The atmosphere of Venus contains 96.5% CO$_2$ at 95 atm of pressure, leading to an average global surface temperature of 462°C. The energy density of solar radiation striking Venus is 2625 J m$^{-2}$ s$^{-1}$. The radius of Venus is 6052 km, and the average albedo (the fraction of solar radiation reflected back into space) of its surface is 0.90. Calculate the magnitude of the greenhouse effect on Venus.

An albedo of 0.90 means that 90% of the solar energy is reflected and only 10% is available to heat the planet. If Venus has a radius $R$, the energy input from the Sun is:

$$E_{\text{in}} = (2625 \times \pi R^2 \times 0.10) \text{ J}$$

The energy output from the surface area $4\pi R^2$ is:

$$E_{\text{out}} = (4\pi R^2 \times 5.67 \times 10^{-8} \times T^4) \text{ J}$$

At equilibrium, the energy input and output are equal and so the temperature can be calculated:

$$2625 \times \pi R^2 \times 0.10 = 4\pi R^2 \times 5.67 \times 10^{-8} \times T^4$$

$$T^4 = 0.10 \times 2625 / (4 \times 5.67 \times 10^{-8}) \text{ K}$$

so $T = 184 \text{ K}$

As the actual temperature on Venus is 462°C = 735 K, the magnitude of the greenhouse effect is:

$$\text{greenhouse effect} = (735 - 185) \text{ K} = 551 \text{ K}$$

Answer: 551 K

The main absorption bands of CO$_2$ lie in the energy range 600 – 750 cm$^{-1}$. What range of wavelengths (in nm) corresponds to this energy range?

600 cm$^{-1}$ corresponds to a wavelength of (1/600) cm = 0.00167 cm. As 1 cm = 0.01 m and 1 nm = 10$^{-9}$ m, this corresponds to 16700 nm.

750 cm$^{-1}$ corresponds to a wavelength of (1/750) cm = 0.00133 cm. As 1 cm = 0.01 m and 1 nm = 10$^{-9}$ m, this corresponds to 13300 nm.

Answer continues on the next page
Sketch the emission spectrum of Venus on the axes below. Note the wavelength of maximum intensity, and point out any other important features.

The wavelength corresponding to the intensity maximum is given by Wien’s displacement law:

\[ T \lambda_{\text{max}} \approx 2.898 \times 10^6 \text{ K nm} \]

Using \( T = 735 \text{ K} \), \( \lambda_{\text{max}} \approx (2.898 \times 10^6 \text{ K nm}) / (735 \text{ K}) = 3940 \text{ nm} \)
The structural formula of nitroglycerine, $C_3H_5N_3O_9$, is shown below.

Write a balanced equation for the explosive decomposition of liquid nitroglycerine. The products are water, carbon dioxide, nitrogen and oxygen.

$$2C_3H_5N_3O_9(l) \rightarrow 5H_2O(g) + 6CO_2(g) + 3N_2(g) + \frac{1}{2}O_2(g)$$

The standard enthalpy change associated with this explosive decomposition is $-1414$ kJ mol$^{-1}$. What other factor(s) would contribute to the free energy released in the decomposition of nitroglycerine?

As $\Delta G = \Delta H - T\Delta S$, a highly negative value for $\Delta G$ can arise through a highly negative $\Delta H$ value (as here) and also a positive $\Delta S$ value.

In the reaction, each mole of liquid reactant is converted into 7.25 mol of gases. This gives a highly positive $\Delta S$ value.

Briefly describe a calorimetry experiment that could reliably measure the enthalpy of decomposition of nitroglycerine.

A bomb calorimeter (i.e. a constant volume calorimeter) of known heat capacity would be used.

It would be charged with a known amount of water and nitroglycerine, which is then decomposed. By measuring the temperature of the water in the calorimeter before and after decomposition, the enthalpy change for the reaction can be calculated.
When 20.0 mL of 0.250 M Ba(OH)$_2$ at 47.5 °C is added to a constant pressure ("coffee cup") calorimeter containing 200.0 mL of 0.500 M H$_2$SO$_4$ also at 47.5 °C, a white precipitate is formed. The final temperature of the solution is 46.4 °C. Given that the enthalpy of neutralisation of H$^+$ (aq) and OH$^-$ (aq) is $-56.5$ kJ mol$^{-1}$, and assuming that the specific heat capacity and density of all solutions involved are the same as that of pure water ($c = 4.184$ J K$^{-1}$ g$^{-1}$ and $\rho = 1.000$ g mL$^{-1}$), calculate the enthalpy of solution of BaSO$_4$ in kJ mol$^{-1}$.

The number of moles of H$^+$ = 0.2000 L $\times$ 0.500 mol L$^{-1}$ $\times$ 2) = 0.200 mol. The number of moles of OH$^-$ = 0.0200 L $\times$ 0.250 mol L$^{-1}$ $\times$ 2) = 0.0100 mol. Hence, the limiting reagent is OH$^-$.

The enthalpy change due to neutralisation is therefore

$$\Delta_{\text{neutralisation}}H^0 = (0.0100 \text{ mol}) \times (-56.5 \times 10^3 \text{ J mol}^{-1}) = -565 \text{ J}$$

The volume of the combined solutions is 220.0 mL. As the density is 1.000 g mL$^{-1}$, the mass of the solution is 220.0 g. Using $q = mc\Delta T$, the temperature rise from the neutralisation reaction is

$$\Delta T_{\text{neutralisation}} = \frac{q_{\text{neutralisation}}}{mc}$$
$$\Delta T_{\text{neutralisation}} = \frac{(565 \text{ J})}{(220.0 \text{ g} \times 4.184 \text{ J K}^{-1} \text{ g}^{-1})} = +0.614 \text{ K}$$

As an overall temperature decrease from 47.5 °C to 46.4 °C, corresponding to 1.1 K, is observed:

$$\Delta T_{\text{overall}} = \Delta T_{\text{neutralisation}} + \Delta T_{\text{precipitation}}$$
$$\Delta T_{\text{precipitation}} = \Delta T_{\text{overall}} - \Delta T_{\text{precipitation}} = [(-1.1) - (0.614)] = -1.7 \text{ K}$$

The heat change due to precipitation is therefore

$$q_{\text{precipitation}} = mc\Delta T_{\text{precipitation}} = (220.0 \text{ g}) \times (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (-1.7 \text{ K}) = 1570 \text{ J}$$

The number of moles of Ba$^{2+}$ is 0.050 mol so this amount of BaSO$_4$ precipitates. Hence, the molar enthalpy of precipitation is:

$$\Delta_{\text{precipitation}}H^0 = (1570 \text{ J}) / (0.050 \text{ mol}) = 320 \text{ kJ mol}^{-1}$$

Hence, for dissolution:

$$\Delta_{\text{solution}}H^0 = -320 \text{ kJ mol}^{-1}$$

Answer: -320 kJ mol$^{-1}$
• 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 CaCl$_2$ (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 CaCl$_2$.

<table>
<thead>
<tr>
<th>Marks</th>
<th>3</th>
</tr>
</thead>
</table>

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 $(28.97 - 27.00) ^\circ\text{C} = 1.97 ^\circ\text{C} = 1.97 \text{ K}$ 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 CaCl$_2$ is $(40.08 + 2 \times 35.45) \text{ g mol}^{-1} = 110.98 \text{ g mol}^{-1}$. Hence, 1.14 g corresponds to

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

The enthalpy of solution is therefore

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

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
A new process has been developed for converting cellulose from corn waste into the biofuel butanol, C₄H₉OH. A bomb calorimeter with a heat capacity of 3250 J K⁻¹ was used to determine the calorific value by burning 5.0 g of butanol in excess oxygen.

Write a balanced reaction for the combustion of butanol in oxygen.

\[
\text{C}_4\text{H}_9\text{OH}(l) + 6\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(g)
\]

Calculate the heat released from this combustion if the temperature of the calorimeter increased from 23.0 to 78.6 °C during the test.

The heat, \(q\), required to change the temperature of the bomb calorimeter by \(\Delta T\) is given by:

\[
q = C \Delta T
\]

The temperature increases from 23.0 to 78.6 °C corresponding to \(\Delta T = 55.6 \, ^\circ\text{C} = 55.6 \, \text{K}\). Hence:

\[
q = (3250 \, \text{J} \, \text{K}^{-1})(55.6 \, \text{K}) = 181000 \, \text{J} = 181 \, \text{kJ}
\]

Answer: 181 kJ

Use this value to determine the calorific value and molar enthalpy of combustion of butanol.

The calorific value is the energy content per gram. As 5.0 g of butanol releases 181 kJ, the calorific value is:

\[
\text{calorific value} = \frac{181 \, \text{kJ}}{5.0 \, \text{g}} = 36 \, \text{kJ g}^{-1}
\]

The molar enthalpy of combustion is the energy released by combusting one mole. The molar mass of C₄H₉OH is:

\[
\text{molar mass} = (4 \times 12.01 \, (\text{C}) + 10 \times 1.008 \, (\text{H}) + 16.00 \, (\text{O})) \, \text{g} \, \text{mol}^{-1} = 74.12 \, \text{g} \, \text{mol}^{-1}
\]

5.0 g of butanol thus corresponds to:

\[
\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.0 \, \text{g}}{74.12 \, \text{g} \, \text{mol}^{-1}} = 0.067 \, \text{mol}
\]

As 0.067 mol generates 181 kJ when combusted, the molar enthalpy of combustion is negative and is given by:

\[
\Delta H = \frac{-181 \, \text{kJ}}{0.067 \, \text{mol}} = -2.7 \times 10^3 \, \text{kJ} \, \text{mol}^{-1}
\]
Write a balanced equation for (i) the explosive decomposition, and (ii) the combustion
in air, of TNT, C\(_7\)H\(_5\)N\(_3\)O\(_6\)(s).

(i) \(2\text{C}_7\text{H}_5\text{N}_3\text{O}_6\text{(s)} \rightarrow \text{12CO(g)} + \text{3N}_2\text{(g)} + \text{5H}_2\text{(g)} + \text{2C(s)}\)

(ii) \(2\text{C}_7\text{H}_5\text{N}_3\text{O}_6\text{(s)} + \frac{21}{2}\text{O}_2\text{(g)} \rightarrow 14\text{CO}_2\text{(g)} + \text{5H}_2\text{O(g)} + \text{3N}_2\text{(g)}\)

What is the essential difference between these two processes?

In the combustion reaction, the oxidant comes from an external source (air). In the explosion, the oxidant is contained in the explosive material.

What is the increase in the number of moles of gas (per mole of TNT consumed) for each of these two processes?

For process (i), the change in the number of moles of gas, \(\Delta n\), is:

\[
\Delta n = n(\text{moles of gaseous products}) - n(\text{moles of gaseous reactants})
\]
\[
= ((12 + 3 + 5) - (0)) \text{ mol} = 20 \text{ mol}
\]

As (i) involves 2 mol of TNT, \(\Delta n = 10 \text{ mol per mole of TNT}\)

Answer: (i) 10 mol

For process (ii), the change in the number of moles of gas, \(\Delta n\), is:

\[
\Delta n = n(\text{moles of gaseous products}) - n(\text{moles of gaseous reactants})
\]
\[
= ((14 + 5 + 3) - (\frac{21}{2})) \text{ mol} = \frac{23}{2} \text{ mol}
\]

As (i) involves 2 mol of TNT, \(\Delta n = \frac{1}{2} \times \frac{23}{2} \text{ mol per mole of TNT}\)

Answer: (ii) \(\frac{23}{4}\) mol

Which of these two processes releases more energy into the surroundings?

Data: \(\Delta H^\circ(\text{TNT}) = 6.9 \text{ kJ mol}^{-1}\) \(\Delta H^\circ(\text{CO(g)}) = -111 \text{ kJ mol}^{-1}\) \(\Delta H^\circ(\text{CO}_2\text{(g)}) = -393 \text{ kJ mol}^{-1}\) \(\Delta H^\circ(\text{H}_2\text{O(g)}) = -242 \text{ kJ mol}^{-1}\)

Using \(\Delta r H^\circ = \Sigma m \Delta r H^\circ(\text{products}) - \Sigma m \Delta r H^\circ(\text{reactants})\), the enthalpy change for reaction (i) can be written as

\[
\Delta_r H^\circ = [12\Delta r H^\circ(\text{CO(g)})] - [2\Delta r H^\circ(\text{C}_7\text{H}_5\text{N}_3\text{O}_6\text{(s)})]
\]
\[
= ([12 \times -111] - [2 \times 6.9]) \text{ kJ mol}^{-1} = -1346 \text{ kJ mol}^{-1}
\]
Similarly, the enthalpy change for reaction (ii) can be written as

\[ \Delta_r H^\circ = [14\Delta_f H^\circ(CO_2(g)) + 5\Delta_f H^\circ(H_2O(g))] - [2\Delta_f H^\circ(C_7H_5N_3O_6(s))] \]

\[ = ([14 \times -393 + 5 \times -242] - [2 \times 6.9]) \text{ kJ mol}^{-1} = -6726 \text{ kJ mol}^{-1} \]

\( \Delta_f H^\circ(N_2(g)), \Delta_f H^\circ(H_2(g)) \) and \( \Delta_f H^\circ(C(s)) \) all represent formation of the elements from their standard states and are all zero.

The combustion reaction releases more energy.

Answer: combustion reaction
A calorimeter containing 300.0 mL of water at 25 °C was calibrated as follows. A 1000.0 W heating coil was run for 10.0 s, after which time the temperature had increased by 7.5 °C. Calculate the heat capacity of the empty calorimeter. The specific heat of water is 4.184 J K⁻¹ g⁻¹.

With a power of 1000.0 W = 1000.0 J s⁻¹, the amount of heat generated by the coil is:

\[ q = (1000.0 \text{ J s}^{-1}) \times (10.0 \text{ s}) = 1.00 \times 10^3 \text{ J} \]

As the density of water at 25 °C is 0.997 g mL⁻¹, 300.0 mL of water corresponds to:

\[ \text{mass of water} = m = \text{density} \times \text{volume} = (0.997 \text{ g mL}^{-1}) \times (300.0 \text{ mL}) = 299 \text{ g} \]

The heat required to heat this quantity of water by 7.5 °C is:

\[ q = c_{H_2O} \times m_{H_2O} \times \Delta T = (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (299 \text{ g}) \times (7.5 \text{ K}) = 9380 \text{ J} \]

The remaining heat, \((1.00 \times 10^3 - 9380) \text{ J} = 620 \text{ J}\), is used to heat the calorimeter. This also increases in temperature by 7.5 °C so the heat capacity of the calorimeter is:

\[ c_{\text{calorimeter}} = \frac{q}{\Delta T} = \frac{620 \text{ J}}{7.5} = 82 \text{ J K}^{-1} \]

Answer: 82 J K⁻¹

A solution containing 0.040 mol Ag⁺(aq) was mixed with a second solution containing 0.050 mole Br⁻(aq) in this calorimeter, causing AgBr(s) to precipitate. The temperature increased by 2.4 °C. Given the solubility product constant is \(K_{sp}(AgBr) = 5 \times 10^{-13} \text{ M}^2\), calculate the equilibrium concentrations of Ag⁺(aq) and Br⁻(aq) present in the final solution of volume 320 mL.

To calculate the equilibrium constants of Ag⁺(aq) and Br⁻(aq), a reaction table can be used, with \(x\) representing the number of moles which do not precipitate:

<table>
<thead>
<tr>
<th></th>
<th>Ag⁺(aq)</th>
<th>Br⁻(aq)</th>
<th>AgBr(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial (mol)</td>
<td>0.040</td>
<td>0.050</td>
<td>0</td>
</tr>
<tr>
<td>final (mol)</td>
<td>(x)</td>
<td>(0.010 + x)</td>
<td>0.040 - (x)</td>
</tr>
</tbody>
</table>

The concentrations in the final solution of volume 320 mL are therefore:

\[
[\text{Ag}^+(\text{aq})] = \frac{x \text{ mol}}{0.320 \text{ L}} \quad \text{and} \quad [\text{Br}^-(\text{aq})] = \frac{(0.010 - x) \text{ mol}}{0.320 \text{ L}}
\]

Hence, the solubility product is:

**ANSWER CONTINUES ON THE NEXT PAGE**
\[ K_{sp} = [\text{Ag}^+(aq)][\text{Br}^-(aq)] = \left( \frac{x}{0.320} \right) \left( \frac{0.010 - x}{0.320} \right) = 5 \times 10^{-13} \]

\[ K_{sp} \text{ is very small, } x \text{ is tiny and so } 0.010 - x \sim 0.010. \text{ This approximation gives:} \]

\[ \left( \frac{x}{0.320} \right) \left( \frac{0.010}{0.320} \right) = 5 \times 10^{-13} \]

or

\[ [\text{Ag}^+(aq)] = \left( \frac{x}{0.320} \right) = (5 \times 10^{-13}) \times \left( \frac{0.320}{0.010} \right) \text{ M} = 1.6 \times 10^{-11} \text{ M} \]

\[ [\text{Br}^-] = \frac{0.010}{0.320} \text{ M} = 0.031 \text{ M} \]

<table>
<thead>
<tr>
<th>[\text{Ag}^+(aq)]: 1.6 \times 10^{-11} \text{ M}</th>
<th>[\text{Br}^-(aq)]: 0.031 \text{ M}</th>
</tr>
</thead>
</table>

Calculate the enthalpy of solution of AgBr(s).

As the final solution has a volume of 320 mL, its mass is:

\[ \text{mass} = \text{density} \times \text{volume} = (0.997 \text{ g mL}^{-1}) \times (320 \text{ mL}) = 319 \text{ g} \]

The heat produced causes the temperature of this mass of solution and the calorimeter to rise by 2.4 °C:

\[ q = (c_{H_2O} \times m_{H_2O} \times \Delta T) + (c_{\text{calorimeter}} \times \Delta T) \]
\[ = ((4.184 \text{ J K}^{-1} \text{ mol}^{-1}) \times (319 \text{ g}) \times (2.4 \text{ K})) + ((82 \text{ J K}^{-1}) \times (2.4 \text{ K})) \]
\[ = 3400 \text{ J} \]

This corresponds to the heat given out in the precipitation of 0.040 mol of AgBr(s). As the precipitation is exothermic, the heat of solution is endothermic:

\[ \text{heat of solution} = \frac{3400 \text{ J}}{0.040 \text{ mol}} = +85 \text{ kJ mol}^{-1} \]

Answer: +85 kJ mol\(^{-1}\)
Use the figure below to help answer the following.

Write a balanced equation for the smelting of one of these metal oxides with coke in which a major product is CO₂. Give the approximate temperature range over which this reaction is spontaneous and state what happens outside this temperature range.

Between 400 – 950 K, the Ni – NiO lines is below the C – CO₂ line and hence the oxide will be reduced by coke to produce CO₂:

\[ 2\text{NiO}(s) + \text{C}(s) \rightarrow 2\text{Ni}(l) + \text{CO}_2(g) \]

Below 400 K, it appears that the Ni – NiO will be above the C – CO₂ line so this reduction will not occur.

Above 950 K, the C – CO line is higher than the C – CO₂ line so the reduction produces CO₂. (Any CO₂ produced would be reduced by C to produce CO.)

Over what temperature range can ZnO be reduced by Fe? What other metal could be used instead to increase the temperature range in which metallic Zn was produced?

The Zn – ZnO line falls below the Fe – FeO line at approximately 1450 K and reduction of ZnO by Fe will thus occur above this temperature.

The Zn – ZnO line is below the Ca – CaO, Al – Al₂O₃ and Mn – MnO lines over the entire temperature range of the diagram and so Ca, Al or Mn could be used to reduce ZnO at these temperatures.

THIS QUESTION CONTINUES ON THE NEXT PAGE.
Estimate the partial pressure of CO that would be expected at equilibrium in the smelting of ZnO by coke at 1500 K.

At 1500 K,

\[ C + \frac{1}{2}O_2 \rightarrow CO \quad \ln K_p(1) \sim 21 \]
\[ Zn + \frac{1}{2}O_2 \rightarrow ZnO \quad \ln K_p(2) \sim 14 \]

Hence, for:

\[ ZnO + C \rightarrow Zn + CO \]

\[ K_p = p(CO) = \frac{K_p(1)}{K_p(2)} \]

or

\[ \ln K_p = \ln \left( \frac{K_p(1)}{K_p(2)} \right) = \ln K_p(1) - \ln K_p(2) = 21 - 14 = 7 \]

\[ K_p \sim 10^3 \quad \text{and hence } p(CO) \sim 1000 \text{ atm} \]

Metallic copper is produced by smelting chalcopyrite, CuFeS\(_2\)(s), directly in oxygen to produce iron oxides and SO\(_2\). Write a balanced equation for this reaction, and sketch the \(\ln K_p\) versus temperature curve for Cu-CuO on the diagram on page 24. Clearly label the curve you have drawn.

\[ \text{CuFeS}_2(s) + \frac{5}{2}O_2(g) \rightarrow \text{Cu(s)} + \text{FeO(s)} + 2\text{SO}_2(g) \]

The \(\ln K_p\) curve for Cu – CuO lies below Fe – FeO at all temperatures. A sketch (in bold / red) is shown below.
• Write a balanced equation for the combustion of methylhydrazine, CH₃NHNH₂(g).

\[
\text{CH}_3\text{NHNH}_2(g) + \frac{5}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{N}_2(g) + 3\text{H}_2\text{O}(g)
\]

Using bond enthalpies, estimate the enthalpy of combustion of methylhydrazine.

<table>
<thead>
<tr>
<th>Bond</th>
<th>ΔH / kJ mol⁻¹</th>
<th>Bond</th>
<th>ΔH / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–N</td>
<td>285</td>
<td>O–H</td>
<td>464</td>
</tr>
<tr>
<td>N–N</td>
<td>159</td>
<td>O=O</td>
<td>498</td>
</tr>
<tr>
<td>C–H</td>
<td>416</td>
<td>C=O</td>
<td>806</td>
</tr>
<tr>
<td>N–H</td>
<td>391</td>
<td>N≡N</td>
<td>945</td>
</tr>
</tbody>
</table>

\[
\Delta_{\text{atom}}H(\text{CH}_3\text{NHNH}_2) = 3\Delta H(\text{C-H}) + \Delta H(\text{C-N}) + 3\Delta H(\text{N-H}) + \Delta H(\text{N-N})
\]

\[
= (3 \times 416) + (285) + (3 \times 391) + (159) = 2865 \text{ kJ mol}^{-1}
\]

\[
\Delta_{\text{atom}}H(\text{O}_2) = \Delta H(\text{O}=\text{O}) = 498 \text{ kJ mol}^{-1}
\]

\[
\Delta_{\text{atom}}H(\text{CO}_2) = 2 \times \Delta H(\text{C}=\text{O}) = (2 \times 806) = 1612 \text{ kJ mol}^{-1}
\]

\[
\Delta_{\text{atom}}H(\text{N}_2) = \Delta H(\text{N}≡\text{N}) = 945 \text{ kJ mol}^{-1}
\]

\[
\Delta_{\text{atom}}H(\text{H}_2\text{O}) = 2\Delta H(\text{O}=\text{H}) = (2 \times 464) = 928 \text{ kJ mol}^{-1}
\]

\[
\Delta_{\text{comb}}H = \Delta_{\text{atom}}H(\text{reactants}) - \Delta_{\text{atom}}H(\text{products}) =
\]

\[
= [\Delta_{\text{atom}}H(\text{CH}_3\text{NHNH}_2) + \frac{5}{2}\Delta_{\text{atom}}H(\text{O}_2)]
\]

\[
- [\Delta_{\text{atom}}H(\text{CO}_2) + \Delta_{\text{atom}}H(\text{N}_2) + 3\Delta_{\text{atom}}H(\text{H}_2\text{O})]
\]

\[
= [(2865) + (\frac{5}{2} \times 498)] - [(1612) + (945) + (3 \times 928)] = -1231 \text{ kJ mol}^{-1}
\]

Answer: \(-1231 \text{ kJ mol}^{-1}\)

ANSWERS CONTINUES ON THE NEXT PAGE
Liquid methylhydrazine and liquid oxygen can be used as a rocket fuel. Calculate the calorific value (in kJ g\(^{-1}\)) of this fuel.

The molar mass of O\(_2\) is \((2 \times 16.00) = 32.00\). The molar mass of CH\(_3\)NHNH\(_2\) is:

\[
(12.01 \text{ (C)}) + (6 \times 1.008 \text{ (H)}) + (2 \times 14.01 \text{ (N)}) = 46.078
\]

To burn one mole of methylhydrazine requires \(\frac{5}{2}\) moles of liquid O\(_2\) to be carried so the combined mass is \((46.078) + (\frac{5}{2} \times 32.00) = 126.078\).

The calorific value is therefore:

\[
\text{calorific value} = \frac{\Delta_{\text{comb}} H}{\text{molar mass}} = \frac{1231}{126.078} = 9.8 \text{kJ g}^{-1}
\]

Answer: 9.8 kJ g\(^{-1}\)

When methylhydrazine is used as a rocket fuel, the usual oxidant is dinitrogen tetroxide rather than liquid oxygen. Why?

N\(_2\)O\(_4\) has a boiling point of 21 °C, so there are no problems associated with handling cryogenic liquids. N\(_2\)O\(_4\) and methylhydrazine are hypergolic - the reaction occurs spontaneously on contact.
Estimate the average temperature of Mercury given the solar power density at its surface of \(9150 \text{ J m}^{-2} \text{ s}^{-1}\), and assuming an average albedo of 6% and zero Greenhouse effect.

With an albedo of 6%, 94% is not reflected. Hence,

\[
\begin{align*}
E_{\text{out}} &= 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4 \text{ J s}^{-1} \\
E_{\text{in}} &= \pi r^2 \times 9150 \times 0.94 \text{ J s}^{-1}
\end{align*}
\]

These balance at a temperature:

\[
T = \sqrt[4]{\frac{E_{\text{out}}}{E_{\text{in}}}} = 441 \text{ K}
\]

Answer: 441 K
A calorimeter containing 300 mL of water at 25 °C was calibrated as follows. A 1000 W heating coil was run for 10 s, after which time the temperature had increased by 7.5 °C. Calculate the heat capacity of the empty calorimeter. The specific heat of water is 4.184 J K\(^{-1}\) g\(^{-1}\).

The heat generated by running a 1000 W coil for 10 s is \((1000 \times 10) = 1 \times 10^4\) J.

The density of water at 25 °C is 0.997 g cm\(^{-3}\) so 300 mL has a mass of \((300 \times 0.997) = 299\) g.

As \(q = c \times m \times \Delta T\), the heat change of the combined calorimeter and water is:

\[
q = (c_{\text{water}} \times m_{\text{water}} \times \Delta T) + (c_{\text{calorimeter}} \times m_{\text{calorimeter}} \times \Delta T)
\]

\[
= [(4.184 \times 299) + (c_{\text{calorimeter}} \times m_{\text{calorimeter}})] \times 7.5 = 1 \times 10^4
\]

Hence,

\[
c_{\text{calorimeter}} \times m_{\text{calorimeter}} = 82\ J\ K^{-1}
\]

Answer: 82 J K\(^{-1}\)

15.0 g of sodium nitrite was dissolved into this calorimeter, and the temperature of the solution was found to decrease by 2.6 °C. Calculate the enthalpy of solution of sodium nitrite.

From above,

\[
q = [(c_{\text{water}} \times m_{\text{water}}) + (c_{\text{calorimeter}} \times m_{\text{calorimeter}}) \times \Delta T
\]

\[
= [(4.184 \times 299) + (82)] \times 2.6 = 3500\ J
\]

The formula mass of NaNO\(_2\) is \((22.99\) (Na) + 14.01 (N) + \(2 \times 16.00\) (O)) = 69.00.

The number of moles present in 15.0 g is therefore:

\[
\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{15.0}{69.00} = 0.217\ \text{mol}
\]

Hence, the enthalpy of solution is:

\[
\Delta_{\text{solution}}H = \frac{3500}{0.217} = +16100\ J\ \text{mol}^{-1} = +16.1\ kJ\ \text{mol}^{-1}
\]

(The reaction leads to a decrease in the temperature of the water and hence it is endothermic.)

Answer: +16.1 kJ mol\(^{-1}\)
• Use the figure below to help answer the following.

Write a balanced equation for the smelting of NiO by coke. In what temperature range will this process be spontaneous?

\[
\text{NiO}(s) + C(s) \rightleftharpoons \text{Ni}(l) + \text{CO}(g)
\]

The reaction is spontaneous at temperatures where the C-CO line is above the Ni-NiO line.

As marked on the diagram, this occurs at temperatures above \(~620\text{ K}\).

Why are (a) aluminium and (b) tungsten not recovered from their oxides by smelting with coke? What alternative processes are used and why?

Tungsten forms tungsten carbide if smelted with coke. The oxide is usually reduced using another reductant such as \(\text{H}_2\).

Aluminium is usually recovered electrolytically as smelting only occurs at temperatures well above \(1800\text{ K}\), which are not readily achieved.
• Write the equation whose enthalpy change represents the standard enthalpy of formation of hydrazine, $\text{N}_2\text{H}_4(\text{g})$.

$$\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2\text{H}_4(\text{g})$$

Write the equation whose enthalpy change represents the enthalpy of combustion of hydrazine, $\text{N}_2\text{H}_4(\text{g})$ to produce water vapour.

$$\text{N}_2\text{H}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$$

Given the following data, calculate the standard enthalpy of formation of $\text{N}_2\text{H}_4(\text{g})$.

$$\Delta H^\circ_f (\text{H}_2\text{O}(\text{g})) = -242 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{comb}} (\text{N}_2\text{H}_4(\text{g})) = -580 \text{ kJ mol}^{-1}$$

Using $\Delta_{\text{rxn}} H^\circ = \sum m\Delta_f H^\circ(\text{products}) - \sum n\Delta_f H^\circ(\text{reactants})$, the enthalpy change for the combustion reaction is:

$$\Delta_{\text{comb}} H^\circ = [2\Delta_f H^\circ (\text{H}_2\text{O}(\text{g}))] - [\Delta_f H^\circ (\text{N}_2\text{H}_4(\text{l}))]$$ as the remaining compounds are elements in their standard states.

Hence:

$$[2 \times -242] - [\Delta_f H^\circ (\text{N}_2\text{H}_4(\text{l}))] = -580 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{N}_2\text{H}_4(\text{l})) = +96 \text{ kJ mol}^{-1}$$

Answer: $+96 \text{ kJ mol}^{-1}$
• In an experiment, 1.76 g of sodium nitrate was dissolved in water inside a calorimeter. Give a balanced equation for the reaction that took place.

\[
\text{NaNO}_3(s) \rightarrow \text{Na}^+(aq) + \text{NO}_3^-(aq)
\]

The temperature of the solution was found to decrease by 1.22 °C. If the heat capacity of the calorimeter was 77.0 J K\(^{-1}\) and the heat capacity of the solution was 268 J K\(^{-1}\), determine the molar heat of reaction.

The heat change is given by:

\[
q = (c_{\text{calorimeter}} \times \Delta T) + (c_{\text{solution}} \times \Delta T) = (77.0 \times 1.22) + (268 \times 1.22) = 421 \text{ J}
\]

The process is endothermic as the temperature of the solution decreases.

The molar mass of NaNO\(_3\) is \((22.99 \text{ (Na)}) + (14.01 \text{ (N)}) + (3 \times 16.00 \text{ (O)}) = 85\)

The molar heat of reaction is therefore:

\[
q_m = \frac{85}{1.76} \times 421 = 20300 \text{ J mol}^{-1} = 20.3 \text{ kJ mol}^{-1}
\]

Answer: 20.3 kJ mol\(^{-1}\)

How long would it take a 250 W power supply to reheat the calorimeter to its starting temperature?

A 250 W power supply delivers 250 J s\(^{-1}\). As 410 J was removed from the calorimeter and the water inside it to reduce the temperature by 1.22 °C, the power supply will take:

\[
t = \frac{421}{250} = 1.68 \text{ s}
\]
• In an experiment, 50.0 mL of 1.00 M HNO$_3$ was combined with 50.0 mL of 0.540 M NaOH in a calorimeter. Give an equation for the reaction that took place.

H$_3$O$^+$ (aq) + OH$^-$ (aq) $\rightarrow$ 2H$_2$O(l)

The temperature of the solution was found to increase by 2.98 °C. If the heat capacity of the calorimeter was 80.0 J K$^{-1}$ and the heat capacity of the final solution was 426 J K$^{-1}$, determine the molar heat of reaction.

As $q = C \times \Delta T$ for both the calorimeter and the solution,

$q = ((80.0 \times 2.98) \ J) + ((426 \times 2.98) \ J) = 1510 \ J$

As the reaction is a 1:1 reaction and fewer moles of OH$^-$ are present, it is rate limiting. The number of moles of OH$^-$ is:

\[
\text{number of moles of OH}^-= \text{concentration} \times \text{volume} = 0.0500 \ L \times 0.540 \ \text{mol L}^{-1} = 0.027 \ \text{mol}
\]

This number of moles generates 1510 J of heat. The reaction is exothermic as the temperature increases. The enthalpy change for one mole is therefore:

\[
\Delta_rH = \frac{-1510 \ J}{0.027 \ \text{mol}} = -55800 \ \text{J mol}^{-1} = -55.8 \ \text{kJ mol}^{-1}
\]

Answer: $-55.8 \ \text{kJ mol}^{-1}$

The average bond enthalpy of the O-H bond is 463 kJ mol$^{-1}$. Explain briefly why the heat of neutralisation calculated in the first part of this question differs significantly from this value.

The bond enthalpy refers to half the enthalpy change for the reaction H$_2$O(g) $\rightarrow$ O(g) + 2H(g) rather than the transfer of a proton from H$_3$O$^+$ to OH$^-$ in aqueous solution.
When 156 g of aluminium metal at 50.0 °C is added to 100 g of water at 20.0 °C, the final temperature becomes 30.0 °C. The heat capacity of water is 4.18 J K⁻¹ g⁻¹. Calculate the specific heat capacity of aluminium.

Assuming equilibrium has been established and no heat is lost to the surroundings, the heat lost by the aluminium is gained by the water. As \( q = c \times m \times \Delta T \):

\[
c_{\text{water}} \times m_{\text{water}} \times \Delta T_{\text{water}} = c_{\text{aluminium}} \times m_{\text{aluminium}} \times \Delta T_{\text{aluminium}}
\]

or

\[
(4.18 \text{ J K}^{-1} \text{ g}^{-1}) \times (100 \text{ g}) \times ((30.0 - 20.0) \text{ K}) = c_{\text{aluminium}} \times (156 \text{ g}) \times ((50.0 - 30.0) \text{ K})
\]

so,

\[
c_{\text{aluminium}} = 1.34 \text{ J g}^{-1} \text{ mol}^{-1}
\]

Answer: 1.34 J g⁻¹ mol⁻¹

What would the final temperature have been if the 156 g of aluminium metal at 50 °C had been added to iced water containing 10 g ice and 90 g water at 0 °C? \( \Delta H \) for the freezing of water is –6.02 kJ mol⁻¹.

In this case, some of the heat will be used to melt the ice. As the molar mass of H₂O is (2 × 1.008 (H) + 16.00) g mol⁻¹ = 18.016 g mol⁻¹, the number of moles in 10 g of ice is:

\[
\text{moles of ice} = \frac{10 \text{ g}}{18.016 \text{ g mol}^{-1}} = 0.555 \text{ mol}
\]

Hence, the heat required to melt 10 g of ice is

\[
q = (6.02 \times 10^3 \text{ kJ mol}^{-1}) \times (0.555 \text{ mol}) = 3340 \text{ J}
\]

If \( T \) is the final temperature of the water, the overall heat change for the water is the heat required to melt 10 g of ice plus the heat required to warm 100 g of water from 0 °C to \( T \):

\[
q_{\text{water}} = q_{\text{melt}} + (c_{\text{water}} \times m_{\text{water}} \times \Delta T_{\text{water}}) = (3340 + (4.18 \times 100 \times (T - 0))) \text{ J}
\]

This heat is provided by cooling the aluminium from 50 °C to \( T \):

\[
q_{\text{aluminium}} = c_{\text{aluminium}} \times m_{\text{aluminium}} \times \Delta T_{\text{aluminium}} = (1.34 \times 156 \times (50 - T)) \text{ J}
\]

As \( q_{\text{water}} = q_{\text{aluminium}} \),

\[
(3340 + (4.18 \times 100 \times T)) \text{ J} = (1.34 \times 156 \times (50 - T)) \text{ J}
\]

This rearranges to give \( T = 11 \text{ °C} \)

Answer: 11 °C
- If wet silver carbonate is dried in a stream of hot air, the air must have a certain concentration level of carbon dioxide to prevent decomposition by the reaction

\[
\text{Ag}_2\text{CO}_3(s) \rightleftharpoons \text{Ag}_2\text{O}(s) + \text{CO}_2(g)
\]

The enthalpy change, \(\Delta H^\circ\), for this reaction is 79.14 kJ mol\(^{-1}\) in the temperature range of 25 to 125 °C. Given that the partial pressure of CO\(_2\) in equilibrium with solid Ag\(_2\)CO\(_3\) is 8.20 \times 10\(^{-6}\) atm at 25 °C, calculate the partial pressure of CO\(_2\) necessary to prevent decomposition of Ag\(_2\)CO\(_3\) at 110 °C. Assume that \(\Delta S^\circ\) does not change over this temperature range.

As Ag\(_2\)CO\(_3\) and Ag\(_2\)O are present as solids, they are not involved in the equilibrium expression which is simply, \(K_p = p_{\text{CO}_2} = 8.20 \times 10^{-6} \text{ atm} = (8.20 \times 10^{-6} \times 1.01325 \times 10^5) \text{ Pa} = 0.831 \text{ Pa at 298 K.}\)

This is related to \(\Delta_{\text{universe}} S^\circ\) by:

\[
\Delta_{\text{universe}} S^\circ = R \ln K_p = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln(0.831) = -1.54 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
= \Delta_{\text{rxn}} S^\circ - \frac{\Delta_{\text{rxn}} H^\circ}{T} = \{\Delta_{\text{rxn}} S^\circ - \frac{79.14 \times 10^3}{298}\} \text{ J K}^{-1} \text{ mol}^{-1}
\]

Hence, \(\Delta_{\text{rxn}} S^\circ = 264 \text{ J K}^{-1} \text{ mol}^{-1}\).

If \(\Delta_{\text{rxn}} H^\circ\) and \(\Delta_{\text{rxn}} S^\circ\) are the same at 110 °C (378 K), \(\Delta_{\text{universe}} S^\circ\) becomes:

\[
\Delta_{\text{universe}} S^\circ = \Delta_{\text{rxn}} S^\circ - \frac{\Delta_{\text{rxn}} H^\circ}{T} = \{264 - \frac{79.14 \times 10^3}{383}\} \text{ J K}^{-1} \text{ mol}^{-1}
\]

The equilibrium constant at 110 °C (383 K) is then:

\[
K_p = \exp\left(\frac{\Delta_{\text{universe}} S^\circ}{R}\right)
\]

\[
= \exp\left(\frac{57.4}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\right) = 992 \text{ Pa} = 0.00979 \text{ atm} = P_{\text{CO}_2}
\]

\(K_p\) increases with temperature for an endothermic reaction.)

---

Answer: 0.00979 atm