

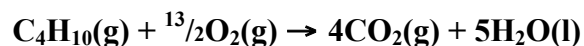
- The Second Law states that all observable processes must involve a net increase in entropy. When liquid water freezes into ice at 0 °C, the entropy of the water decreases. Since the freezing of water is certainly observable, the processes must still satisfy the Second Law. Provide a brief explanation of how this is so.

The freezing of water is exothermic and the heat evolved is passed to the surroundings. This causes an increase in the entropy of the surroundings equal to $\Delta S_{\text{surroundings}} = q/T$ where q is the heat gained by the surroundings and T is the temperature of the surroundings.

As long as the T is *low* enough, the *gain* in entropy in the surroundings, $\Delta S_{\text{surroundings}}$, overcomes the loss in entropy in the water, ΔS_{system} , so that the entropy of the universe increases. Freezing is spontaneous at temperatures below the freezing point.

- Give the balanced chemical equation for the combustion of butane gas, C₄H₁₀, in oxygen to produce CO₂ and water.

Marks
3



Use the standard enthalpies of formation provided to calculate the molar heat of combustion of butane gas. Show all working.

Data:	Compound	H ₂ O(l)	CO ₂ (g)	C ₄ H ₁₀ (g)
	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-285.8	-393.5	-125.6

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

$$\Delta_{\text{combustion}} H^\circ = [4\Delta_f H^\circ(\text{CO}_2(\text{g})) + 5\Delta_f H^\circ(\text{H}_2\text{O}(\text{g}))] - [\Delta_f H^\circ(\text{C}_4\text{H}_{10}(\text{g}))]$$

$\Delta_f H^\circ(\text{O}_2(\text{g}))$ is zero as O₂(g) is already an element in its standard state. Hence:

$$\Delta_{\text{combustion}} H^\circ = ([4 \times -393.5 + 5 \times -285.8] - [-125.6]) \text{ kJ mol}^{-1} = -2877.4 \text{ kJ mol}^{-1}$$

Answer: -2877.4 kJ mol⁻¹

- The Second Law states that all observable processes must involve a net increase in entropy. When liquid water freezes into ice at 0 °C, the entropy of the water decreases. Since the freezing of water is certainly observable, the processes must still satisfy the Second Law. Provide a brief explanation of how this is so.

The Second Law requires that there is a net increase in the entropy of universe:

$$\Delta_{\text{universe}}S = \Delta_{\text{system}}S + \Delta_{\text{surroundings}}S > 0$$

When water freezes, $\Delta_{\text{system}}S < 0$. However, freezing is an exothermic process: heat is given out to the surroundings. The heat gain in the surroundings is equal and opposite to the heat lost in the system: $q_{\text{surr}} = -\Delta_{\text{freezing}}H$. This increases the entropy in the surroundings:

$$\Delta_{\text{surroundings}}S = -\Delta_{\text{freezing}}H / T$$

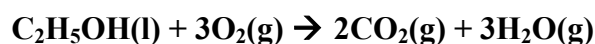
Overall:

$$\Delta_{\text{universe}}S = \Delta_{\text{system}}S - \Delta_{\text{freezing}}H / T$$

As long as the second term is larger than the first, $\Delta_{\text{universe}}S > 0$. This is true at low temperatures.

- Ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$, is increasingly being used as a fuel. Give the balanced chemical equation for the combustion of ethanol in oxygen to produce carbon dioxide and water.

Marks
5



Use the standard enthalpies of formation given below to calculate the molar heat of combustion of gaseous ethanol. Show all working.

Compound	$\text{C}_2\text{H}_5\text{OH}(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-235.3	-393.5	-285.8

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

$$\begin{aligned} \Delta H^\circ &= (2\Delta_f H^\circ(\text{CO}_2(\text{g})) + 3\Delta_f H^\circ(\text{H}_2\text{O}(\text{l}))) - (\Delta_f H^\circ(\text{C}_2\text{H}_5\text{OH}(\text{l})) + 3\Delta_f H^\circ(\text{O}_2(\text{g}))) \\ &= [(2 \times -393.5 + 3 \times -285.8) - (-235.3 + 0)] \text{ kJ mol}^{-1} = -1409.1 \text{ kJ mol}^{-1} \end{aligned}$$

where $\Delta_f H^\circ(\text{O}_2(\text{g}))$ is zero for an element in its standard state.

Answer: **-1409.1 kJ mol⁻¹**

Calculate the volume change when 150 g of liquid ethanol is burnt in an engine at 1500 °C and 2.0 atm pressure. Assume all gases behave as ideal gases. Show all working.

The molar mass of ethanol is:

$$\begin{aligned} \text{molar mass} &= (2 \times 12.01 (\text{C}) + 6 \times 1.008 (\text{H}) + 16.00 (\text{O})) \text{ g mol}^{-1} \\ &= 46.07 \text{ g mol}^{-1} \end{aligned}$$

The number of moles in 150 g is therefore:

$$\text{number of moles} = \text{mass} / \text{molar mass} = 150 \text{ g} / 46.07 \text{ g mol}^{-1} = 3.3 \text{ mol}$$

From the chemical equation when 1 mol of ethanol burns, there is a net increase of 2 mol of gas (3 mol of $\text{O}_2(\text{g})$ is lost and 2 mol of $\text{CO}_2(\text{g})$ and 3 mol of $\text{H}_2\text{O}(\text{g})$ is made). When 3.3 mol of ethanol burns, there is a net increase of 6.6 mol of gas.

With $P = 2.0 \text{ atm}$ and $T = 1500 \text{ }^\circ\text{C}$, the volume increase will be:

$$\begin{aligned} \Delta V &= \Delta n RT / P \\ &= (6.6 \text{ mol}) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times ((1500 + 273) \text{ K}) / 2.0 \text{ atm} \\ &= 470 \text{ L} \end{aligned}$$

Answer: **470 L**

Why can the volume occupied by the liquid ethanol be ignored in this calculation?

The volume occupied by 150 g of ethanol is very small compared to the volume occupied by the gases.

- The Second Law states that all observable processes must involve a net increase in entropy. When liquid water freezes into ice at 0 °C, the entropy of the water decreases. Explain how this is consistent with the Second Law.

Marks
2

The freezing of water is exothermic and the heat evolved is passed to the surroundings. This causes an *increase* in the entropy of the surroundings with $\Delta_{\text{surrounding}}S = \Delta q/T$ where Δq is the heat passed to the surroundings from the freezing of the water.

At low temperatures (below 0 °C), the increase in the entropy of the surroundings is larger than the reduction in entropy of the water itself. There is a net increase in entropy of the universe (system + surroundings) therefore increases, consistent with the Second Law.

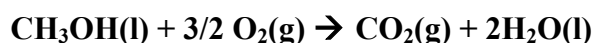
Above 0 °C, $\Delta_{\text{surrounding}}S = \Delta q/T$ is smaller and not enough to overcome the decrease in the entropy of the freezing water.

- Use the standard heats of formation provided to calculate the molar heat of combustion of liquid methanol, CH₃OH, in oxygen to produce CO₂ and water. Your answer must include a balanced chemical equation for this reaction. Show all working.

Marks
2

Data:	Compound	H ₂ O(l)	CH ₃ OH(l)	CO ₂ (g)
	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-285.9	-238.6	-393.5

The chemical equation for the combustion of methanol is:



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

$$\begin{aligned} \Delta H^\circ &= (\Delta_f H^\circ(\text{CO}_2\text{(g)}) + 2\Delta_f H^\circ(\text{H}_2\text{O(l)})) - (\Delta_f H^\circ(\text{CH}_3\text{OH(l)}) + 3/2 \Delta_f H^\circ(\text{O}_2\text{(g)})) \\ &= [(-393.5 + 2 \times -285.9) - (-238.6 + 0)] \text{kJ mol}^{-1} = -726.7 \text{kJ mol}^{-1} \end{aligned}$$

where $\Delta_f H^\circ(\text{O}_2\text{(g)})$ is zero for an element in its standard state.

Answer: **-726.7 kJ mol⁻¹**

- Two samples of iron are prepared so that the heavier has a heat capacity of 50.0 J K^{-1} and the lighter has a heat capacity of 19 J K^{-1} . Initially, the heavier sample is at a temperature of $100.0 \text{ }^\circ\text{C}$ and the lighter sample is at $20.0 \text{ }^\circ\text{C}$. Calculate the final equilibrium temperature after the two samples have been placed in thermal contact. Show working.

Marks
2

The heat lost by the heavier sample is gained by the lighter sample until they reach the same final temperature, T_f .

For the heavier sample, the heat change is:

$$\begin{aligned}q_{\text{heavier}} &= C_{\text{heavier}} \times \Delta T_{\text{heavier}} \\ &= 50.0 \times (T_f - 100.0) \text{ J}\end{aligned}$$

For the lighter sample, the heat change is:

$$\begin{aligned}q_{\text{lighter}} &= C_{\text{lighter}} \times \Delta T_{\text{lighter}} \\ &= 19 \times (T_f - 20.0) \text{ J}\end{aligned}$$

As $q_{\text{heavier}} = -q_{\text{lighter}}$:

$$\begin{aligned}50.0 \times (T_f - 100.0 \text{ }^\circ\text{C}) &= -19 \times (T_f - 20.0 \text{ }^\circ\text{C}) \\ 69 T_f &= 5380\end{aligned}$$

So, $T_f = 78 \text{ }^\circ\text{C}$.

Answer: $78 \text{ }^\circ\text{C}$

- Paraffin wax candles primarily consist of long, saturated, hydrocarbon chains such as triacontane ($C_{30}H_{62}$). Assuming a 1.00 kg candle is made of pure triacontane, how many moles of triacontane will it contain?

Marks
6

The molar mass of $C_{30}H_{62}$ is $(30 \times 12.01 \text{ (C)} + 62 \times 1.008 \text{ (H)}) \text{ g mol}^{-1} = 422.80 \text{ g mol}^{-1}$. The number of moles in 1.00 kg is therefore:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} \\ &= 1.00 \times 10^3 \text{ g} / 422.80 \text{ g mol}^{-1} = 2.37 \text{ mol} \end{aligned}$$

Answer: **2.37 mol**

Estimate the atomisation enthalpy, $\Delta_{\text{atom}}H$, for triacontane, based on the following tabulated average bond enthalpies.

bond	$\Delta H / \text{kJ mol}^{-1}$	bond	$\Delta H / \text{kJ mol}^{-1}$
C–C	346	C–H	414
C–O	358	O–H	463
C=O	804	O=O	498

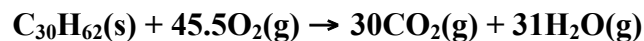
We are told that $C_{30}H_{62}$ is a long, saturated hydrocarbon: it contains a chain of C-C bonds with no branches or double bonds.

As there are 30 C atoms in the chain, there must be 29 C-C bonds. If there are 62 H in the molecule, there must be 62 C-H bonds.

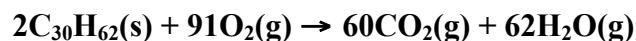
$$\begin{aligned} \Delta_{\text{atom}}H &= 29 \times \Delta H (\text{C-C}) + 62 \times \Delta H (\text{C-H}) \\ &= (29 \times 346 + 62 \times 414) \text{ kJ mol}^{-1} = 3.57 \times 10^4 \text{ kJ mol}^{-1} \end{aligned}$$

Answer: **$3.57 \times 10^4 \text{ kJ mol}^{-1}$**

Write out a chemical equation for the complete combustion of triacontane.



or



ANSWER CONTINUES ON THE NEXT PAGE

Using the same table of average bond enthalpies, estimate the atomisation enthalpy of each product of the complete combustion.

CO₂ contains 2 C=O bonds:

$$\Delta_{\text{atom}}H = 2 \times \Delta H (\text{C=O}) = 2 \times 804 \text{ kJ mol}^{-1} = 1608 \text{ kJ mol}^{-1}$$

H₂O contains 2 O-H bonds:

$$\Delta_{\text{atom}}H = 2 \times \Delta H (\text{O-H}) = 2 \times 463 \text{ kJ mol}^{-1} = 926 \text{ kJ mol}^{-1}$$

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Estimate the molar enthalpy of combustion of triacontane, $\Delta_c H$.

Marks
4

The balanced equation for the combustion is:



The reaction involves (i) atomising $\text{C}_{30}\text{H}_{62}(\text{s})$ and $45.5\text{O}_2(\text{g})$ and (ii) forming 30CO_2 and $31\text{H}_2\text{O}$ from the atoms. Hence:

$$\begin{aligned}\Delta_c H &= \Delta_{\text{atom}} H (\text{C}_{30}\text{H}_{62}) + 45.5 \Delta_{\text{atom}} H (\text{O}_2) \\ &\quad - 30 \Delta_{\text{atom}} H (\text{CO}_2) - 31 \Delta_{\text{atom}} H (\text{H}_2\text{O}) \\ &= ((3.57 \times 10^4) + 45.5 \times (498) \\ &\quad - 30 \times (1608) - 31 \times (926)) \text{ kJ mol}^{-1} \\ &= -1.86 \times 10^4 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Answer: } -1.86 \times 10^4 \text{ kJ mol}^{-1}$$

Using this enthalpy of combustion, calculate the energy released by the combustion of the candle.

As 1.86×10^4 kJ is released per mol, 2.37 mol will release:

$$\Delta H = (1.86 \times 10^4 \text{ kJ mol}^{-1}) \times (2.37 \text{ mol}) = 4.40 \times 10^4 \text{ kJ}$$

$$\text{Answer: } 4.40 \times 10^4 \text{ kJ}$$

- Explain why quartz, $\text{SiO}_2(\text{s})$, does not spontaneously decompose into silicon and oxygen at $25\text{ }^\circ\text{C}$, even though the standard entropy change of the reaction is large and positive.

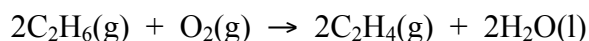


Spontaneity requires a negative Gibbs free energy, *i.e.* $\Delta G = \Delta H - T\Delta S < 0$.

The ΔH component is very large and positive because of the very strong Si-O bonds in SiO_2 , a network covalent compound.

Although ΔS is large and positive, it is not large enough to make the above expression negative, except at very high temperatures when $T\Delta S > \Delta H$.

- In a process called pyrolysis, a hydrocarbon fuel is partially dehydrogenated to produce hydrogen gas, which can then be combined with oxygen to produce water. Using ethane C_2H_6 as the fuel, the overall process is described by the following balanced equation:



$H_2O(l)$	$C_2H_6(g)$	$C_2H_4(g)$	$CO_2(g)$	$CO(g)$
-285.9	-84.67	52.28	-393.5	-110.5

Using heats of formation, calculate the heat of reaction per mole of ethane consumed in the reaction described above.

Using $\Delta_{rxn}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - \sum n\Delta_fH^\circ(\text{reactants})$, the enthalpy of this reaction is:

$$\begin{aligned}\Delta H^\circ &= (2\Delta_fH^\circ(C_2H_4(g)) + 2\Delta_fH^\circ(H_2O(l))) - (2\Delta_fH^\circ(C_2H_6(g)) + \Delta_fH^\circ(O_2(g))) \\ &= [(2 \times 52.28 + 2 \times -285.9) - (2 \times -84.67 + 0)] \text{ kJ mol}^{-1} = -297.9 \text{ kJ mol}^{-1}\end{aligned}$$

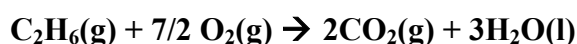
This is for the reaction as written, which consumes 2 mol of C_2H_6 . The heat of reaction per mole of ethane is therefore

$$\Delta H^\circ = \frac{1}{2} \times -297.9 \text{ kJ mol}^{-1} = -149.0 \text{ kJ mol}^{-1}$$

Answer: **-149.0 kJ mol⁻¹**

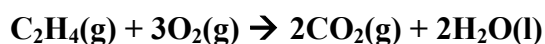
Simply burning ethane in oxygen to produce carbon dioxide and water releases 1560 kJ per mole of ethane consumed. Provide a brief explanation of the difference between the heats of combustion and the pyrolysis-based process described above.

The heat of combustion is for the reaction



This reaction produces much more energy per mole of ethane as its products are more stable.

The C_2H_4 produced in the pyrolysis reaction can itself be burnt to produce more energy



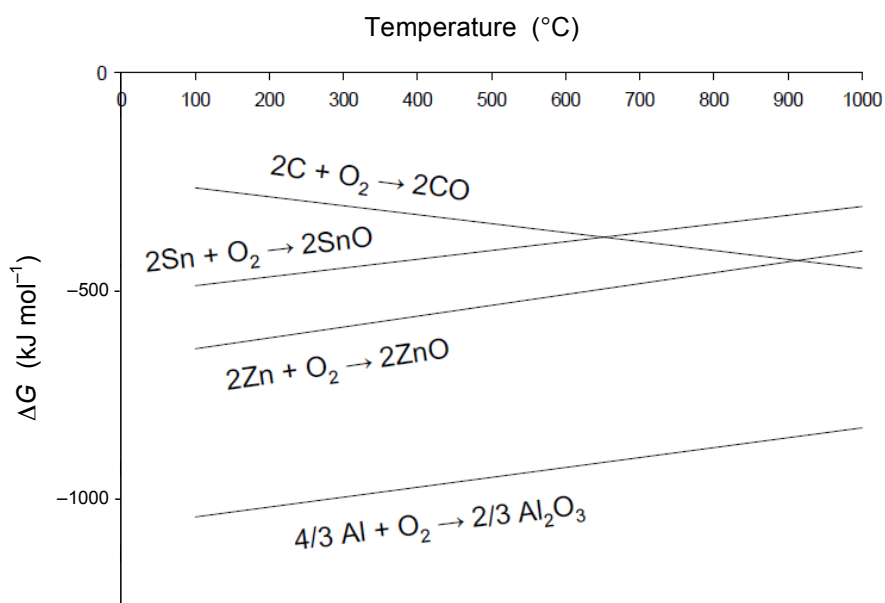
Briefly describe one environmental benefit of using the pyrolysis-based process for energy production.

The pyrolysis reaction does not produce $CO_2(g)$ which is known to contribute to the greenhouse effect.

However, the C_2H_4 gas produced is likely to be a greenhouse gas so would have to be removed and stored for its effect to be removed.

- The diagram below represents the Gibbs Free energy change associated with the formation of 4 different oxides.

Marks
4



Using the free energy data above, write down the equation and indicate with an arrow the direction of the expected spontaneous reaction under the following conditions. If you think no reaction would occur, write “no reaction”.

a) C and SnO are mixed at 400 $^{\circ}\text{C}$

At 400 $^{\circ}\text{C}$, the Sn / SnO line is *below* the C / CO line. Hence, there is no reaction.

b) C and SnO are mixed at 900 $^{\circ}\text{C}$

$\text{SnO} + \text{C} \rightarrow \text{Sn} + \text{CO}$

c) SnO, Sn, Zn and ZnO are mixed at 900 $^{\circ}\text{C}$

$\text{Zn} + \text{SnO} \rightarrow \text{ZnO} + \text{Sn}$

Of the 4 oxide formation reactions, write down one for which the entropy change is negative. Provide a brief explanation for your choice.

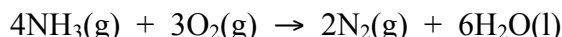
The entropy change is likely to be negative in three of them:

- $2\text{Sn} + \text{O}_2 \rightarrow 2\text{SnO}$**
- $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$**
- $4/3\text{Al} + \text{O}_2 \rightarrow 2/3\text{Al}_2\text{O}_3$**

Each of these involves a *decrease* in the number of moles of gas. Gases have far higher entropy than solids.

The fourth reaction involves an increase in the number of moles of gas so is likely to produce an increase in entropy.

- Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel that produces no greenhouse gases on combustion. In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the following equation.



The initial and final states are at 298 K. After combustion with 14.40 g of O_2 , some NH_3 remains unreacted. Calculate the enthalpy change during the process, given the following data.

$$\Delta_f H^\circ(\text{NH}_3(\text{g})) = -46.11 \text{ kJ mol}^{-1} \text{ and } \Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) = -285.83 \text{ kJ mol}^{-1}$$

O_2 is the limiting reagent and so determines the enthalpy change. The molar mass of O_2

$$\text{molar mass} = (2 \times 16.00) \text{ g mol}^{-1} = 32.00 \text{ g mol}^{-1}.$$

The number of moles in 14.40 g is therefore:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} \\ &= (14.40 \text{ g}) / (32.00 \text{ g mol}^{-1}) = 0.4500 \text{ mol} \end{aligned}$$

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

$$\begin{aligned} \Delta H^\circ &= (2\Delta_f H^\circ(\text{N}_2(\text{g})) + 6\Delta_f H^\circ(\text{H}_2\text{O}(\text{l}))) - (4\Delta_f H^\circ(\text{NH}_3(\text{g})) + 3\Delta_f H^\circ(\text{O}_2(\text{g}))) \\ &= [(0 + 6 \times -285.83) - (4 \times -46.11 + 0)] \text{ kJ mol}^{-1} = -1530.54 \text{ kJ mol}^{-1} \end{aligned}$$

where $\Delta_f H^\circ$ for $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ are zero because they are elements in their standard states.

This quantity is for the reaction as written: it is for the consumption of 3 mol of O_2 . The enthalpy change per mole of O_2 is therefore:

$$\Delta H^\circ = (-1530.54 / 3) \text{ kJ mol}^{-1} = -510.18 \text{ kJ mol}^{-1}$$

The enthalpy change for 0.4500 mol of O_2 is therefore:

$$\Delta H^\circ = (-510.18 \text{ kJ mol}^{-1}) \times (0.4500 \text{ mol}) = -229.6 \text{ kJ}$$

Answer: -229.6 kJ

ANSWER CONTINUES ON THE NEXT PAGE

- ANFO (ammonium nitrate fuel oil) is a powerful explosive used recently in the Oslo bombing. If the fuel oil is replaced by carbon in the form of graphite, calculate what mass of carbon needs to be added to 1.0 kg of ammonium nitrate so that the products of the detonation are N_2 , CO_2 and H_2O .

The molar mass of NH_4NO_3 is:

$$\begin{aligned}\text{molar mass} &= (2 \times 14.01 \text{ (N)}) + (4 \times 1.008 \text{ (H)}) + (3 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} \\ &= 80.052 \text{ g mol}^{-1}\end{aligned}$$

The number of moles in 1.0 kg is therefore:

$$\begin{aligned}\text{number of moles} &= \text{mass} / \text{molar mass} \\ &= (1.0 \times 10^3 \text{ g}) / (80.052 \text{ g mol}^{-1}) = 12.5 \text{ mol}\end{aligned}$$

The balanced equation for the detonation reaction is:



From the chemical equation, the amount of C(s) required is therefore:

$$\text{number of moles} = (12.492 / 2) \text{ mol} = 6.25 \text{ mol}$$

As the molar mass of C is 12.01 g mol^{-1} , this corresponds to:

$$\text{mass} = \text{number of moles} \times \text{molar mass} = (6.25 \text{ mol}) \times (12.01 \text{ g mol}^{-1}) = 75 \text{ g}$$

Answer: 75 g

Marks
3

- Consider the process $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$

Give the sign of ΔH° at 273 K and explain your choice.

ΔH° is positive: the ice is melting so the reaction is endothermic. Energy must be put into the system to break the hydrogen bonds.

Give the sign of ΔS° at 273 K and explain your choice.

ΔS° is positive: the ice is melting so the system goes from solid ice to liquid water. There is increased spreading out of the energy of the system.

How does ΔG° change with an increase in temperature? Explain your answer.

Using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, increasing the temperature will increase the effect of the entropy term.

As ΔS° is positive, $-T\Delta S^\circ$ is negative so that ΔG° will become smaller as the temperature increases. When the temperature exceeds a certain value, this negative term is large enough to overcome the positive ΔH° term and ΔG° will become negative. The process is then spontaneous.

This temperature is the melting point: 273 K.

- Ethane C_2H_6 can be burnt in the presence of an excess of oxygen to give $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ or under restricted oxygen conditions to give $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. A balanced equation for the first process is



Write a balanced equation for the combustion under restricted oxygen where $\text{CO}(\text{g})$ rather than $\text{CO}_2(\text{g})$ is produced.



Using the heats of formation, calculate the difference (in kJ per mole of ethane) in heat released by the two different types of combustion of ethane, *i.e.* combustion with excess O_2 and combustion under restricted O_2 conditions.

Compound	$\Delta_f H^\circ$ (kJ mol ⁻¹)
$\text{H}_2\text{O}(\text{l})$	-285.9
$\text{C}_2\text{H}_6(\text{g})$	-84.67
$\text{CO}_2(\text{g})$	-393.5
$\text{CO}(\text{g})$	-110.5

Using $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ(\text{products}) - \sum n \Delta_f H^\circ(\text{reactants})$, the enthalpy of the combustion of the reaction with excess O_2 is:

$$\begin{aligned} \Delta H^\circ(\text{A}) &= (4\Delta_f H^\circ(\text{CO}_2(\text{g})) + 6\Delta_f H^\circ(\text{H}_2\text{O}(\text{l}))) - (2\Delta_f H^\circ(\text{C}_2\text{H}_6(\text{g}))) \\ &= [(4 \times -393.5 + 6 \times -285.9) - (2 \times -84.67)] \text{ kJ mol}^{-1} = -3120.1 \text{ kJ mol}^{-1} \end{aligned}$$

For the reaction in restricted O_2 , this becomes:

$$\begin{aligned} \Delta H^\circ(\text{B}) &= (4\Delta_f H^\circ(\text{CO}(\text{g})) + 6\Delta_f H^\circ(\text{H}_2\text{O}(\text{l}))) - (2\Delta_f H^\circ(\text{C}_2\text{H}_6(\text{g}))) \\ &= [(4 \times -110.5 + 6 \times -285.9) - (2 \times -84.67)] \text{ kJ mol}^{-1} = -1988.1 \text{ kJ mol}^{-1} \end{aligned}$$

The difference between them is thus $(3120.1 - 1988.1) \text{ kJ mol}^{-1} = 1132 \text{ kJ mol}^{-1}$.

Both reactions were written for the combustion of two moles of ethane. The difference per mole of ethane is therefore $\frac{1}{2} \times 1132 \text{ kJ mol}^{-1} = 566 \text{ kJ mol}^{-1}$.

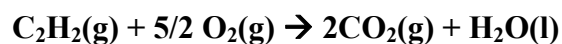
Answer: **566 kJ mol⁻¹**

Marks
4

- The heat of combustion of acetylene, $\text{C}_2\text{H}_2(\text{g})$, is $-1301 \text{ kJ mol}^{-1}$. What is the heat of formation of acetylene gas?

Data: $\Delta_f H^\circ$ of $\text{CO}_2(\text{g}) = -393.5 \text{ kJ mol}^{-1}$ $\Delta_f H^\circ$ of $\text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ mol}^{-1}$

The heat of combustion corresponds to the reaction below in which one mol of $\text{C}_2\text{H}_2(\text{g})$ is burnt:



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

$$\Delta_{\text{combustion}} H^\circ = [2 \times \Delta_f H^\circ (\text{CO}_2(\text{g})) + \Delta_f H^\circ (\text{H}_2\text{O}(\text{l}))] - [\Delta_f H^\circ (\text{C}_2\text{H}_2(\text{g}))]$$

or

$$\begin{aligned} [\Delta_f H^\circ (\text{C}_2\text{H}_2(\text{g}))] &= [2 \times \Delta_f H^\circ (\text{CO}_2(\text{g})) + \Delta_f H^\circ (\text{H}_2\text{O}(\text{l}))] - \Delta_{\text{combustion}} H^\circ \\ &= [(2 \times -393.5) + (-285.8) - (-1301)] \text{ kJ mol}^{-1} \\ &= +228 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta_f H^\circ = +228 \text{ kJ mol}^{-1}$$

- A gaseous hydrocarbon is found to contain 85.6 % carbon and 17.4 % hydrogen by mass. A 10.0 L sample of this gas has a mass of 23.78 g at 1.00 atm and 298 K. Show that the hydrocarbon is butane, C₄H₁₀.

From the percentages:

	C	H
percentage	85.6	17.4
divide by atomic mass	$\frac{85.6}{12.01} = 7.13$	$\frac{17.4}{1.008} = 17.3$
divide by smallest value	1	2.44

The ratio 1 : 2.44 is consistent with the empirical formula C₂H₅.

Alternatively, using the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(10.0 \text{ L})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 0.409 \text{ mol}$$

As this has a mass of 23.78 g, the molar mass, corresponding to 1 mol, is:

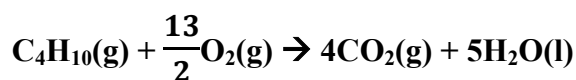
$$\text{molar mass} = \frac{\text{mass}}{\text{number of moles}} = \frac{23.78 \text{ g}}{0.409 \text{ mol}} = 58.1 \text{ g}$$

The molar mass of C₄H₁₀ is (4 × 12.01 + 10 × 1.008) g mol⁻¹ = 58.12 g mol⁻¹, which is again consistent with the experimental data.

Using the data below, calculate the heat generated when this quantity of butane is burnt in air.

$$\Delta_f H^\circ: \text{C}_4\text{H}_{10}(\text{g}) -126 \text{ kJ mol}^{-1}, \text{CO}_2(\text{g}) -394 \text{ kJ mol}^{-1}, \text{H}_2\text{O}(\text{l}) = -286 \text{ kJ mol}^{-1}$$

The combustion reaction is:



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

$$\begin{aligned} \Delta_{\text{comb}} H^\circ &= (4\Delta_f H^\circ(\text{CO}_2(\text{g})) + 5\Delta_f H^\circ(\text{H}_2\text{O}(\text{l}))) - (\Delta_f H^\circ(\text{C}_4\text{H}_{10}(\text{g}))) \\ &= [(4 \times -394 + 5 \times -286) - (-126)] \text{ kJ mol}^{-1} = -2880 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, for 0.409 mol, the enthalpy change is:

$$\Delta_{\text{comb}} H^\circ = (-2880 \text{ kJ mol}^{-1}) \times (0.498 \text{ mol}) = -1180 \text{ kJ}$$

Answer: 1180 kJ

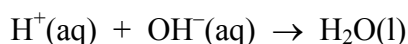
Marks
4

- A 50.0 mL solution contained 5.00 g of NaOH in water at 25.00 °C. When it was added to a 250.0 mL solution of 0.100 M HCl at 25.00 °C in a “coffee cup” calorimeter, the temperature of the solution rose to 26.12 °C.

Is the process an endothermic or exothermic reaction?

exothermic

Assuming the specific heat of the solution is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$, that the calorimeter absorbs a negligible amount of heat, and that the density of the solution is 1.00 g mL^{-1} , calculate $\Delta_r H$ (in kJ mol^{-1}) for the following reaction.



The total volume of the solution after mixing is $(50.0 + 250.0) \text{ mL} = 300.0 \text{ mL}$. As the density of the solution is 1.00 g mL^{-1} , the mass of the solution is:

$$\text{mass} = \text{density} \times \text{volume} = (1.00 \text{ g mL}^{-1}) \times (300.0 \text{ mL}) = 300. \text{ g}$$

The reaction produces a temperature change $\Delta T = (26.12 - 25.00) \text{ }^\circ\text{C} = 1.12 \text{ K}$. The heat change is therefore:

$$q = mC_v\Delta T = (300. \text{ g}) \times (4.18 \text{ J K}^{-1} \text{ g}^{-1}) \times (1.12 \text{ K}) = 1404 \text{ J}$$

The formula mass of NaOH is $(22.99 \text{ (Na)} + 16.00 \text{ (O)} + 1.008 \text{ (H)}) \text{ g mol}^{-1} = 40.00 \text{ g mol}^{-1}$. 5.00 g of NaOH therefore corresponds to:

$$\text{moles of NaOH} = \text{moles of OH}^- = \frac{\text{mass}}{\text{molar mass}} = \frac{5.00 \text{ g}}{40.00 \text{ mol}} = 0.125 \text{ mol}$$

A 250.0 mL solution of 0.100 M HCl corresponds to

$$\begin{aligned} \text{moles of HCl} &= \text{moles of H}^+ = \text{concentration} \times \text{volume} \\ &= (0.100 \text{ mol L}^{-1}) \times (0.250 \text{ L}) = 0.0250 \text{ mol} \end{aligned}$$

H^+ is therefore the limiting reagent in the reaction. The heat change of 1404 J corresponds to 0.025 mol of H^+ reacting with 0.025 mol of OH^- . The reaction is exothermic as it causes a temperature increase.

The molar enthalpy of reaction is $\frac{-1404 \text{ J}}{0.025 \text{ mol}} = -56200 \text{ J mol}^{-1} = -56.2 \text{ kJ mol}^{-1}$.

Answer: **-56.2 kJ mol⁻¹**

- Indicate the relative entropy of each system in the following pairs of systems. Use: “>”, “<”, or “=”.

$\text{H}_2\text{O}(\text{g})$

>

$\text{H}_2\text{O}(\text{s})$

$3\text{O}_2(\text{g})$

>

$2\text{O}_3(\text{g})$

- Consider butane (C_4H_{10}) and pentane (C_5H_{12}). Which gas has the higher entropy at 40 °C? Give reasons for your answer.

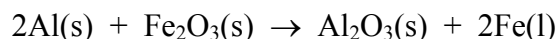
Pentane. It has more bonds and can therefore take on more conformations so has the higher entropy (disorder).

1

2

- 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.

Marks
6



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

Assume there is 1 mol of reactants at an 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 *and* heat all the products (2 mol of Fe + 1 mol of Al₂O₃) to the melting point of Fe.

For the reaction:

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

To melt 2 mol of Fe and heat all products to the melting point of Fe:

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

$$\Delta H = nC_p\Delta T = (2 \text{ mol}) \times (25 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((1535-25) \text{ K}) = 75.5 \text{ kJ}$$

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

$$\Delta H = nC_p\Delta T = (1 \text{ mol}) \times (79 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((1535-25) \text{ K}) = 119 \text{ kJ}$$

(iii) ΔH to melt 2 mol of Fe

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

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

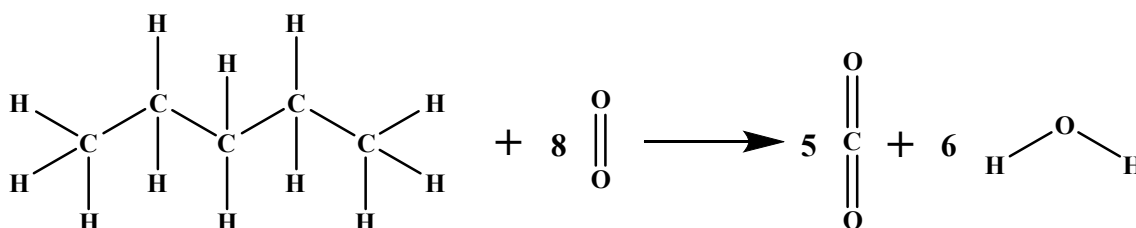
There is more than enough energy generated in the reaction for iron to be produced as a liquid.

- Pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, burns completely in oxygen to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. Use the bond enthalpies given below to estimate the enthalpy change for this process.

Marks
3

Bond	Bond enthalpy (kJ mol^{-1})	Bond	Bond enthalpy (kJ mol^{-1})
C-H	414	O-H	463
C-C	346	O-O	144
C=O	804	O=O	498

The combustion reaction is:



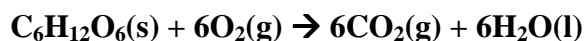
$$\begin{aligned} \Delta_{\text{comb}}H &= \{ [\Delta_{\text{atom}}H(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)] + 8 \times [\Delta_{\text{atom}}H(\text{O}_2)] \} \\ &\quad - \{ 5 \times [\Delta_{\text{atom}}H(\text{CO}_2)] + 6 \times \Delta_{\text{atom}}H(\text{H}_2\text{O}) \} \\ &= \{ [4 \times 346 (\text{C-C}) + 12 \times 414 (\text{C-H})] + 8 \times [498 (\text{O=O})] \} \\ &\quad - \{ 5 \times [2 \times 804 (\text{C=O})] + 6 \times [2 \times 463] \} \text{ kJ mol}^{-1} \\ &= \{ [10336] - [13596] \} \text{ kJ mol}^{-1} \\ &= -3260 \text{ kJ mol}^{-1} \end{aligned}$$

Answer: $-3260 \text{ kJ mol}^{-1}$

- The net amount of carbon dioxide fixed by photosynthesis on Earth has been estimated as 5.5×10^{16} g year⁻¹. Calculate the energy stored by photosynthesis each year, assuming that all this carbon is converted into glucose, C₆H₁₂O₆.

$$\Delta_f H^\circ: \text{C}_6\text{H}_{12}\text{O}_6(\text{s}): -1273 \text{ kJ mol}^{-1}, \text{H}_2\text{O}(\text{l}): -285.8 \text{ kJ mol}^{-1}, \text{CO}_2(\text{g}): -393.5 \text{ kJ mol}^{-1}$$

The chemical reaction for the combustion of glucose into carbon dioxide and water is:



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

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= [6\Delta_f H^\circ (\text{CO}_2(\text{g})) + 6\Delta_f H^\circ (\text{H}_2\text{O}(\text{l}))] - [\Delta_f H^\circ (\text{C}_6\text{H}_{12}\text{O}_6(\text{s}))] \\ &= [6 \times -393.5 + 6 \times -285.8] \text{ kJ mol}^{-1} - [-1273] \text{ kJ mol}^{-1} \\ &= -2803 \text{ kJ mol}^{-1} \end{aligned}$$

This is the energy released when 1 mol of glucose combusts. As this generates 6 mol of CO₂(g), the energy release per mol of CO₂(g) is

$$\text{energy released per mol of CO}_2(\text{g}) = (-2803/6) \text{ kJ mol}^{-1} = 467.1 \text{ kJ mol}^{-1}$$

The molar mass of CO₂ is (12.01 (C) + 2 × 16.00 (O)) g mol⁻¹ = 44.01 g mol⁻¹.

The number of moles of CO₂ fixed per year is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.5 \times 10^{16} \text{ g}}{44.01 \text{ g mol}^{-1}} = 1.25 \times 10^{15} \text{ mol}$$

As combustion of glucose generates -467.1 kJ mol⁻¹ per mole of CO₂(g) produced, photosynthesis of this amount stores

$$\text{energy stored} = (467.1 \text{ kJ mol}^{-1}) \times (1.25 \times 10^{15} \text{ mol}) = 5.8 \times 10^{17} \text{ kJ}$$

Answer: 5.8×10^{17} kJ

- Sulfuric acid produced industrially must be diluted for many of its applications. This process is always carried out by adding the acid to water rather than by adding water to the acid. Use the data below to show that $\Delta_r H^\circ$ for the dilution of 50.0 mL of $\text{H}_2\text{SO}_4(\text{l})$ to 1.00 L of $\text{H}_2\text{SO}_4(\text{aq})$ is -89 kJ.

$$\text{H}_2\text{SO}_4(\text{l}): \Delta_f H^\circ = -814 \text{ kJ mol}^{-1}, \text{ density} = 1.831 \text{ g mL}^{-1}, C = 1.42 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\text{H}_2\text{SO}_4(\text{aq}): \Delta_f H^\circ = -909 \text{ kJ mol}^{-1}, \text{ density} = 1.060 \text{ g mL}^{-1}, C = 3.50 \text{ J g}^{-1} \text{ K}^{-1}$$

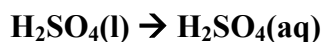
As the density of $\text{H}_2\text{SO}_4(\text{l})$ is 1.831 g mL^{-1} and the dilution is of 50.0 mL, the mass of $\text{H}_2\text{SO}_4(\text{l})$ requiring dilution is:

$$\text{mass} = \text{density} \times \text{volume} = (1.831 \text{ g mL}^{-1}) \times (50.0 \text{ mL}) = 91.55 \text{ g}$$

The molar mass of H_2SO_4 is $(2 \times 1.008 \text{ (H)} + 32.07 \text{ (S)} + 4 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 98.086 \text{ g mol}^{-1}$. This mass therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{91.55 \text{ g}}{98.086 \text{ g mol}^{-1}} = 0.9334 \text{ mol}$$

The dilution process involves the reaction:



For which:

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants}) \\ &= \Delta_f H^\circ (\text{H}_2\text{SO}_4(\text{aq})) - \Delta_f H^\circ (\text{H}_2\text{SO}_4(\text{l})) \\ &= (-909 \text{ kJ mol}^{-1}) - (-814 \text{ kJ mol}^{-1}) = -95 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, 0.9334 mol will generate:

$$\Delta_{\text{rxn}} H^\circ = (0.9334 \text{ mol}) \times (-95 \text{ kJ mol}^{-1}) = -89 \text{ kJ mol}^{-1}$$

The dilution is carried out in a calorimeter. If the initial temperature of the system is 25.0°C , what is the final temperature after dilution?

After dilution, the calorimeter contains 1.00 L of $\text{H}_2\text{SO}_4(\text{aq})$. As this has a density of 1.060 g mL^{-1} , this corresponds to a mass of:

$$\text{mass} = \text{density} \times \text{volume} = (1.060 \text{ g mL}^{-1}) \times (1.00 \times 10^3 \text{ mL}) = 1060 \text{ g}$$

The dilution generates 89 kJ, causing the solution to warm. The temperature change is related to the heat change by:

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

ANSWER CONTINUES ON THE NEXT PAGE

Hence,

$$89 \times 10^3 \text{ J} = (3.50 \text{ J g}^{-1} \text{ K}^{-1}) \times (1060 \text{ g}) \times \Delta T$$

Note that the heat capacity of H₂SO₄(aq) has been used as this is what the calorimeter contains.

Hence,

$$\Delta T = 24 \text{ K} = 24 \text{ }^\circ\text{C}$$

As the original temperature is 25.0 °C, the final temperature after this increase is

$$T_{\text{final}} = T_{\text{initial}} + \Delta T = (25.0 + 24) \text{ }^\circ\text{C} = 49 \text{ }^\circ\text{C}$$

Final temperature: **49 °C**

Using the concept of heat capacity, explain why the dilution of sulfuric acid is carried out by adding acid to water rather than water to acid.



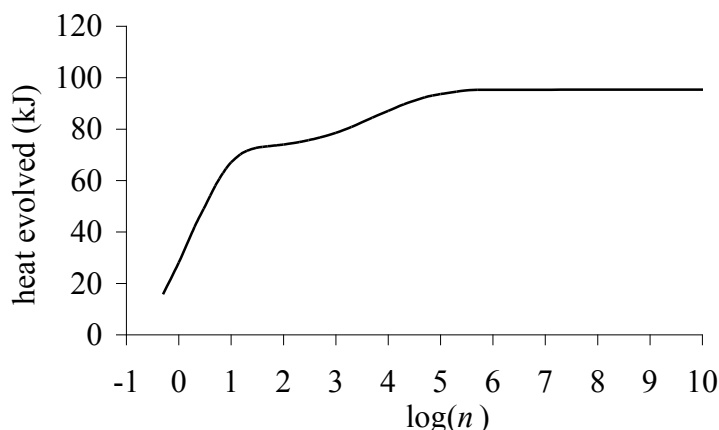
The dilution of sulfuric acid generates 95 kJ mol^{-1} of heat.

As $q = Cm\Delta T$, the temperature change when a quantity of heat is generated is *inversely* proportional to the heat capacity of the substance.

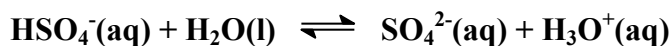
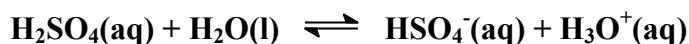
If water is added to $\text{H}_2\text{SO}_4(\text{l})$, the *same* quantity of heat generates a much *larger* temperature change than occurs if $\text{H}_2\text{SO}_4(\text{l})$ is added to water as the heat capacity of $\text{H}_2\text{SO}_4(\text{l})$ is much *smaller* than that of water.

If water is added to acid, the temperature change is so large so it produces localized boiling of the solution at the surface. This causes the acid to spit out causing potential safety issues.

The figure below shows the heat evolved when one mole of H_2SO_4 is mixed with n moles of H_2O . Explain the shape of curve.



H_2SO_4 is a diprotic acid as it has two acidic protons:

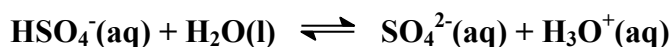
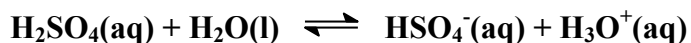


At normal dilutions levels, $\text{H}_2\text{SO}_4(\text{aq})$ is completely ionized into SO_4^{2-} . A 1 M solution contains roughly a 1 : 55 molar ratio of acid : water.

However, in the dilution curve above, the amount of H_2O is initially very low – when $\log(n) = 0$, $n_{\text{water}} = 1 \text{ mol}$ so there is a 1 : 1 molar ratio of acid : water. Low amounts of water lead both equilibria to shift towards the left.

Hence, the curve shows an initial increase in temperature as the first ionization occurs. Increasing the amount of water causes a higher percentage to be ionized and more heat to be generated.

H₂SO₄ is a diprotic acid as it has two acidic protons:



At normal dilutions levels, H₂SO₄(aq) is completely ionized into SO₄²⁻. A 1 M solution contains roughly a 1 : 55 molar ratio of acid : water.

However, in the dilution curve above, the amount of H₂O is initially very low – when log(*n*) = 0, *n*_{water} = 1 mol so there is a 1 : 1 molar ratio of acid : water. Low amounts of water lead both equilibria to shift towards the left.

Hence, the curve shows an initial increase in temperature as the first ionization occurs. Increasing the amount of water causes a higher percentage to be ionized and more heat to be generated.

When log(*n*) ~ 1, *n*_{water} = 10 mol. At this point, the first ionization is essentially complete and further dilution up to log(*n*) ~ 3 generates little extra heat as all the solution contains HSO₄⁻(aq).

As more water is added, the second ionization begins to occur. Again, addition of more water causes a higher percentage of the HSO₄⁻ to ionize, generating more heat.

When log(*n*) ~ 5, the second ionization is essentially completely and the solution contains only SO₄²⁻(aq). Further addition of water does not cause any additional ionization and no more heat is evolved.

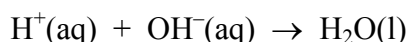
Marks
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- A 50.0 mL solution contained 10.00 g of NaOH in water at 25.00 °C. When it was added to a 250.0 mL solution of 0.200 M HCl at 25.00 °C in a “coffee cup” calorimeter, the temperature of the solution rose to 27.24 °C.

Is the process an endothermic or exothermic reaction?

Exothermic ($\Delta H < 0$) as the reaction causes the temperature of the solution to rise.

Assuming the specific heat of the solution is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$, that the calorimeter absorbs a negligible amount of heat, and that the density of the solution is 1.00 g mL^{-1} , calculate $\Delta_r H$ (in kJ mol^{-1}) for the following reaction.



The formula mass of NaOH is $(22.99 \text{ (Na)} + 16.00 \text{ (O)} + 1.008 \text{ (H)}) \text{ g mol}^{-1} = 39.998 \text{ g mol}^{-1}$. Hence the number of moles in 10.00 g is:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{10.00 \text{ g}}{39.998 \text{ g mol}^{-1}} = 0.2500 \text{ mol}$$

The number of moles of H^+ in 250.0 mL of a 0.200 M solution is

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (0.200 \text{ mol L}^{-1}) \times (0.2500 \text{ L}) = 0.0500 \text{ mol} \end{aligned}$$

NaOH is in excess and H^+ is the limiting reagent.

After the solutions are mixed, the total volume = $(50.0 + 250.0) \text{ mL} = 300.0 \text{ mL}$. If the density is 1.00 g mL^{-1} , this corresponds to a mass of:

$$\text{mass} = \text{density} \times \text{volume} = (1.00 \text{ g mL}^{-1}) \times (300.0 \text{ mL}) = 300. \text{ g}$$

The temperature change, ΔT , of a substance with mass, m , is related to the heat change, q , using the specific heat capacity of the substance, c :

$$q = c \times m \times \Delta T$$

In the experiment, $\Delta T = (27.24 - 25.00) \text{ K} = 2.24 \text{ K}$. Hence,

$$q = (4.18 \text{ J K}^{-1} \text{ g}^{-1}) \times (300. \text{ g}) \times (2.24 \text{ K}) = 28.1 \times 10^2 \text{ J}$$

This is the heat from the reaction of 0.0500 mol, so the molar enthalpy change is:

$$\Delta_r H = -(28.1 \times 10^2 \text{ J}) / (0.0500 \text{ mol}) = -56200 \text{ J mol}^{-1} = -56.2 \text{ kJ mol}^{-1}$$

where the negative sign corresponds to an exothermic reaction (see above).

Answer: **-56.2 kJ mol⁻¹**

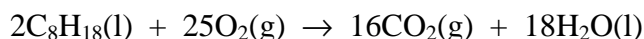
ANSWER CONTINUES ON THE NEXT PAGE

When the experiment was repeated using 12.00 g of NaOH in water, the temperature increase was the same. Explain.

$\text{H}^+(\text{aq})$ is the limiting reagent.

There is not enough $\text{H}^+(\text{aq})$ available to react with 10.0 g of NaOH, so no further reaction occurs when using 12.0 g instead.

- The current “petrochemical economy” is based on the combustion of fossil fuels, of which octane is a typical example.



Calculate the heat of combustion of octane using the supplied heat of formation data.

Data: $\text{C}_8\text{H}_{18}(\text{l})$: $-249.9 \text{ kJ mol}^{-1}$; $\text{CO}_2(\text{g})$: $-393.5 \text{ kJ mol}^{-1}$; $\text{H}_2\text{O}(\text{l})$: $-285.8 \text{ kJ mol}^{-1}$

Marks
5

Using $\Delta_{\text{rxn}}\text{H}^\circ = \sum m\Delta_{\text{f}}\text{H}^\circ(\text{products}) - \sum n\Delta_{\text{f}}\text{H}^\circ(\text{reactants})$, the heat of the reaction as written is:

$$\begin{aligned}\Delta_{\text{rxn}}\text{H}^\circ &= [16\Delta_{\text{f}}\text{H}^\circ(\text{CO}_2(\text{g})) + 18\Delta_{\text{f}}\text{H}^\circ(\text{H}_2\text{O}(\text{l}))] - [2\Delta_{\text{f}}\text{H}^\circ(\text{C}_8\text{H}_{18}(\text{l}))] \\ &= [(16 \times -393.5) + (18 \times -285.8)] - [(2 \times -249.9)] \\ &= -10940 \text{ kJ mol}^{-1}\end{aligned}$$

where $\Delta_{\text{f}}\text{H}^\circ(\text{O}_2(\text{g})) = 0$ has been used for the formation of an element in its standard state.

The enthalpy of combustion is defined per mole of fuel. The above reaction is for the combustion of two moles of C_8H_{18} .

Hence, $\Delta_{\text{comb}}\text{H}^\circ = \frac{1}{2} \times -10940 = -5470 \text{ kJ mol}^{-1}$

Answer: **-5470 kJ mol⁻¹**

How much energy is released when 1.00 L of octane is burned?

Data: Density of octane is 0.67 kg L^{-1}

As density = $\frac{\text{mass}}{\text{volume}}$, 1.00 L corresponds to:

$$\text{mass} = \text{density} \times \text{volume} = 0.67 \times 1.00 = 0.67 \text{ kg} = 670 \text{ g.}$$

The molar mass of octane, C_8H_{18} , is $8 \times 12.01 (\text{C}) + 18 \times 1.008 (\text{H}) = 114.224$.

This mass of octane therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{670}{114.224} = 5.9 \text{ mol}$$

From above, 1 mole releases 5470 kJ mol^{-1} . Therefore, this amount release:

$$\text{energy released} = 5.9 \times 5470 = 32 \times 10^3 \text{ kJ} = 32 \text{ MJ}$$

Answer: **$32 \times 10^3 \text{ kJ}$ or **32 MJ****

- The so-called "hydrogen economy" is based on $\text{H}_2(\text{g})$ produced from water by solar energy. The gas is then burned as fuel:



Calculate the volume of H_2 gas at 25°C and 1 atm required to produce 1.0×10^4 kJ of heat.

From the chemical equation, burning of two moles of $\text{H}_2(\text{g})$ produces 571.6 kJ. so one mole produces $\frac{1}{2} \times 571.6 = 285.8$ kJ mol.

To produce 1.0×10^4 kJ therefore requires:

$$\text{amount of } \text{H}_2(\text{g}) \text{ required} = \frac{1.0 \times 10^4}{285.8} = 35 \text{ mol}$$

At 25°C and 1 atm, 1 mole of an ideal gas has a volume of 24.5 L. This amount therefore has a volume of:

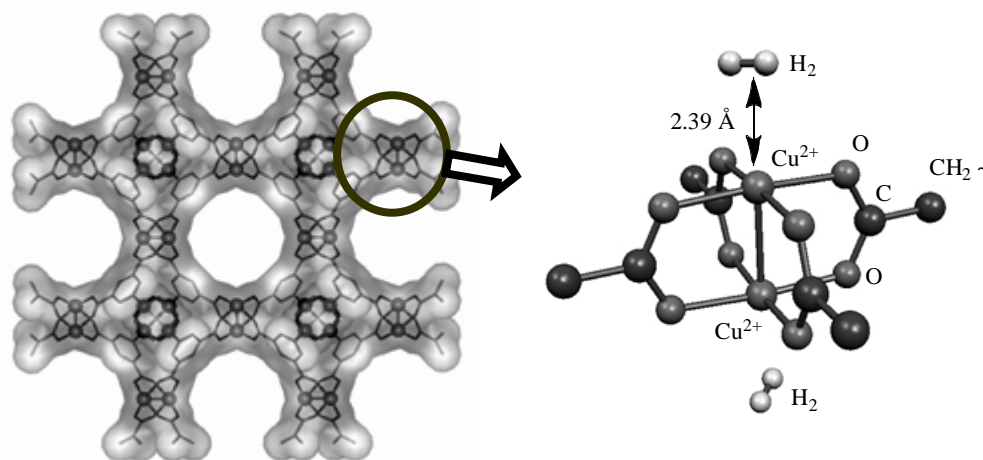
$$\text{volume} = 35 \times 24.5 = 860 \text{ L}$$

Alternatively, and entirely equivalently, the ideal gas law $PV = nRT$ can be used:

$$V = \frac{nRT}{P} = \frac{(35) \times (0.08206) \times (25 + 273)}{(1)} = 860 \text{ L}$$

Answer: 860 L

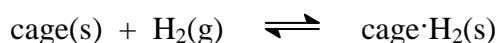
A major disadvantage of hydrogen as a fuel is that it is a gas, and therefore hard to store. There is an enormous world-wide effort, including research performed in the University of Sydney, to develop novel chemical structures in which H_2 can be stored much more efficiently. One of the structures being tested in the School of Chemistry is shown below.



What type of intermolecular force (or forces) are responsible for the binding between the Cu^{2+} and the H_2 ?

There are ion-induced dipole forces between Cu^{2+} and the H_2 molecules as well as weak dispersion (London or induced dipole-induced dipole) forces.

In order that such a material be useful for fuel storage, the binding of the H_2 must be reversible:



One simple way to reverse the binding is to increase the temperature, so that at low temperature the equilibrium lies to the right and at high temperature to the left. Use this information, plus any chemical knowledge or intuition to infer the sign of ΔG , ΔH and ΔS at “low” and “high” temperatures. (You may assume that ΔH and ΔS do not change greatly with temperature.)

At low temperature, the equilibrium lies to the right favouring products: $\Delta G < 0$. At high temperature, it lies to the left favouring reactants: $\Delta G > 0$.

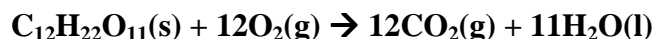
The reaction involves formation of a solid from a solid and a gas. There is therefore a decrease in the entropy: $\Delta S < 0$. This is true at all temperatures.

The forward reaction becomes less favourable as the temperature is increased. Le Chatelier’s principle therefore suggests that the reaction is exothermic: $\Delta H < 0$. This is true at all temperatures. (If the temperature is increased, the equilibrium shifts to remove heat by increasing the backward reaction.)

Temperature	ΔG	ΔS	ΔH
low	< 0	< 0	< 0
high	> 0	< 0	< 0

- Normal table sugar is pure sucrose, $C_{12}H_{22}O_{11}(s)$. Give the equation for the complete combustion of sucrose.

Marks
9



A standard can (375 mL) of soft drink contains 795 kJ of energy. Assume the only ingredients are water and sucrose and that the energy obtained from sucrose by the body is the same as that obtained by combustion. Tagatose, $C_6H_{12}O_6$, is a low-calorie sweetener with a calorific value to humans of only 6.2 kJ g^{-1} . On a weight for weight basis, it is 92% as sweet as sucrose. What mass of tagatose would be needed to produce a 375 mL can of drink with the same sweetness as a standard soft drink?

Data: $\Delta_f H^\circ (C_{12}H_{22}O_{11}(s)) = -2221.7 \text{ kJ mol}^{-1}$
 $\Delta_f H^\circ (CO_2(g)) = -393.5 \text{ kJ mol}^{-1}$
 $\Delta_f H^\circ (H_2O(l)) = -285.8 \text{ kJ mol}^{-1}$

The molar mass of sucrose, $C_{12}H_{22}O_{11}$ is:

$$M_{\text{sucrose}} = 12 \times 12.01 \text{ (C)} + 22 \times 1.008 \text{ (H)} + 11 \times 16.00 \text{ (O)} = 342.296 \text{ g mol}^{-1}$$

As $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants})$, the $\Delta_{\text{comb}} H^\circ$ (sucrose) is given by:

$$\begin{aligned} \Delta_{\text{comb}} H^\circ &= \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants}) \\ &= (12 \Delta_f H^\circ (CO_2(g)) + 11 \Delta_f H^\circ (H_2O(l))) \\ &\quad - (\Delta_f H^\circ (C_{12}H_{22}O_{11}(g)) + 12 \Delta_f H^\circ (O_2(g))) \\ &= (12 \times -393.5 + 11 \times -285.8) - (-2221.7 + 12 \times 0) = -5644.1 \text{ kJ mol}^{-1} \end{aligned}$$

As a standard can generates 795 kJ of energy, it must contain $\frac{795 \text{ kJ}}{5644.1 \text{ kJ mol}^{-1}} =$

0.141 mol of sucrose. Using the molar mass from above, this corresponds to a mass of:

$$\text{mass} = \text{number of moles} \times \text{molar mass} = 0.141 \times 342.296 = 48.2 \text{ g}$$

As tagatose only has 92% of the sweetness of sucrose, more is required to match the sweetness provided by sucrose:

$$\text{mass of tagatose required} = \frac{48.2}{0.92} = 52.4 \text{ g}$$

Answer: **52.4 g**

ANSWER CONTINUES ON THE NEXT PAGE

How much energy will a person obtain from this reduced-calorie can of soft drink?

As tagatose has a calorific value of 6.2 kJ g^{-1} , 52.4 g will provide:

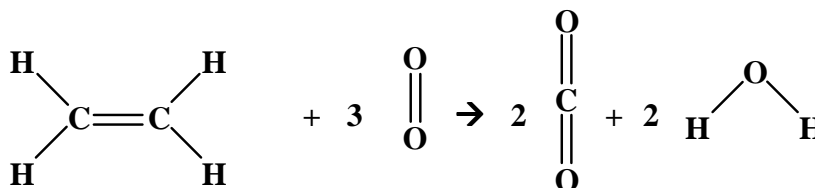
$$\text{energy obtained} = 52.4 \text{ g} \times 6.2 \text{ kJ g}^{-1} = 330 \text{ kJ}$$

Answer: **330 kJ**

- Calculate the molar enthalpy of combustion of ethylene (C_2H_4) using bond dissociation energies.

Data:	Bond	Bond enthalpy (in kJ mol^{-1})	Bond	Bond enthalpy (in kJ mol^{-1})
	C-H	413	C=C	614
	O-H	467	C=O	799
			O=O	498

The combustion reaction is: $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$



$$\Delta H = \{ [\Delta_{\text{atom}}H (C_2H_4)] + 3 \times [\Delta_{\text{atom}}H (O_2)] \}$$

$$- \{ 2 \times [\Delta_{\text{atom}}H (CO_2)] + 2 \times \Delta_{\text{atom}}H (H_2O) \}$$

$$= \{ [614 (C=C) + 4 \times 413 (C-H)] + 3 \times [498 (O=O)] \}$$

$$- \{ 2 \times [2 \times 799 (C=O)] + 2 \times [2 \times 467] \} = (3760) - (5064) = -1304 \text{ kJ mol}^{-1}$$

Answer: $-1304 \text{ kJ mol}^{-1}$

The heat of combustion of ethane (C_2H_6) is $-1560 \text{ kJ mol}^{-1}$, while that of ethanol (C_2H_5OH) is $-1367 \text{ kJ mol}^{-1}$. Comment on which of ethylene, ethane and ethanol is the most efficient fuel.

The molar masses of ethane, ethene and ethanol are:

molar mass of ethane is $(2 \times 12.01 (C)) + (6 \times 1.008 (H)) = 30.068$

molar mass of ethene is $(2 \times 12.01 (C)) + (4 \times 1.008 (H)) = 28.052$

molar mass of ethanol is $(2 \times 12.01 (C)) + (6 \times 1.008 (H)) + (16.00 (O)) = 45.068$

The best comparison of the fuel efficiencies are the heats of combustion per gram:

$$\Delta_{\text{comb}}H (\text{ethane}) = -1560 \text{ kJ mol}^{-1} = \frac{-1560}{30.068} = -51.9 \text{ kJ g}^{-1}$$

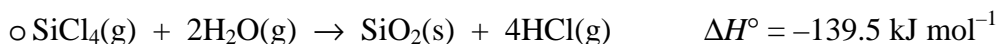
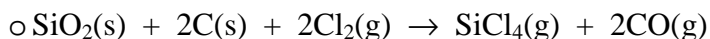
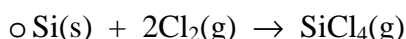
$$\Delta_{\text{comb}}H (\text{ethene}) = -1304 \text{ kJ mol}^{-1} = \frac{-1304}{28.052} = -46.5 \text{ kJ g}^{-1}$$

$$\Delta_{\text{comb}}H (\text{ethanol}) = -1367 \text{ kJ mol}^{-1} = \frac{-1367}{46.068} = -29.7 \text{ kJ g}^{-1}$$

On this basis, ethane is the most efficient and ethanol is the least efficient.

Marks
5

- Silicon tetrachloride (SiCl_4) is produced annually on a kilotonne scale for making transistor-grade silicon. It can be made directly from the elements (reaction 1), or, more cheaply, by heating sand and graphite with chlorine gas (reaction 2). If water is present, some SiCl_4 may be lost in an unwanted side-reaction (reaction 3).



Calculate the heats of reaction of reactions 1 and 2.

Compound	$\Delta H^\circ_f / \text{kJ mol}^{-1}$
$\text{SiO}_2(\text{s})$	-910.9
HCl(g)	-92.3
$\text{H}_2\text{O(g)}$	-241.8
CO(g)	-110.5

Using $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants})$ and recalling that the enthalpy of formation of an element in its standard state is zero:

$$\Delta_{\text{rxn}} H^\circ (1) = \Delta_f H^\circ (\text{SiCl}_4(\text{g}))$$

$$\Delta_{\text{rxn}} H^\circ (2) = [\Delta_f H^\circ (\text{SiCl}_4(\text{g})) + 2\Delta_f H^\circ (\text{CO(g)})] - [\Delta_f H^\circ (\text{SiO}_2(\text{s}))]$$

$$\Delta_{\text{rxn}} H^\circ (3) = [\Delta_f H^\circ (\text{SiO}_2(\text{s})) + 4\Delta_f H^\circ (\text{HCl(g)})] - [\Delta_f H^\circ (\text{SiCl}_4(\text{g})) + 2\Delta_f H^\circ (\text{H}_2\text{O(g)})]$$

As $\Delta_{\text{rxn}} H^\circ (3) = -139.5 \text{ kJ mol}^{-1}$, using the tabulated values of $\Delta_f H^\circ$ for $\text{SiO}_2(\text{s})$, HCl(g) and $\text{H}_2\text{O(g)}$ gives:

$$-139.5 = [(-910.9) + (4 \times -92.3)] - [\Delta_f H^\circ (\text{SiCl}_4(\text{g})) + (2 \times -241.8)]$$

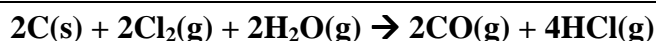
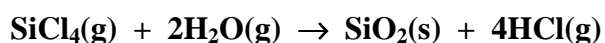
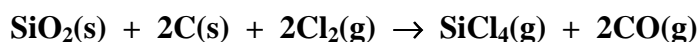
Hence, $\Delta_{\text{rxn}} H^\circ (1) = \Delta_f H^\circ (\text{SiCl}_4(\text{g})) = -657 \text{ kJ mol}^{-1}$.

$$\Delta_{\text{rxn}} H^\circ (2) = [(-657) + (2 \times -110.5)] - [(-910.9)] = +32.9 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{(\text{reaction 1})} = -657 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{(\text{reaction 2})} = +32.9 \text{ kJ mol}^{-1}$$

Write down the new reaction that is the sum of reactions 2 and 3. What is the heat of reaction for this new reaction?



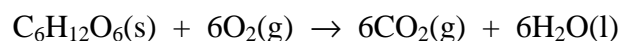
$$\Delta_{\text{rxn}} H^\circ (2) = \Delta_{\text{rxn}} H^\circ (2) + \Delta_{\text{rxn}} H^\circ (3) = (+32.9) + (-139.5) = -106.6 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ = -106.6 \text{ kJ mol}^{-1}$$

Marks
3

- Glucose is a common food source. The net reaction for its metabolism in humans is:



Calculate ΔH° for this reaction given the following heats of formation.

$$\Delta H^\circ_f(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) = -1274 \text{ kJ mol}^{-1}$$

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

$$\Delta H^\circ_f(\text{H}_2\text{O}(\text{l})) = -285 \text{ kJ mol}^{-1}$$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - \sum n\Delta_fH^\circ(\text{reactants})$ and recalling that the enthalpy of formation of an element in its standard state is zero, the reaction enthalpy is:

$$\begin{aligned}\Delta_{\text{rxn}}H^\circ &= [(6 \times \Delta_fH^\circ(\text{CO}_2(\text{g})) + (6 \times \Delta_fH^\circ(\text{H}_2\text{O}(\text{g}))) - [(\Delta_fH^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})))] \\ &= [(6 \times -393) + (6 \times -285)] - [-1274] = -2794 \text{ kJ mol}^{-1}\end{aligned}$$

Answer: **-2794 kJ mol⁻¹**

If the combustion of glucose is carried out in air, water is produced as a vapour. Calculate ΔH° for the combustion of glucose in air given that



As energy is required to convert the liquid water into vapour, the combustion enthalpy will be lower:

$$\Delta_{\text{rxn}}H^\circ = (-2794 + 6 \times 44) \text{ kJ mol}^{-1} = -2540 \text{ kJ mol}^{-1}$$

Answer: **-2540 kJ mol⁻¹**

Will ΔS be different for the two oxidation reactions? If so, how will it differ and why?

Marks
4

The reaction in the body gives rise to an increase in entropy as a solid and 6 moles of gas react to give 6 moles of liquid and 6 moles of gas, which have higher entropy.

In air, the reaction gives rise to 12 moles of gas so will give rise to an even higher entropy increase.

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of glucose.

The molar mass of glucose is:

$$(6 \times 12.01 \text{ (C)}) + (12 \times 1.008 \text{ (H)}) + (6 \times 16.00 \text{ (O)}) = 180.156$$

$$1.0 \text{ g of glucose corresponds to } \frac{\text{mass}}{\text{molar mass}} = \frac{1.00}{180.156} = 0.00555 \text{ mol}$$

From the chemical equation, oxidation of 1 mol of glucose leads 6 mol of CO_2 . Hence the number of moles of CO_2 produced is $6 \times 0.00555 = 0.0333 \text{ mol}$.

$$\text{The molar mass of } \text{CO}_2 \text{ is } (12.01 \text{ (C)}) + (2 \times 16.00 \text{ (O)}) = 44.01$$

Therefore, the number of mass of CO_2 produced is:

$$\text{mass} = \text{number of moles} \times \text{molar mass} = 0.0333 \times 44.01 = 1.47$$

Answer: **1.47 g**

Calculate the volume of this mass of carbon dioxide at 0.50 atm pressure and 37 °C.

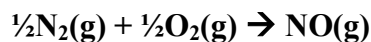
The ideal gas law gives $PV = nRT$, hence:

$$V = \frac{nRT}{P} = \frac{(0.0333) \times (0.08206) \times (273+37)}{(0.50)} = 1.7 \text{ L}$$

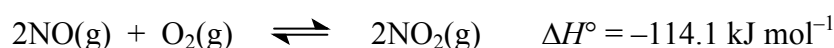
Answer: **1.7 L**

- Write the equation whose enthalpy change represents the standard enthalpy of formation of NO(g).

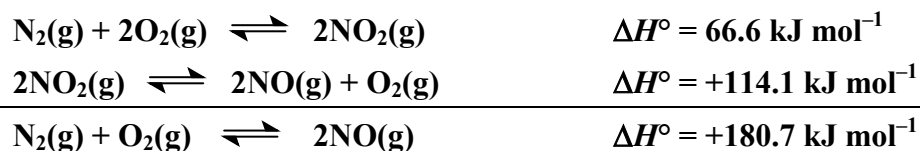
Marks
3



Given the following data, calculate the standard enthalpy of formation of NO(g).



Reversing the second reaction (changing sign of ΔH°) and adding this to the first reaction gives:



This gives the enthalpy of formation of two moles of NO hence:

$$\Delta_f H^\circ = +90.4 \text{ kJ mol}^{-1}$$

Answer: $\Delta_f H^\circ = +90.4 \text{ kJ mol}^{-1}$

- Hydrazine, N₂H₄, burns completely in oxygen to form N₂(g) and H₂O(g). Use the bond enthalpies given below to estimate the enthalpy change for this process.

3

Bond	Bond enthalpy (kJ mol ⁻¹)	Bond	Bond enthalpy (kJ mol ⁻¹)
N-H	391	O=O	498
N-N	158	O-O	144
N=N	470	O-H	463
N≡N	945	N-O	214

The equation for the combustion is: N₂H₄(g) + O₂(g) → N₂(g) + 2H₂O(l)

Thus the process involves breaking 4 N-H, 1 N-N and 1 O=O bonds and making 1 N≡N and 4 O-H bonds. Using the bond enthalpies, the reaction enthalpy is therefore:

ANSWERS CONTINUES ON THE NEXT PAGE

$$\begin{aligned}\Delta_{\text{comb}} H^{\circ} &= \left[\Delta_{\text{atm}} H^{\circ}(\text{N}_2\text{H}_4) + \Delta_{\text{atm}} H^{\circ}(\text{O}_2) \right] \\ &\quad - \left[\Delta_{\text{atm}} H^{\circ}(\text{N}_2(\text{g})) + 2\Delta_{\text{atm}} H^{\circ}(\text{H}_2\text{O}(\text{g})) \right] \\ &= [(4 \times 391 + 1 \times 158) + (1 \times 498)] \\ &\quad - [(1 \times 945) + 2 \times (2 \times 463)] \text{kJ mol}^{-1} \\ &= -577 \text{kJ mol}^{-1}\end{aligned}$$

Answer: **-577 kJ mol⁻¹**