04013 = 0.0801. This is present in 250 mL at 33.16 °C. Using the ideal gas law,

$$P = \frac{nRT}{V} = \frac{(0.0801) \times (0.08206) \times (273 + 33.16)}{0.250} = 8.05 \text{ atm}$$

Answer: 8.05 atm

Marks
2

- The specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and the specific heat capacity of copper is $0.39 \text{ J g}^{-1} \text{ K}^{-1}$. If the same amount of energy were applied to a 1.0 mol sample of each substance, both initially at $25 \text{ }^\circ\text{C}$, which substance would get hotter? Show all working.

Using $q = C \times m \times \Delta T$, the temperature change for a substance of mass m and specific heat capacity C when an amount of heat equal to q is supplied is given by:

$$\Delta T = \frac{q}{C \times m}$$

The atomic mass of copper is 63.55. Hence, the temperature change for 1.0 mol of copper is

$$\Delta T (\text{copper}) = \frac{q}{(0.39 \times 63.55)} = \frac{q}{24.8} \text{ }^\circ\text{C}$$

The molar mass of H_2O is $(2 \times 1.008 (\text{H})) + 16.00 (\text{O}) = 18.016$. Hence, the temperature change for 1.0 mol of water is

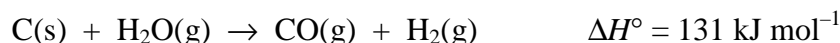
$$\Delta T (\text{water}) = \frac{q}{(4.18 \times 18.016)} = \frac{q}{75.3} \text{ }^\circ\text{C}$$

Hence,

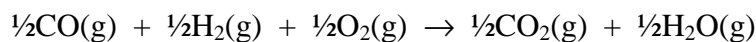
$$\Delta T (\text{copper}) > \Delta T (\text{water})$$

Answer: **Copper**

- “Water gas” is a mixture of combustible gases produced from steam and coal according to the following reaction:



The equation for the complete combustion of 1 mol of water gas (*i.e.* 0.5 mol CO(g) and 0.5 mol H₂(g)) can be written as:



Calculate the standard enthalpy of combustion of water gas, given the following thermochemical data.

$$\Delta H^\circ_{\text{vap}}(\text{H}_2\text{O}) = 44 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{H}_2\text{O(l)}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{CO}_2\text{(g)}) = -393 \text{ kJ mol}^{-1}$$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_{\text{f}}H^\circ(\text{products}) - \sum n\Delta_{\text{f}}H^\circ(\text{reactants})$ for the vaporization of water ($\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$) gives

$$\begin{aligned} \Delta_{\text{vap}}H^\circ &= [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})] - [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(l)})] \\ &= [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})] - (-286) = +44 \end{aligned}$$

Hence $\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)}) = (+44) + (-286) = -242 \text{ kJ mol}^{-1}$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_{\text{f}}H^\circ(\text{products}) - \sum n\Delta_{\text{f}}H^\circ(\text{reactants})$ for the reaction,

$\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2\text{(g)}$ gives

$$\begin{aligned} \Delta_{\text{rxn}}H^\circ &= [\Delta_{\text{f}}H^\circ(\text{CO(g)})] - [\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})] \\ &= [\Delta_{\text{f}}H^\circ(\text{CO(g)})] - (-242) = +131 \end{aligned}$$

as $\Delta_{\text{f}}H^\circ(\text{H}_2\text{(g)})$ and $\Delta_{\text{f}}H^\circ(\text{C(s)})$ are both zero for elements in their standard states. Hence $\Delta_{\text{f}}H^\circ(\text{CO(g)}) = -111 \text{ kJ mol}^{-1}$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_{\text{f}}H^\circ(\text{products}) - \sum n\Delta_{\text{f}}H^\circ(\text{reactants})$ for the reaction,

$\frac{1}{2}\text{CO(g)} + \frac{1}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \frac{1}{2}\text{CO}_2\text{(g)} + \frac{1}{2}\text{H}_2\text{O(g)}$ gives

$$\Delta_{\text{comb}}H^\circ = \left[\frac{1}{2}\Delta_{\text{f}}H^\circ(\text{CO}_2\text{(g)}) + \frac{1}{2}\Delta_{\text{f}}H^\circ(\text{H}_2\text{O(g)})\right] - \left[\frac{1}{2}\Delta_{\text{f}}H^\circ(\text{CO(g)})\right]$$

as the enthalpy of formation of H₂(g) and O₂(g) are both zero for elements in their standard states. Hence,

$$\Delta_{\text{comb}}H^\circ = \left[\left(\frac{1}{2} \times -393\right) + \left(\frac{1}{2} \times -242\right)\right] - \left[\left(\frac{1}{2} \times -111\right)\right] = -262 \text{ kJ mol}^{-1}$$

Answer: -262 kJ mol⁻¹

THIS QUESTION CONTINUES ON THE NEXT PAGE.

- A solution of 2.00 M NaOH (50.0 mL) at 44.9 °C is added to a constant pressure (“coffee cup”) calorimeter containing 250.0 mL of 0.70 M HNO₃ at 21.5 °C. The final temperature of the solution is 29.9 °C. Calculate the enthalpy of neutralisation of OH⁻(aq) and H⁺(aq) in kJ mol⁻¹. Assume the density of these solutions is 1.000 g mL⁻¹ and the specific heat capacity of the solutions is 4.184 J K⁻¹ g⁻¹.

The final temperature is due to both the mixing of two solutions with different initial temperatures and the chemical reaction. It is convenient to treat these two processes separately.

(i) Temperature change due to mixing:

The NaOH(aq) and HNO₃(aq) solutions are initially at 44.9 °C and 21.5 °C. When mixed, heat from the former will warm up the latter to give a solution with temperature T_m .

50.0 mL of NaOH(aq) corresponds to $(50.0 \text{ mL} \times 1.000 \text{ g mL}^{-1}) = 50.0 \text{ g}$. The heat *lost* by this mass is given by:

$$q_1 = mC\Delta T = 50.0 \times 4.184 \times (T_m - 44.9)$$

250.0 mL of HNO₃(aq) corresponds to $(250.0 \text{ mL} \times 1.000 \text{ g mL}^{-1}) = 250.0 \text{ g}$. The heat *gained* by this mass is given by:

$$q_2 = mC\Delta T = 250.0 \times 4.184 \times (T_m - 21.5)$$

As the heat lost by NaOH(aq) is gained by the HNO₃(aq), $q_1 = -q_2$ and so:

$$50.0 \times 4.184 \times (T_m - 44.9) = -1 \times 250.0 \times 4.184 \times (T_m - 21.5)$$

so $T_m = 25.4 \text{ °C}$

(ii) Temperature change due to reaction:

The final temperature is 29.9 °C so the temperature change due to the reaction must be $(29.9 - T_m) = (29.9 - 25.4) = 4.5 \text{ °C}$. The mixed solution has a total volume of $(50.0 + 250.0) = 300.0 \text{ mL}$.

This volume has a mass of $(300.0 \text{ mL} \times 1.000 \text{ g mL}^{-1}) = 300.0 \text{ g}$. The heat change corresponding to this mass and temperature increase is therefore:

$$q_r = mC\Delta T = 300.0 \times 4.184 \times 4.5 = 5600 \text{ J} = 5.6 \text{ kJ}$$

The reaction is a 1:1 neutralization reaction, $\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{aq})$.

ANSWER CONTINUES ON THE NEXT PAGE

The number of moles of $\text{OH}^{\text{-(aq)}}$ present in 50.0 mL of the 2.00 M NaOH solution is:

$$\text{number of moles} = \text{concentration} \times \text{volume} = 2.00 \times 0.0500 = 0.100 \text{ mol}$$

The number of moles of $\text{H}^{\text{+(aq)}}$ present in 250.0 mL of the 0.70 M HNO_3 solution is:

$$\text{number of moles} = \text{concentration} \times \text{volume} = 0.70 \times 0.2500 = 0.175 \text{ mol}$$

The $\text{H}^{\text{+}}$ is therefore in excess and the $\text{OH}^{\text{-}}$ is the limiting reagent.

As 0.100 mol generates a heat change of 5.6 J, the enthalpy of neutralization is:

$$\Delta_{\text{r}}H = \frac{-5.6 \text{ kJ}}{0.1 \text{ mol}} = -56 \text{ kJ mol}^{-1}$$

The reaction increases the temperature and so must be exothermic.

Answer: **56 kJ mol⁻¹**

Calculate the pH in the combined solution in the calorimeter at 21.5 °C.

As 0.100 mol of $\text{OH}^{\text{-(aq)}}$ reacts with 0.175 mol of $\text{H}^{\text{+(aq)}}$, the final solution contains $(0.175 - 0.100) = 0.075$ mol of unreacted $\text{H}^{\text{+(aq)}}$.

The final solution has a volume of 300.0 mL so,

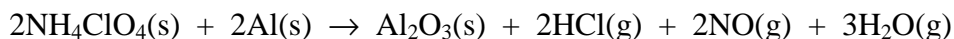
$$[\text{H}^{\text{+(aq)}}] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.075 \text{ mol}}{0.3000 \text{ L}} = 0.25 \text{ M}$$

Hence,

$$\text{pH} = -\log_{10}[\text{H}^{\text{+(aq)}}] = -\log_{10}(0.25) = 0.60$$

Answer: **pH = 0.60**

- Ammonium perchlorate mixed with powdered aluminium powers the space shuttle booster rockets:



Given the following thermochemical data, how much heat would be released per gram of Al(s)?

$$\Delta H_f^\circ (\text{H}_2\text{O}(\text{l})) = -285.1 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (\text{Al}_2\text{O}_3(\text{s})) = -1669.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (\text{NO}(\text{g})) = 90.4 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (\text{NH}_4\text{ClO}_4(\text{s})) = -290.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (\text{HCl}(\text{g})) = -92.3 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vap}}^\circ (\text{H}_2\text{O}) = 44.1 \text{ kJ mol}^{-1}$$

Marks
3

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

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= \sum \Delta_f H^\circ (\text{Al}_2\text{O}_3(\text{s})) + 2\Delta_f H^\circ (\text{HCl}(\text{g})) + 2\Delta_f H^\circ (\text{NO}(\text{g})) + 3\Delta_f H^\circ (\text{H}_2\text{O}(\text{g})) \\ &\quad - \sum 2\Delta_f H^\circ (\text{NH}_4\text{ClO}_4(\text{s})) + 2\Delta_f H^\circ (\text{Al}(\text{s})) \\ &= [(-1669.8) + 2(-92.3) + 2(90.4) + 3(-285.1 + 44.1)] - [2(-290.6) + 2(0)] \\ &= -1815.4 \text{ kJ mol}^{-1} \end{aligned}$$

In this calculation, $\Delta_f H^\circ (\text{Al}(\text{s})) = 0$ for an element in its standard state and $\Delta_f H^\circ (\text{H}_2\text{O}(\text{g})) = \Delta_f H^\circ (\text{H}_2\text{O}(\text{l})) + \Delta_{\text{vap}} H^\circ (\text{H}_2\text{O})$ have been used.

As written, this enthalpy change is for the reaction of two moles of Al(s). Therefore, per mole of Al(s), $\Delta H^\circ = \frac{1}{2} \times -1815.4 \text{ kJ mol}^{-1} = -907.7 \text{ kJ mol}^{-1}$.

As the atomic mass of aluminium is 26.98 g mol^{-1} , the heat released per gram of Al is:

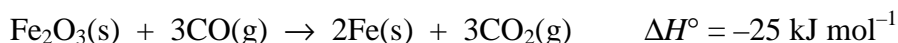
$$q = \frac{-907.7 \text{ kJ mol}^{-1}}{26.98 \text{ g mol}^{-1}} = 33.64 \text{ kJ g}^{-1}$$

Answer: **33.64 kJ g⁻¹**

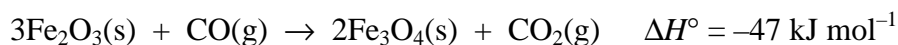
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

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:

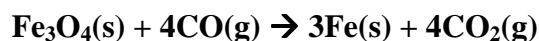


Incomplete reduction, however, results in the formation of magnetite, Fe_3O_4 :

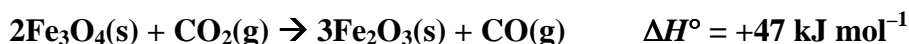


Use these heats of reaction to calculate the enthalpy change when one mole of magnetite is reduced to iron metal using carbon monoxide.

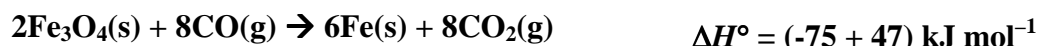
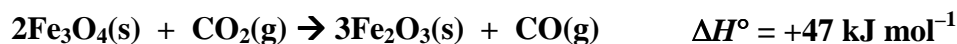
The required reaction is:



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 :

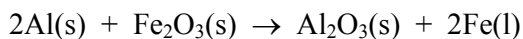
$$q = m \times C \times \Delta T = (150.0 \text{ g}) \times (0.450 \text{ J K}^{-1} \text{ g}^{-1}) \times \Delta T = 32990 \text{ J}$$

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

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**

- The thermite reaction is written below. Show that the heat released in this reaction is sufficient for the iron to be produced as molten metal.



Assume that the values in the table are independent of temperature.

Substance	Enthalpy of formation, $\Delta_f H^\circ$ kJ mol ⁻¹	Molar heat capacity, C_p J K ⁻¹ mol ⁻¹	Melting point °C	Enthalpy of fusion kJ mol ⁻¹
Al	0	24	660	11
Al ₂ O ₃	-1676	79	2054	109
Fe	0	25	1535	14
Fe ₂ O ₃	-824	104	1565	138

Marks
6

Assume 1 mol of reactants at initial temperature of 25 °C. Need to show that ΔH for the reaction is *greater* than the amount of energy required to melt 2 mol of Fe(s) and heat all the products (2 mol of Fe(s) + 1 mol of Al₂O₃(s)) to the melting point of Fe.

$$\begin{aligned}\Delta H &= \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants}) \\ &= \Delta_f H(\text{Al}_2\text{O}_3\text{(s)}) + 2\Delta_f H(\text{Fe(s)}) - (2\Delta_f H(\text{Al(s)}) + \Delta_f H(\text{Fe}_2\text{O}_3\text{(s)})) \\ &= [(-1676 + 2 \times 0) - (-824 + 2 \times 0)] \text{ kJ mol}^{-1} \\ &= -852 \text{ kJ mol}^{-1}\end{aligned}$$

ΔH to heat 2 mol of Fe(s) to its melting point

$$\begin{aligned}\Delta H &= n_{\text{Fe(s)}} \times C_p(\text{Fe(s)}) \times \Delta T \\ &= (2 \text{ mol}) \times (25 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1535 - 25) \text{ K} = 75.5 \text{ kJ}\end{aligned}$$

ΔH to heat 1 mol of Al₂O₃(s) to melting point of Fe(s)

$$\begin{aligned}\Delta H &= n_{\text{Al}_2\text{O}_3\text{(s)}} \times C_p(\text{Al}_2\text{O}_3\text{(s)}) \times \Delta T \\ &= (1 \text{ mol}) \times (79 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1535 - 25) \text{ K} = 119 \text{ kJ}\end{aligned}$$

ΔH to melt 2 mol of Fe(s)

$$\Delta H = 2 \times \Delta_{\text{fus}} H^\circ = (2 \text{ mol}) \times (14 \text{ kJ mol}^{-1}) = 28 \text{ kJ}$$

Total energy required to melt the iron = (75.5 + 119 + 28) kJ = +222.5 kJ.

The energy generated by the reaction is more than enough to melt the iron.