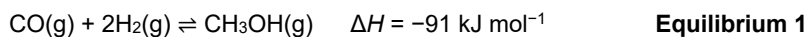# Enthalpy and Entropy

1.   Methanol, CH3OH, can be made industrially by the reaction of carbon monoxide with hydrogen, as shown in **equilibrium 1**.

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H = -91$ kJ mol^{-1} **Equilibrium 1**

Standard entropy values are given below.

Substance	CO(g)	H$_2$(g)	CH$_3$OH(g)
S^{θ} / J K^{-1} mol^{-1}	198	131	238

A chemist proposed producing methanol at 525 K using **equilibrium 1**.

Explain, with a calculation, whether the production of methanol is feasible at 525 K.

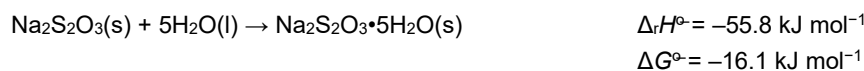--

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[5]
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2.   The standard enthalpy change of reaction, $\Delta_r H^{\ominus}$, and the standard free energy change, $\Delta G^{\ominus}$, for converting anhydrous sodium thiosulfate to hydrated sodium thiosulfate are shown below.

$Na_2S_2O_3(s) + 5H_2O(l) \rightarrow Na_2S_2O_3 \cdot 5H_2O(s)$ $\Delta_r H^{\ominus} = -55.8$ kJ mol^{-1}

$\Delta G^{\ominus} = -16.1$ kJ mol^{-1}

Standard entropies are given in the table.

Compound	$S^{\ominus}$ / J K^{-1} mol^{-1}
Na$_2$S$_2$O$_3$·5H$_2$O(s)	372.4
H$_2$O(l)	69.9

Determine the **standard** entropy, $S^\ominus$, of anhydrous sodium thiosulfate, $Na_2S_2O_3(s)$.

Give your answer to **3** significant figures.

$S^\ominus$... J K^{-1} mol^{-1} **[4]**

3. Two changes are described below.

For each change,

- write an equation, including state symbols,
- state and explain how the entropy changes.

   i. The reaction of aqueous barium nitrate with aqueous sodium sulfate.

     Full equation with state symbols

     Explanation of entropy change

---**[2]**

ii.   The change that accompanies the standard enthalpy change of atomisation of iodine.

Equation with state symbols

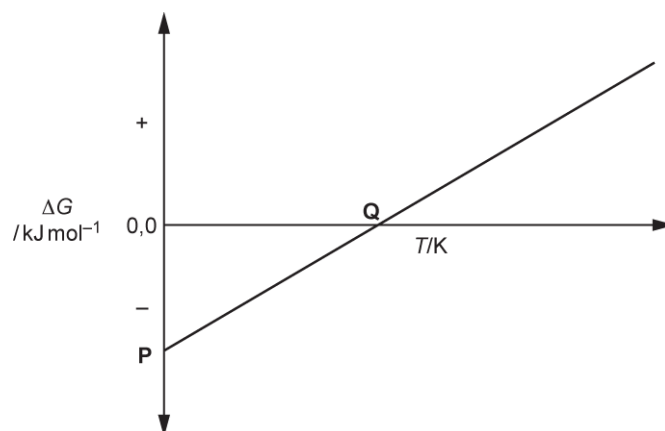
Explanation of entropy
change

---**[2]**

4(a).   This question is about free energy changes, ΔG, enthalpy changes, ΔH, and temperature, T.

The Gibbs' equation is shown below.

$\Delta G = \Delta H - T\Delta S$

A chemist investigates a reaction to determine how ΔG varies with T.
The results are shown in **Fig. 18.1**.

Fig. 18.1

What is significant about the gradient of the line and the values **P** and **Q** shown in **Fig. 18.1**?
Explain your reasoning.

---**[4]**

(b). Iron can be extracted from its ore Fe_3O_4 using carbon.
Several equilibria are involved including **equilibrium 18.1**, shown below.

equilibrium 18.1	$Fe_3O_4(s) + 4C(s) \rightleftharpoons 3Fe(s) + 4CO(g)$	$\Delta H = +676.4$ kJ mol^{-1} $\Delta S = +703.1$ J K^{-1} mol^{-1}

   i.   Why is **equilibrium 18.1** a *heterogeneous* equilibrium?

---**[1]**

   ii.   Write the expression for K_p for **equilibrium 18.1**.

[1]

   iii.   The forward reaction in **equilibrium 18.1** is only feasible at high temperatures.
   o   Show that the forward reaction is **not** feasible at 25 °C.
   o   Calculate the minimum temperature, in K, for the forward reaction to be
       feasible.

minimum temperature = _____ K
[3]

iv.   Another equilibrium involved in the extraction of iron from Fe_3O_4 is shown below.

$$Fe_3O_4(s) + 4CO(g) \rightleftharpoons 3Fe(s) + 4CO_2(g) \qquad \Delta H = -13.5 \text{ kJ mol}^{-1}$$
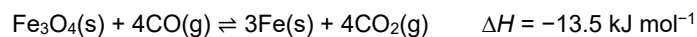
Enthalpy changes of formation, $\Delta_f H$, for $Fe_3O_4(s)$ and $CO_2(g)$ are shown in the table.

Compound	$\Delta_f H$ / kJ mol^{-1}
$Fe_3O_4(s)$	−1118.5
$CO_2(g)$	−393.5

Calculate the enthalpy change of formation, $\Delta_f H$, for CO(g).

$\Delta_f H$, for CO(g) = _____ kJ mol^{-1}
[3]

5(a).   Much of the sulfur required for production of sulfuric acid is obtained from sulfur impurities in natural gas, such as hydrogen sulfide, H_2S.

The H_2S is converted into sulfur in two steps.

Step 1:   Some of the H_2S is reacted with oxygen to form sulfur dioxide, SO_2.
$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$$

Step 2:   The remaining H_2S is reacted with the SO_2 to produce sulfur.
$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(g)$$

i.   Construct the overall equation for the two steps above.

_____**[1]**

ii.   A natural gas supply contains 16.0% H_2S by volume.
The $H_2S(g)$ in 1.50×10^8 dm^3 of this natural gas supply, measured at RTP, is processed into sulfur with an overall percentage yield of 95.0%.

Calculate the mass of sulfur, in g, obtained from 1.50×10^8 dm^3 of natural gas supply.

Give your answer to **three** significant figures and in standard form.

mass of sulfur = ……………………………………………… g **[3]**

(b).   The enthalpy change for the equation in **step 2** is shown below.

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(g) \qquad \Delta H = -145.6 \text{ kJ mol}^{-1}$$
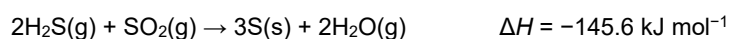
Standard entropies, S, and enthalpy changes of formation, $\Delta_f H$, are given in the table.

Substance	$H_2S(g)$	$SO_2(g)$	$S(s)$	$H_2O(g)$
S / J mol^{-1} K^{-1}	205.7	248.1	31.8	188.7
$\Delta_f H$ / kJ mol^{-1}	−20.6		0	−241.8

i.   Calculate ΔG at 25 °C, and explain whether the reaction in **step 2** is feasible at 25 °C.

Calculate the temperature, in K, at which the feasibility changes.

Show your working and explain your reasoning.

[5]

ii.   Calculate $\Delta_f H$ for $SO_2(g)$.

$\Delta_f H$ for $SO_2(g)$ = ……………………………………………kJ mol^{-1} **[2]**

6(a). This question is about four enthalpy changes, **A**–**D**, that can be linked to the dissolving of potassium sulfate, K_2SO_4, in water.

	Name of enthalpy change	Enthalpy change / kJ mol^{-1}
A	lattice enthalpy of potassium sulfate	−1763
B	enthalpy change of solution of potassium sulfate	+24
C	enthalpy change of hydration of potassium ions	−320
D	enthalpy change of hydration of sulfate ions	

Table 3.1

Define the term *enthalpy change of hydration.*

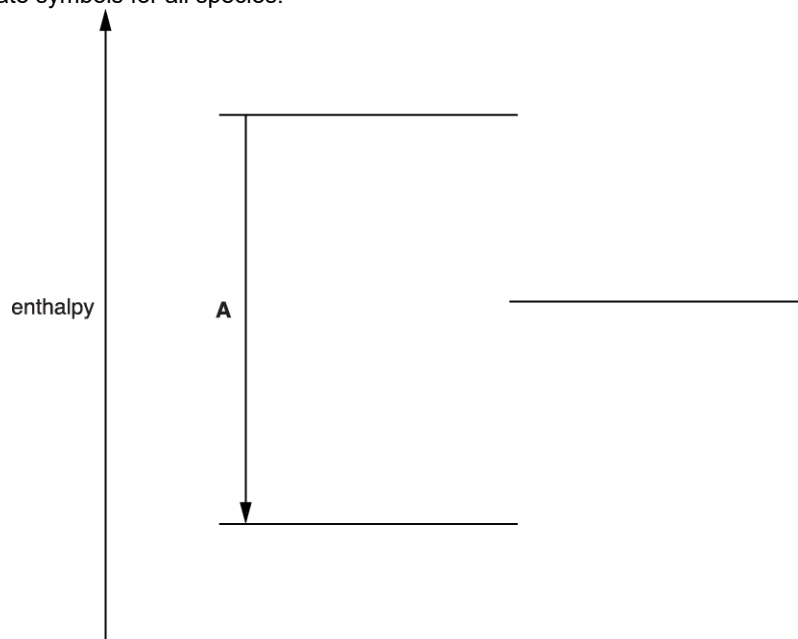---**[2]**

(b). The diagram below is an incomplete energy cycle linking the four enthalpy changes in **Table 3.1**. One of the four energy levels is missing.

Include state symbols for all species.

     i.   Complete the energy cycle as follows.
- o   Add the missing energy level to the diagram. Add the species on all **four** energy levels.
- o   Add arrows to show the direction of the three missing enthalpy changes. Label these enthalpy changes using the letters **B–D** from **Table 3.1**.

[5]

     ii.   Calculate the enthalpy change of hydration of sulfate ions.

ΔH = ……………………………………………… kJ mol^{-1} **[1]**

(c).   The entropy change of solution of K_2SO_4 is +225 J K^{-1} mol^{-1}.

     i.   Suggest, in terms of the states of the particles involved, why this entropy change is positive.

---**[1]**

     ii.   Explain, using a calculation, why K_2SO_4 dissolves in water at 25 °C, despite the enthalpy change of solution being endothermic.
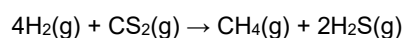

---**[3]**

7.   This question looks at two reactions involving sulfur compounds.

Hydrogen reacts with carbon disulfide as shown below.

$$4H_2(g) + CS_2(g) \rightarrow CH_4(g) + 2H_2S(g)$$

For this reaction, $\Delta H = -234$ kJ mol^{-1} and $\Delta S = -164$ J K^{-1} mol^{-1}.

i.   Why does the reaction have a negative entropy change?

---**[1]**

ii.   Standard entropies are shown in the table below.

substance	$CS_2(g)$	$CH_4(g)$	$H_2S(g)$
$S^{\ominus}$/ JK^{-1} mol^{-1}	238	186	206

Calculate the standard entropy for H_2.

$S^{\ominus}=$ ………………………………………… J K^{-1} mol^{-1} **[2]**

iii.   Explain, with a calculation, whether this reaction is feasible at 25°C.

Show your working.

---**[3]**

iv.   Explain, with a calculation, the significance of temperatures above 1154°C for this
reaction.

---**[2]**

8(a) This question looks at different aspects of entropy.

Three processes are given below.

For each process, state and explain whether the change would be accompanied by an increase or decrease in entropy.

    i.   The freezing of water.

    increase or decrease

    ……

    ……….

    explanation

    ……

    ……………………

----

[1]

    ii.   The reaction of calcium carbonate with hydrochloric acid.

    increase or decrease

    ……

    ……….

    explanation

    ……

    ……………………

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[1]

    iii.   The formation of $O_3(g)$ from $O_2(g)$.

    increase or decrease

    ……

    ……….
    explanation

    ……

    ……………………

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[1]

(b).   The enthalpy and entropy changes of a reaction both have a negative sign.

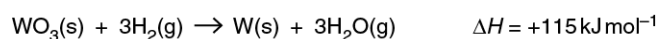Discuss how the feasibility of this reaction will change as the temperature increases.

-- **[2]**

(c).   The metal tungsten is obtained on a large scale from its main ore, wolframite.
Wolframite contains tungsten(VI) oxide, WO_3.

Tungsten is extracted from wolframite by reduction with hydrogen:

$$WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g) \qquad \Delta H = +115\,kJ\,mol^{-1}$$

Standard entropies are given in the table below.

Substance	$WO_3(s)$	$H_2(g)$	$W(s)$	$H_2O(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	76	131	33	189

i.   Calculate the free energy change, ΔG, in kJ mol^{-1}, for this reaction at 25 °C.

Show your working.

ΔG at 25 °C = ………………………………………………… kJ mol^{-1} **[2]**

ii.   Calculate the minimum temperature, in K, at which this reaction becomes feasible.

Show your working.

minimum temperature = ………………………………………………… K **[2]**

9. A student is asked to calculate ΔG at 25 °C for the combustion of butan-1-ol. The teacher provides two pieces of information.
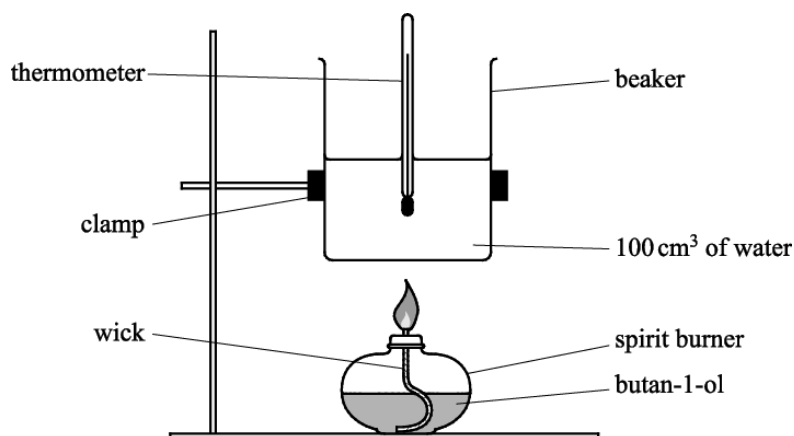
    o   The equation for the combustion of butan-1-ol.

$$CH_3(CH_2)_3OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \qquad \textbf{Equation 2}$$

• Standard entropies of butan-1-ol, oxygen, carbon dioxide and water.

	$CH_3(CH_2)_3OH(l)$	$O_2(g)$	$CO_2(g)$	$H_2O(l)$
$S^\ominus$ / J K^{-1} mol^{-1}	228	205	214	70

The student carries out an experiment using the apparatus below and obtains the following results. The specific heat capacity of water is 4.18 J g^{-1} K^{-1}.

Mass of burner and butan-1-ol before burning / g	98.997
Mass of burner and butan-1-ol after burning / g	98.738
Initial temperature / °C	18.5
Maximum temperature reached / °C	39.0

Use the information on the previous page to calculate ΔG, in kJ mol^{-1}, for the combustion of butan-1-ol according to **Equation 2** at 25 °C.

Show **all** your working.

ΔG = …………………………………kJ mol^{-1} **[7]**

END OF QUESTION PAPER