# 2.3 Energetics and Thermodynamics: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

**Answer ALL questions. Show all your working.**

**1** This question uses standard enthalpies of formation and Hess's law to calculate the enthalpy of combustion of propane.

**(a)** Write a balanced symbol equation, including state symbols, for the complete combustion of propane, $C_3H_8$. **(2)**

**(b)** Standard enthalpies of formation (kJ/mol): $C_3H_8(g)$ = -104, $CO_2(g)$ = -393, $H_2O(l)$ = -286. Calculate the standard enthalpy of combustion of propane using Hess's law. **(5)**

**(c)** The literature value for the enthalpy of combustion of propane is -2220 kJ/mol. Comment on the agreement between this value and your calculated value in (b). **(2)**

**(Total for Question 1 is 9 marks)**


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**2** The table gives enthalpy data needed to construct a Born-Haber cycle for magnesium chloride, $MgCl_2$.

Enthalpy of formation of $MgCl_2$(s), delta Hf = -641 kJ/mol
Enthalpy of atomisation of Mg(s), delta Hat = +148 kJ/mol
First ionisation energy of Mg, IE1 = +738 kJ/mol
Second ionisation energy of Mg, IE2 = +1451 kJ/mol
Enthalpy of atomisation of chlorine (per mole of Cl atoms), delta Hat = +122 kJ/mol
Electron affinity of Cl, EA = -349 kJ/mol

**(a)** Define the term first ionisation energy. **(2)**

**(b)** Explain why the enthalpy of atomisation of chlorine is given as a value per mole of Cl atoms, rather than per mole of $Cl_2$ molecules. **(1)**

**(c)** Using the data given, construct a Born-Haber cycle and calculate the lattice enthalpy of formation of magnesium chloride, $MgCl_2$. Show all steps in your working. **(4)**

**(d)** The theoretical (calculated) lattice enthalpy of $MgCl_2$, based on a perfect ionic model, is -2326 kJ/mol. Compare this with your Born-Haber (experimental) value from part (c), and suggest what this comparison indicates about the bonding in $MgCl_2$. **(2)**

**(Total for Question 2 is 9 marks)**


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**3** This synoptic question links the thermodynamics of the $N_2O_4/NO_2$ equilibrium to its equilibrium constant and the effect of temperature.

**(a)** For the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, delta H = +57.2 kJ/mol and delta S = +176 J/(K mol) (assume both are constant with temperature). Calculate delta G for this reaction at 298 K, in kJ/mol. **(3)**

**(b)** State what the sign of delta G found in (a) indicates about the position of equilibrium at 298 K, and relate this to the fact that $N_2O_4$ is the predominant species present at room temperature. **(2)**

**(c)** Use the relationship delta G = -RT ln K, with R = 8.31 J/(K mol), to calculate the equilibrium constant, K, for this reaction at 298 K. **(4)**

**(d)** Calculate delta G and hence K at 350 K (assume delta H and delta S remain constant), and use your results to explain, in terms of Le Chatelier's principle, why K increases with temperature for this reaction. **(3)**

**(Total for Question 3 is 12 marks)**

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**4** This question uses a Born-Haber cycle to determine the lattice enthalpy of formation of calcium oxide.

**(a)** The bond dissociation enthalpy of $O_2(g)$ is +498 kJ/mol. Calculate the atomisation enthalpy of oxygen, 1/2 $O_2(g)$ -> O(g). **(2)**

**(b)** Explain why the second ionisation energy of calcium, $Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$, is greater than the first ionisation energy, $Ca(g) \rightarrow Ca^+(g) + e^-$. **(2)**

**(c)** Explain why the second electron affinity of oxygen, $O^-(g) + e^- \rightarrow O^{2-}(g)$, is endothermic even though it brings together a negative ion and an electron. **(2)**

**(d)** Using delta Hf(CaO) = -635 kJ/mol, atomisation enthalpy of Ca = +178 kJ/mol, first ionisation energy of Ca = +590 kJ/mol, second ionisation energy of Ca = +1145 kJ/mol, atomisation enthalpy of O (from (a), ft) = +249 kJ/mol, first electron affinity of O = -141 kJ/mol, and second electron affinity of O = +798 kJ/mol, use a Born-Haber cycle (Hess's law) to calculate the lattice enthalpy of formation of CaO ($Ca^{2+}(g) + O^{2-}(g) \rightarrow CaO(s)$). **(6)**

**(Total for Question 4 is 12 marks)**


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# Mark scheme · 2.3 Energetics and Thermodynamics: 1-hour Pack

## Question 1

(a) correct formulae and balancing: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ **B1**

(a) correct state symbols: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ **B1**

**(a) Answer: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$**

(b) correct Hess's law expression: delta Hc = sum(delta Hf products) - sum(delta Hf reactants) **M1**

(b) correct substitution for products: (3 x -393) + (4 x -286) **M1**

(b) products sum = -2323 kJ/mol **A1**

(b) correct subtraction using reactants: delta Hc = -2323 - (-104) **M1**

(b) -2219 kJ/mol, cao **A1**

**(b) Answer: -2219 kJ/mol**

(c) the calculated value (-2219 kJ/mol) agrees very closely with the literature value (-2220 kJ/mol), oe **B1**

(c) this close agreement is expected because the calculation uses accurately known enthalpies of formation and Hess's law, an exact method with no experimental measurement error involved, oe **B1**

**(c) Answer: Very close agreement (within about 1 kJ/mol).**

## Question 2

(a) the energy required to remove one electron from each atom in one mole of gaseous atoms **B1**

(a) to form one mole of gaseous 1+ ions oe (gaseous state must be specified for full credit) **B1**

**(a) Answer: The energy required to remove one electron from each atom in one mole of gaseous atoms, forming one mole of gaseous 1+ ions.**

(b) atomisation is defined as forming one mole of gaseous atoms; $Cl_2(g) \rightarrow 2Cl(g)$ produces 2 mol of atoms per mole of $Cl_2$, so the value must be expressed (halved) per mole of atoms oe **B1**

**(b) Answer: Enthalpy of atomisation is defined per mole of gaseous atoms formed; since 1 mol of $Cl_2$ gives 2 mol of Cl atoms, the value is expressed per mole of atoms.**

(c) correct cycle relationship set up: delta Hf = delta Hat(Mg) + IE1 + IE2 + 2 x delta Hat(Cl) + 2 x EA(Cl) + delta H(lattice) (oe, allow cycle drawn or described) **M1**

(c) correct doubling of the chlorine terms: 2 x 122 and 2 x (-349), since 2 mol of Cl are needed per mole of $MgCl_2$ **M1**

(c) correct sum of all non-lattice terms: 148 + 738 + 1451 + 244 - 698 = 1883 (kJ/mol) **A1**

(c) delta H(lattice) = -641 - 1883 = -2524 (kJ/mol) cao **A1**

**(c) Answer: Lattice enthalpy of formation of $MgCl_2$ = -2524 kJ/mol**

(d) the experimental (Born-Haber) value is more exothermic/larger in magnitude than the theoretical ionic value, ecf from (c) **B1**

(d) this indicates that the bonding in $MgCl_2$ has some covalent character in addition to ionic bonding (the ionic model is not a perfect description) oe **B1**

**(d) Answer: The experimental value (-2524 kJ/mol) is more exothermic than the theoretical ionic value (-2326 kJ/mol), suggesting the bonding in $MgCl_2$ has some covalent character (polarisation of the $Cl^-$ ion), so it is not purely ionic.**


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## Question 3

(a) convert units consistently, e.g. delta H = 57200 J/mol **M1**

(a) correct substitution: delta G = 57200 - (298 x 176) **M1**

(a) +4.75 kJ/mol (accept +4.7 to +4.8), cao **A1**

**(a) Answer: +4.75 kJ/mol**

(b) delta G is positive, so the forward reaction (as written) is not thermodynamically favourable under standard conditions at 298 K, meaning the equilibrium position lies towards the reactant ($N_2O_4$) side, oe **B1**

(b) this is consistent with $N_2O_4$ being the predominant species observed at room temperature, oe **B1**

**(b) Answer: Positive delta G indicates the equilibrium favours $N_2O_4$ at 298 K, consistent with observation.**

(c) correct rearrangement: ln K = -delta G/(RT) **M1**

(c) correct substitution using delta G in J/mol (4750 J/mol, ft) and T = 298 K **M1**

(c) K = 0.15 (accept 0.14-0.15), ft **A1**

(c) K < 1 is consistent with the equilibrium favouring the reactant ($N_2O_4$) side, as found in (b), oe **B1**

**(c) Answer: K = 0.15 (no units)**

(d) delta G(350 K) = 57200 - (350 x 176) = -4400 J/mol (-4.40 kJ/mol) **M1**

(d) correct use of delta G = -RT ln K to find K(350 K) = exp(4400/(8.31 x 350)), giving K = 4.5 (accept 4.3-4.6) **M1**

(d) the forward reaction is endothermic (delta H positive), so by Le Chatelier's principle increasing temperature shifts the equilibrium towards the (endothermic) forward direction/products, increasing K, consistent with the calculated increase from 0.15 to about 4.5, oe **B1**

**(d) Answer: delta G(350K) = -4.40 kJ/mol; K = 4.5; K increases with T because the forward reaction is endothermic.**

## Question 4

(a) correct method: 498/2 **M1**

(a) +249 kJ/mol, cao **A1**

**(a) Answer: +249 kJ/mol**

(b) the second electron is removed from an ion (Ca+) that already carries a net positive charge, so the remaining electrons are held more strongly by the nucleus than in the neutral atom, oe **B1**

(b) removing an electron from a positive ion therefore requires more energy input than removing one from a neutral atom, since there is a greater effective nuclear attraction per remaining electron, oe **B1**

**(b) Answer: More energy is needed to remove an electron from the positively charged Ca+ ion than from the neutral atom.**

(c) the O- ion already carries a net negative charge, so bringing another (negatively charged) electron towards it involves overcoming electrostatic repulsion between like charges, oe **B1**

(c) energy must therefore be put in to overcome this repulsion, rather than being released, making the process endothermic, oe **B1**

**(c) Answer: Repulsion between the electron and the already negative O- ion must be overcome, requiring energy input.**

(d) correct Hess's law cycle: delta Hf(CaO) = atomisation(Ca) + IE1(Ca) + IE2(Ca) + atomisation(O) + EA1(O) + EA2(O) + LE(CaO) **M1**

(d) correct summation of the six known steps: 178 + 590 + 1145 + 249 + (-141) + 798 **M1**

(d) sum = +2819 kJ/mol, ft from (a) **A1**

(d) correct rearrangement: LE(CaO) = delta Hf(CaO) - 2819 **M1**

(d) -3454 kJ/mol, ft, cao **A1**

(d) the large exothermic (negative) value is consistent with the strong electrostatic attraction between the small, highly charged $Ca^{2+}$ and $O^{2-}$ ions in the lattice, oe **B1**

**(d) Answer: -3454 kJ/mol**


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