23. Chemical energetics

23.4 Gibbs free energy change, ΔG

Paper 4

Question Paper

1 **(a)** Carbon disulfide, CS_2, is flammable and reacts readily with oxygen, as shown in reaction 1.

reaction 1 $CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$

Table 3.1 shows the standard enthalpy of formation, $\Delta H_f^\ominus$, and the standard entropy, $S^\ominus$, for some substances.

Table 3.1

	$CS_2(g)$	$O_2(g)$	$CO_2(g)$	$SO_2(g)$
$\Delta H_f^\ominus$ / kJ mol^{-1}	116.7	0.0	–393.5	–296.8
$S^\ominus$ / J K^{-1} mol^{-1}	237.8	205.2	213.8	248.2

Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, in kJ mol^{-1}, for reaction 1 at 25 °C.

$\Delta G^\ominus$ = ... kJ mol^{-1} [3]

(b) Carbon disulfide reacts with chlorine to form tetrachloromethane, as shown in reaction 2.

reaction 2 $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$ $\Delta H^\ominus = -261.6\,kJ\,mol^{-1}$

$\Delta S^\ominus = -365.5\,J\,K^{-1}\,mol^{-1}$

Calculate the maximum temperature, in K, for reaction 2 to be feasible.

temperature = ... K [2]

2 **(d)** At 25 °C the enthalpy change of solution of compound **Z** is +26 kJ mol^{-1}. The entropy change of solution of **Z** at the same temperature is +52 J K^{-1} mol^{-1}.

Calculate the value of the Gibbs free energy change, ΔG, for the solution of **Z** at 25 °C.

ΔG = ... kJ mol^{-1} [2]

(e) **(i)** Use your answer to **(d)** to predict whether or not **Z** is soluble in water at 25 °C. Explain your answer.

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.... [1]

(ii) Predict whether **Z** becomes more or less soluble as the water is heated from 25 °C to 95 °C. Explain your answer.

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.... [1]

3 **(b)** The exhaust systems of many diesel-fuelled cars contain an additional system to reduce vehicle emissions. This uses a liquid that is added to the exhaust system.

This liquid contains urea, $(NH_2)_2CO$, which decomposes on heating to isocyanic acid, HNCO, and ammonia.

reaction 1 $(NH_2)_2CO \rightarrow HNCO + NH_3$

Isocyanic acid reacts with water vapour to form ammonia and carbon dioxide.

reaction 2 $HNCO(g) + H_2O(g) \rightarrow NH_3(g) + CO_2(g)$

Some values for standard enthalpy changes of formation, $\Delta H_f^\ominus$, and standard entropies, $S^\ominus$, are given in Table 5.1.

Table 5.1

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}	$S^\ominus$ / J K^{-1} mol^{-1}
HNCO(g)	–101.7	+238.2
$H_2O(g)$	–241.8	+188.8
$NH_3(g)$	–45.9	+192.8
$CO_2(g)$	–393.5	+213.8

(i) Explain what is meant by the term entropy of a system.

....

.... [1]

(ii) Use the data in Table 5.1 to calculate $\Delta G^\ominus$ for **reaction 2** at 25 °C.
Show your working.

$\Delta G^\ominus$ = ... kJ mol^{-1} [4]

(c) The ammonia formed in reactions 1 and 2 can be used to remove nitrogen dioxide from exhaust emissions, as shown.

reaction 3 $8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$

Use the equations for reactions 1, 2 and 3 to construct an overall equation for the reduction of NO_2 by $(NH_2)_2CO$.

.... [1]

4 **(f)** The standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of $AgNO_3(s)$ in water is +22.6 kJ mol^{-1}.

Suggest how the feasibility of dissolving $AgNO_3(s)$ in water changes with temperature.

Explain your answer.

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....

.... [2]

5 Hydrogen peroxide is a liquid at 298 K. It is moderately stable under room conditions but will decompose quickly if a catalyst is added.

reaction 1 $2H_2O_2(l) \rightarrow 2H_2O\ (l) + O_2\ (g)$

(c) Some standard entropies, $S^\ominus$, are shown in Table 3.2.

Table 3.2

substance	$S^\ominus$ / J K^{-1} mol^{-1}
$H_2O_2(l)$	+102
$H_2O(l)$	+70

The enthalpy change and Gibbs free energy change for the following reaction are shown.

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g) \qquad \Delta H^\ominus = -196\ \text{kJ mol}^{-1} \quad \Delta G^\ominus = -238\ \text{kJ mol}^{-1}$$

Use the data given to calculate the standard entropy of oxygen, $S^\ominus$, $O_2(g)$.

$S^\ominus$, $O_2(g)$ = ... J K^{-1} mol^{-1} [3]

6 Some electrode potentials are shown in Table 3.1.

Table 3.1

electrode reaction	$E^\ominus$/V
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89

(f) Iron(II) chloride, $FeCl_2$, is oxidised by chlorine to form iron(III) chloride, $FeCl_3$, under standard conditions.

$$2FeCl_2(s) + Cl_2(g) \rightarrow 2FeCl_3(s) \qquad \Delta H^\ominus = -128\,kJ\,mol^{-1}$$

Table 3.2

species	$S^\ominus$/J K^{-1} mol^{-1}
$Cl_2(g)$	223
$FeCl_2(s)$	120
$FeCl_3(s)$	142

(i) Use Table 3.2 and other data to calculate the Gibbs free energy change, $\Delta G^\ominus$, for this reaction.

Show your working.

$\Delta G^\ominus$ = ... kJ mol^{-1} [3]

(ii) Predict whether this reaction becomes more or less feasible at a higher temperature.

Explain your answer.

The reaction becomes .... feasible.

explanation ....

....
[1]

7 **(e)** The reaction of solid hydrated barium hydroxide, $Ba(OH)_2{\bullet}8H_2O$, with ammonium salts is endothermic.

(i) Calculate the **minimum** temperature at which the reaction of $Ba(OH)_2{\bullet}8H_2O$ with NH_4NO_3 becomes feasible. Show all your working.

$$Ba(OH)_2{\bullet}8H_2O(s) + 2NH_4NO_3(s) \rightarrow 2NH_3(g) + Ba(NO_3)_2(s) + 10H_2O(l) \quad \Delta H_r^\ominus = +132\,kJ\,mol^{-1}$$

$$\Delta S^\ominus = +616\,J\,K^{-1}\,mol^{-1}$$

temperature = ... °C [2]

(ii) Barium hydroxide reacts readily with ammonium chloride on mixing at room temperature.

$$Ba(OH)_2{\bullet}8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + BaCl_2{\bullet}2H_2O(s) + 8H_2O(l) \quad \Delta H_r^\ominus = +133\,kJ\,mol^{-1}$$

Some relevant standard entropies are given in Table 1.2.

Table 1.2

substance	$Ba(OH)_2{\bullet}8H_2O(s)$	$NH_4Cl(s)$	$NH_3(g)$	$BaCl_2{\bullet}2H_2O(s)$	$H_2O(l)$
$S^\ominus / J\,K^{-1}\,mol^{-1}$	427	95	192	203	70

Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for this reaction at 25 °C.

$\Delta G^\ominus$ = ... $kJ\,mol^{-1}$ [3]

8 **(a)** Calcium carbonate decomposes on heating.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

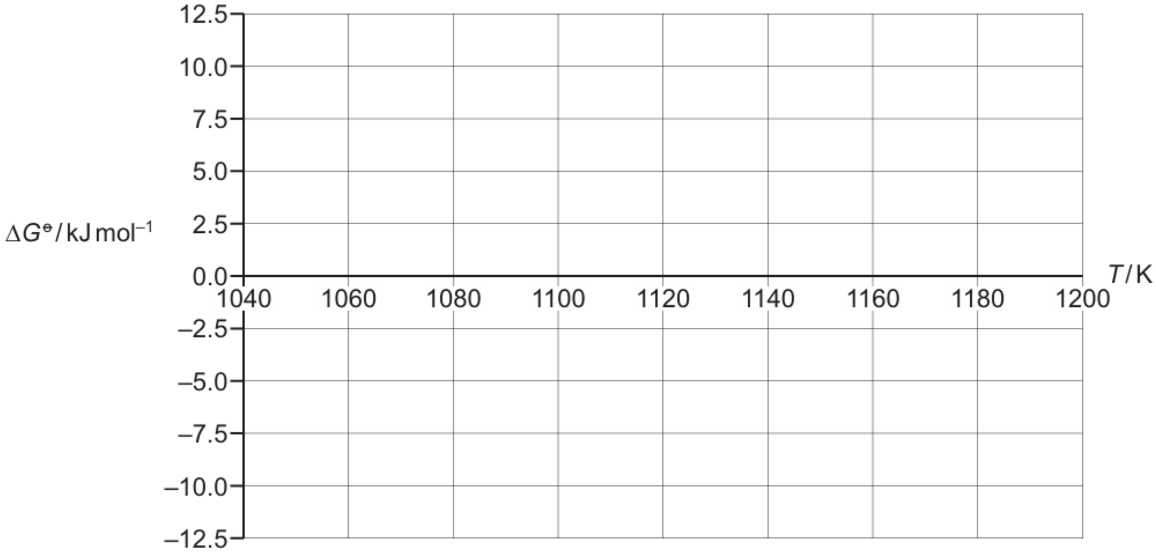
Table 4.1 shows the values of the Gibbs free energy change, $\Delta G^\ominus$, for this reaction at various temperatures.

Table 4.1

T/K	$\Delta G^\ominus$/kJ mol^{-1}
1050	9.9
1085	4.3
1120	–1.3
1148	–5.8
1176	–10.3

Assume the standard enthalpy change, $\Delta H^\ominus$, and the standard entropy change, $\Delta S^\ominus$, for this reaction remain constant over this temperature range.

(i) Use the data in Table 4.1 to plot a graph of $\Delta G^\ominus$ against T on the grid.



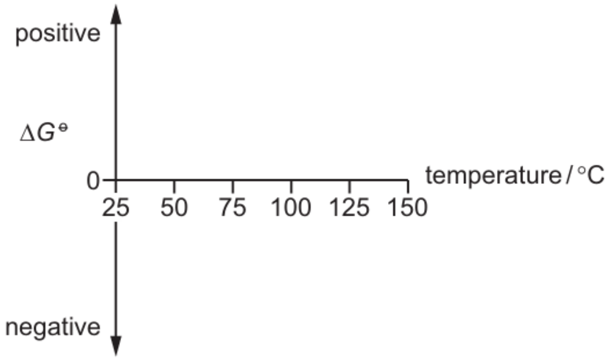
[2]

(ii) Calculate the gradient of your graph. Determine the $\Delta S^\ominus$ in J K^{-1} mol^{-1} for this reaction. Show all working.

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

9 **(c) (iii)** The evaporation of one mole of water has a standard Gibbs free energy change, $\Delta G^{\ominus}$, of +8.6 kJ at 25 °C.

Sketch a graph on the axes to show how $\Delta G^{\ominus}$ changes for this process between 25 °C and 150 °C at 101 kPa.



[2]

(d) The reaction between A and B is feasible at low temperatures but is **not** feasible at high temperatures.

$$A + B \rightleftharpoons C + D$$

Deduce the signs of ΔH and ΔS for this reaction and explain why the feasibility changes with temperature.

sign of ΔH = ... sign of ΔS = ...

....

....

....

.... [2]

10 When dilute sulfuric acid is electrolysed, water is split into hydrogen and oxygen.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

A current of **x** A is passed through the solution for 14.0 minutes. 462 cm^3 of hydrogen are produced at the cathode, measured under room conditions.

(e) The standard entropies, $S^{\ominus}$, of three species are given in the table.

species	$S^{\ominus}$ / $J K^{-1} mol^{-1}$
$H_2O(l)$	+70
$H_2(g)$	+131
$O_2(g)$	+205

(i) Calculate $\Delta S^{\ominus}$ for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$.

$\Delta S^{\ominus}$ = ... $J K^{-1} mol^{-1}$ [1]

(ii) $\Delta H^{\ominus}$ for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ is +572 $kJ mol^{-1}$.

Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.

$\Delta G^{\ominus}$ = ... $kJ mol^{-1}$ [2]

(iii) Predict the effect of increasing temperature on the spontaneity of this reaction.
Explain your answer.

....

.... [1]

11 $EDTA^{4-}$, is a polydentate ligand.

(b) Cadmium ions form complexes with methylamine, CH_3NH_2, and with 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, as shown in equilibriums **2** and **3**. 1,2-diaminoethane is shown as en.

equilibrium **2** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O$ $K_{stab2} = 3.60 \times 10^6$

equilibrium **3** $[Cd(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4H_2O$ $K_{stab3} = 4.20 \times 10^{10}$

An equilibrium is set up between these two complexes as shown in equilibrium **4**.

equilibrium **4** $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4CH_3NH_2$ $\Delta H^\circ = +0.840\,kJ\,mol^{-1}$
$\Delta S^\circ = +80.9\,J\,K^{-1}\,mol^{-1}$

(i) K_{eq4} is the equilibrium constant for equilibrium **4**.

Write an expression for K_{eq4} in terms of K_{stab2} and K_{stab3}.

$K_{eq4} =$

[1]

(ii) Calculate the value of the standard Gibbs free energy change, ΔG°, for equilibrium **4** at 298 K.

(iii) State how the value of ΔG° changes as the temperature increases. Explain your answer.

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.... [1]

12 Pure water is a very poor conductor of electricity. However, when hydrogen chloride gas is dissolved in water, ions are formed and a current flows during electrolysis.

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$$

The overall change after electrolysis is that hydrogen chloride gas is converted into hydrogen and chlorine.

$$2HCl(g) \rightarrow H_2(g) + Cl_2(g)$$

When a current of 3.10 A is passed through the solution for *Y* minutes, 351 cm^3 of chlorine are produced at the anode, measured under room conditions.

(e) The standard entropies, $S^\ominus$, of three species are given in the table.

species	$S^\ominus$ / J K^{-1} mol^{-1}
$HCl(g)$	+187
$H_2(g)$	+131
$Cl_2(g)$	+223

(i) Calculate $\Delta S^\ominus$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$.

$\Delta S^\ominus$ = ... J K^{-1} mol^{-1} [1]

(ii) $\Delta H^\ominus$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$ is +185 kJ mol^{-1}.

Calculate $\Delta G^\ominus$ for this reaction at 298 K.

$\Delta G^\ominus$ = ... kJ mol^{-1} [2]

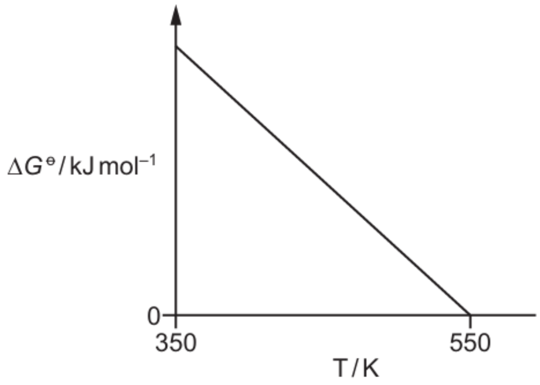
(iii) Predict the effect of increasing temperature on the spontaneity of this reaction. Explain your answer.

....

.... [1]

13 **(e)** For a particular gas phase reaction the variation in standard Gibbs free energy change, ΔG°, with temperature is shown.

Assume standard enthalpy change, ΔH°, and standard entropy change, ΔS°, remain constant with temperature.



(i) Write the equation that relates ΔG° to ΔH° and ΔS°.

.... [1]

(ii) Use this equation to explain why ΔG° becomes **less** positive as temperature increases in this reaction.

....

.... [1]

14 **(c)** The reaction $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$ is not spontaneous at room temperature.

(i) Give the full name for the term $\Delta G^{\ominus}$.

.... [1]

(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.

equation ....

....

....

....

[2]

15 The table shows some standard entropy data.

substance	standard entropy, $S^\ominus$ / J K^{-1} mol^{-1}
$PbO_2(s)$	77
$PbO(s)$	69
$O_2(g)$	205

Lead(IV) oxide, PbO_2, decomposes to lead(II) oxide, PbO, and oxygen when heated.

$$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g) \qquad \Delta H^\ominus = +118\,\text{kJ mol}^{-1}$$

(b) Use the value of $\Delta H^\ominus$ and your answer to **(a)** to calculate the temperature at which this reaction becomes feasible.

T = ... K [3]