23. Chemical energetics

23.3 Entropy change, ΔS

Paper 4

Question Paper

1 **(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 $(NH_2)_2CO \longrightarrow HNCO + NH_3$

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

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

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]

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

(a) **(i)** Define entropy.

.....

..... [1]

(ii) Predict the sign of the standard entropy change of reaction 1.

Explain your answer.

sign .....

explanation .....

.....

[1]

3 Potassium chloride, KCl, and magnesium chloride, MgCl_2, are both ionic solids.

Table 1.1

energy change	value / kJ mol^{-1}
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of KCl	+15
lattice energy, $\Delta H^{\ominus}_{latt}$, of KC$l$(s)	–701
standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of K^+	–322
standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of Cl^-	–364
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of MgCl_2	–155
lattice energy, $\Delta H^{\ominus}_{latt}$, of MgC$l_2$(s)	–2493

(e) (i) Explain what is meant by entropy, *S*.

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..... [1]

(ii) Potassium chloride is very soluble in water at 20 °C.

Explain the solubility of potassium chloride by reference to change in entropy, ΔS.

.....

..... [1]

(iii) Use the Gibbs equation and your answer to **(e)(ii)** to predict whether potassium chloride is more soluble in water at 20 °C or at 80 °C. Explain your answer.

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..... [1]

4 Calcium chloride, $CaCl_2$, is an ionic solid.

The values of some energy changes are shown in Table 1.1.

Table 1.1

energy change	value / kJ mol^{-1}
lattice energy, $\Delta H^{\ominus}_{latt}$, $CaCl_2(s)$	–2237
standard enthalpy change of atomisation of calcium	+193
first ionisation energy of calcium	+590
second ionisation energy of calcium	+1150
standard enthalpy change of atomisation of chlorine	+121
first electron affinity of chlorine	–364

(e) Calcium fluoride, $CaF_2(s)$, can be synthesised directly from its elements.

The value of $\Delta H^{\ominus}_f(CaF_2(s))$ is –1214 kJ mol^{-1}.

(i) Predict the sign of the entropy change, $\Delta S^{\ominus}$, for this synthesis. Explain your answer.

The sign of the entropy change is ..... .

explanation .....

.....

[1]

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

.....

..... [1]

(ii) Place one tick (✓) in each row of the table to show the sign of each entropy change, ΔS.

process	ΔS is negative	ΔS is zero	ΔS is positive
$NaCl$ dissolving in water			
water solidifying to ice			

[1]

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

.....

..... [1]

(b) State and explain whether the entropy change of each of the following processes is positive or negative. Do not consider the entropy change of the surroundings.

- liquid water at 80 °C is cooled to 60 °C

The entropy change is ..... because .....

.....

- solid calcium chloride is added to water and the mixture is stirred

The entropy change is ..... because .....

.....

- the change corresponding to the lattice energy of calcium chloride, ΔH_{latt} $CaCl_2(s)$, takes place

The entropy change is ..... because .....

.....

[3]

7 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.

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

(a) Use the data to calculate the value of $\Delta S^{\ominus}$ for this reaction.

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

(c) Solid lead(II) oxide can be made by heating lead metal in air.

Predict the **sign** of the standard entropy change of this reaction. Explain your answer.

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..... [1]