A LEVEL CHEMISTRY

TOPIC 10 –THERMODYNAMICS

ASSESSED HOMEWORK

Answer all questions

Max 80 marks

Name	…………………………………………………………..
Mark	……../80 ……....% Grade ………

1. Some thermodynamic data for fluorine and chlorine are shown in the table.
In the table, X represents the halogen F or Cl.

	Fluorine	**Chlorine**
Electronegativity	4.0	3.0
Electron affinity / kJ mol^{-1}	–348	–364
Enthalpy of atomisation / kJ mol^{-1}	+79	+121
Enthalpy of hydration of X^-(g) / kJ mol^{-1}	–506	–364

(a) Explain the meaning of the term *electron affinity*.

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(2)

(b) Explain why the electronegativity of fluorine is greater than the electronegativity of chlorine.

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(c) Explain why the hydration enthalpy of the fluoride ion is more negative than the hydration enthalpy of the chloride ion.

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(2)

(d) The enthalpy of solution for silver fluoride in water is –20 kJ mol^{-1}.

The hydration enthalpy for silver ions is –464 kJ mol^{-1}.

(i) Use these data and data from the table to calculate a value for the lattice enthalpy of dissociation of silver fluoride.

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(ii) Suggest why the entropy change for dissolving silver fluoride in water has a positive value.

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(iii) Explain why the dissolving of silver fluoride in water is always a spontaneous process.

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(Total 12 marks)

2. The balance between enthalpy change and entropy change determines the feasibility of a reaction. The table below contains enthalpy of formation and entropy data for some elements and compounds.

	N_2(g)	O_2(g)	NO(g)	C(graphite)	C(diamond)
$\Delta H_f^\ominus$/kJ mol^{-1}	0	0	+90.4	0	+1.9
$S^\ominus$/J K^{-1} mol^{-1}	192.2	205.3	211.1	5.7	2.4

(a) Explain why the entropy value for the element nitrogen is much greater than the entropy value for the element carbon (graphite).

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(b) Suggest the condition under which the element carbon (diamond) would have an entropy value of zero.

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(1)

(c) Write the equation that shows the relationship between Δ*G*, Δ*H* and Δ*S* for a reaction.

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(1)

(d) State the requirement for a reaction to be feasible.

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(1)

(e) Consider the following reaction that can lead to the release of the pollutant NO into the atmosphere.

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$$

Use data from the table above to calculate the minimum temperature above which this reaction is feasible.

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(f) At temperatures below the value calculated in part (e), decomposition of NO into its elements should be spontaneous. However, in car exhausts this decomposition reaction does **not** take place in the absence of a catalyst.
Suggest why this spontaneous decomposition does **not** take place.

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(1)

(g) A student had an idea to earn money by carrying out the following reaction.

$$C(graphite) \longrightarrow C(diamond)$$

Use data from the table above to calculate values for ΔH and $\Delta S^{\ominus}$ for this reaction.
Use these values to explain why this reaction is **not** feasible under standard pressure at any temperature.

$\Delta H^{\ominus}$ ....

$\Delta S^{\ominus}$ ....

Explanation ....

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(3)
(Total 14 marks)

3. Comparison of lattice enthalpies from Born-Haber cycles with lattice enthalpies from calculations based on a perfect ionic model are used to provide information about bonding in crystals.

(a) Define the terms *enthalpy of atomisation* and *lattice dissociation enthalpy*.

Enthalpy of atomisation ....

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Lattice dissociation enthalpy ....

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(4)

(b) Use the following data to calculate a value for the lattice dissociation enthalpy of sodium chloride.

	$\Delta H^{\ominus}$/ kJ mol^{-1}
$Na(s) \longrightarrow Na(g)$	+109
$Na(g) \longrightarrow Na^{+}(g) + e^{-}$	+494
$Cl_2(g) \longrightarrow 2Cl(g)$	+242
$Cl(g) + e^{-} \longrightarrow Cl^{-}(g)$	–364
$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$	–411

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(3)

(c) Consider the following lattice dissociation enthalpy ($\Delta H_L^\ominus$) data.

	NaBr	AgBr
$\Delta H_L^\ominus$(experimental)/kJ mol^{-1}	+733	+890
$\Delta H_L^\ominus$(theoretical)/kJ mol^{-1}	+732	+758

The values of $\Delta H_L^\ominus$ (experimental) have been determined from Born–Haber cycles.

The values of $\Delta H_L^\ominus$ (theoretical) have been determined by calculation using a perfect ionic model.

(i) Explain the meaning of the term *perfect ionic model*.

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(ii) State what you can deduce about the bonding in NaBr from the data in the table.

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(1)

(iii) State what you can deduce about the bonding in AgBr from the data in the table.

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(1)

(Total 11 marks)

4. Thermodynamics can be used to investigate the changes that occur when substances such as calcium fluoride dissolve in water.

(a) Give the meaning of each of the following terms.

(i) enthalpy of lattice formation for calcium fluoride

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(ii) enthalpy of hydration for fluoride ions

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(1)

(b) Explain the interactions between water molecules and fluoride ions when the fluoride ions become hydrated.

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(c) Consider the following data.

	$\Delta H^{\ominus}$/ kJ mol^{-1}
Enthalpy of lattice formation for CaF_2	–2611
Enthalpy of hydration for Ca^{2+} ions	–1650
Enthalpy of hydration for F^- ions	–506

Use these data to calculate a value for the enthalpy of solution for CaF_2

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(2)
(Total 7 marks)

5. Ethyl ethanoate can be prepared by the reactions shown below.

Reaction 1

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ $\Delta H^{\ominus} = -2.0\ kJ\ mol^{-1}$

Reaction 2

$CH_3COCl(l) + C_2H_5OH(l) \rightarrow CH_3COOC_2H_5(l) + HCl(g)$ $\Delta H^{\ominus} = -21.6\ kJ\ mol^{-1}$

Use the information given above and the data below to calculate values for the standard entropy change, $\Delta S^{\ominus}$, and the standard free-energy change, $\Delta G^{\ominus}$, for **Reaction 2** at 298 K.

	$CH_3COCl(l)$	$C_2H_5OH(l)$	$CH_3COOC_2H_5(l)$	$HCl(g)$
$S^{\ominus}/J K^{-1} mol^{-1}$	201	161	259	187

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(Total 6 marks)

6. The feasibility of a physical or a chemical change depends on the balance between the thermodynamic quantities of enthalpy change (ΔH), entropy change (ΔS) and temperature (T).

(a) Suggest how these quantities can be used to predict whether a change is feasible.

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(b) Explain why the evaporation of water is spontaneous even though this change is endothermic.
In your answer, refer to the change in the arrangement of water molecules and the entropy change.

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(c) This table contains some thermodynamic data for hydrogen, oxygen and water.

	$S^\ominus$ / J K^{-1} mol^{-1}	$\Delta H_f^\ominus$/ kJ mol^{-1}
$H_2(g)$	131	0
$O_2(g)$	205	0
$H_2O(g)$	189	−242
$H_2O(l)$	70	

(i) Calculate the temperature above which the reaction between hydrogen and oxygen to form gaseous water is **not** feasible.

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(ii) State what would happen to a sample of gaseous water that was heated to a temperature higher than that of your answer to part (c)(i).
Give a reason for your answer.

What would happen to gaseous water ....

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Reason ....

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(2)

(d) When hydrogen is used as a fuel, more heat energy can be obtained if the gaseous water formed is condensed into liquid water.

Use entropy data from the table in part (c) to calculate the enthalpy change when one mole of gaseous water is condensed at 373 K.
Assume that the free-energy change for this condensation is zero.

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(3)
(Total 15 marks)

7. Chlorine is formed in a reversible reaction as shown by the equation

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$

(a) Use the data below to calculate the standard enthalpy change, $\Delta H^{\ominus}$, and the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

Substance	HCl(g)	O_2(g)	Cl_2(g)	H_2O(g)
$\Delta H_f^{\ominus}$/kJ mol^{-1}	–92	0	0	–242
$S^{\ominus}$/ J K^{-1} mol^{-1}	187	205	223	189

Standard enthalpy change, $\Delta H^{\ominus}$ ....

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Standard entropy change, $\Delta S^{\ominus}$ ....

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(6)

(b) The data below apply to a different gas phase reversible reaction.

Standard enthalpy change, $\Delta H^{\ominus}$ = +208 kJ mol^{-1}
Standard entropy change, $\Delta S^{\ominus}$ = +253 J K^{-1} mol^{-1}

(i) Deduce the effect of an increase in temperature on the position of the equilibrium in this reaction. Use Le Chatelier's principle to explain your answer.

Effect ....

Explanation ....

(ii) Calculate the minimum temperature at which this reaction is feasible.

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(7)
(Total 13 marks)

8. Which one of the equations below represents a reaction that is feasible at all temperatures?

A P(s) → Q(s) + R(g) endothermic

B 2L(g) + M(g) → 2N(g) exothermic

C S(g) → 2T(g) exothermic

D A(g) + B(g) → C(g) endothermic

(Total 1 mark)

9. Using the information below, answer this question.

$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$ $\Delta H^{\ominus} = +96\ kJ\ mol^{-1}$, $\Delta S^{\ominus} = +138\ J\ K^{-1}\ mol^{-1}$

	$Fe_2O_3(s)$	**$H_2(g)$**	**Fe(s)**
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	−822.0	0	0
$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}	90.0	131.0	27.0

The standard enthalpy of formation of steam is

A +286 kJ mol^{-1}

B +242 kJ mol^{-1}

C −242 KJ mol^{-1}

D −286 kJ mol^{-1}

(Total 1 mark)