Chemical Energetics Tutorial

- 1 Write thermochemical equations to represent the following statements:
 - (a) Standard enthalpy change of formation of hydrogen bromide gas is $-36.2 \text{ kJ mol}^{-1}$ $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Br}_2(I) \rightarrow \text{HBr}(g) \ \Delta \text{H}^{e_f} = -36.2 \text{ kJ mol}^{-1}$
 - (b) Standard enthalpy change of combustion of liquid propanol (CH₃CH₂CH₂OH) is $-2017 \text{ kJ mol}^{-1}$

CH₃CH₂CH₂OH(*I*) + $\frac{9}{2}$ O₂(g) → 3CO₂(g) + 4H₂O(*I*) △H^e_c = -2017 kJ mol⁻¹

- (c) Standard enthalpy change of neutralisation of hydrochloric acid and sodium hydroxide is -57 kJ mol⁻¹ NaOH(aq) + HCl(aq) \rightarrow NaCl (aq) + H₂O(l) Δ H°_n= -57 kJ mol⁻¹
- (d) Lattice energy of calcium chloride solid is $-2237 \text{ kJ mol}^{-1}$ $Ca^{2+}(g) + 2Cl^{-}(g) \rightarrow CaCl_{2}(s)$ $\Delta H = -2237 \text{ kJ mol}^{-1}$
- (e) Bond energy of I–I (refer to the Data Booklet for the bond energy) $I_2 (g) \rightarrow 2I (g)$ BE = 151 kJ mol⁻¹ 1 mole of covalent bond in gaseous molecules

2 [N2008 P1 Q32]

Which reactions represent standard enthalpy changes?

- 1 $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
- **2** $C(g) + 6H(g) \rightarrow C_2H_6(g)$
- 3 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
- A 1 only B 1 and 2 only C 2 and 3 only D 1, 2 and 3
- (A) 1. ✓ (True) The physical state of reactants and products given are their corresponding physical states under standard conditions.
 - 2. × (False) Carbon is in solid state and hydrogen exists as $H_2(g)$ under standard conditions.
 - 3. × (False) H_2O is in liquid state under standard conditions.

By using this information, what is the most likely value for the heat liberated in the following neutralisation?

 $Ba(OH)_2(aq) + 2HC/(aq) \rightarrow BaC/_2(aq) + 2H_2O(l)$

- A –57 kJ mol^{−1} B –76 kJ mol^{−1} C –114 kJ mol^{−1} D –228 kJ mol^{−1}
- (C) The standard enthalpy change of neutralisation of an acid with an alkali is the energy evolved when <u>one mole of water is formed</u> from the reaction of the acid and alkali under standard conditions.
 Both reactions involve mixing of a strong base and a strong acid and each gives two moles of water. Therefore, the heat liberated for both reactions is the same.

 $\begin{array}{ll} H_2 SO_4(aq) \ + \ 2NaOH(aq) \ \rightarrow \ Na_2 SO_4(aq) \ + \ \underline{2H_2O(I)} \\ 2HC/(aq) \ + \ Ba(OH)_2(aq) \ \rightarrow \ BaC/_2(aq) \ + \ \underline{2H_2O(I)} \\ \Delta H = -114 \ \text{kJ mol}^{-1} \\ \Delta H = -114 \ \text{kJ mol}^{-1} \end{array}$

- 4 The enthalpy change of neutralisation of ethanoic acid with sodium hydroxide can be found experimentally by mixing known volumes of 1.0 mol dm⁻³ ethanoic acid, CH₃COOH, and 1.0 mol dm⁻³ NaOH. The following results are obtained. Volume of CH₃COOH used = 40.0 cm³ Volume of NaOH used = 30.0 cm³ Initial temperature of mixture = 28.0 °C Final temperature of mixture = 32.6 °C
 - (a) Use the data given to calculate the standard enthalpy change of neutralisation of CH₃COOH with NaOH. [-44.9 kJ mol⁻¹] Amount of water formed = Amount of NaOH reacted (since NaOH is the limiting reagent) $= \frac{30.0}{1000} \times 1.0 = 0.0300 \text{ mol}$

Enthalpy change of neutralisation of CH₃COOH with NaOH

$$\Delta H_{n}^{e} = -\frac{mc\Delta T}{n_{H20}}$$
$$= -\frac{(40+30) \times 4.18 \times (32.6 - 28)}{0.0300}$$
$$= -44.9 \text{ kJ mol}^{-1}$$

(b) The experiment is repeated with NaOH and HC*l* and it is found that the enthalpy change of reaction between NaOH and HC*l* is more exothermic than that calculated in (a). Explain why this is so.

 $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-Na^+(aq) + H_2O(I)$

HCl is a strong acid that ionises completely in aqueous solution.

CH₃COOH is a weak acid that ionises partially in aqueous solution.

Since ionisation of $CH_3COOH(aq)$ is an endothermic process, some heat released from the neutralisation is absorbed to further ionise the weak acid completely.

Therefore, the enthalpy change of neutralisation of $CH_3COOH(aq)$ with NaOH is less exothermic than that of HCl with NaOH.

- **5** When 1.00 g of ethanol in a spirit lamp was burned under a container of water, it was found that 100 cm³ of water was heated from 15 °C to 65 °C. The process was known to be only 70% efficient.
 - (a) Suggest reasons why only 70% of heat released by combustion is transferred to the water.

Heat lost to the surrounding air and to the container Presence of draught (wind currents)

(b) Calculate the standard enthalpy change of combustion of ethanol. [-1370 kJ mol⁻¹] $\Delta H_c = -\frac{mc\Delta T}{n} \times \frac{100}{70}$

$$= -\frac{100 \times 4.18 \times (65-15)}{\frac{1.00}{46.0}} \times \frac{100}{70}$$
$$= -1373$$
$$\approx -1370 \text{ kJ mol}^{-1}$$

(c)By using the value you have obtained in (b) and the following data:
Enthalpy change of combustion of carbon-393.5 kJ mol⁻¹Enthalpy change of combustion of hydrogen-285.8 kJ mol⁻¹

Calculate the enthalpy change of formation of ethanol.

$$2 C(s) + 3 H_2(g) + \frac{1}{2} O_2(g) \longrightarrow CH_3CH_2OH(I) \quad \Delta H_f = ?$$

[-271 kJ mol⁻¹]

 $\Delta H_{r}^{\circ} = \sum n \Delta H_{c}^{\circ}$ (reactants) – $\sum m \Delta H_{c}^{\circ}$ (products)

 $\Delta H_{f}(CH_{3}CH_{2}OH) = 2(-393.5) + 3(-285.8) - (-1373)$ = -271.4 $\approx -271 \text{ kJ mol}^{-1}$

When 6 g each of carbon, hydrogen and methanol, CH₃OH (I), are completely burnt in oxygen, 196.8, 857.7 and 136.2 kJ of heat are evolved respectively. Calculate the enthalpy change of formation of liquid methanol. [- 239 kJ mol⁻¹]

$$\Delta H_{c} = -\frac{4}{n_{\text{substance burnt}}}$$

$$\Delta H_{c}(C) = -\frac{196.8}{\frac{6}{12.0}} = -393.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{c}(H_{2}) = -\frac{857.7}{\frac{6}{2.0}} = -285.9 \text{ kJ mol}^{-1}$$

$$\Delta H_{c}(CH_{3}OH) = -\frac{136.2}{\frac{6}{32.0}} = -726.4 \text{ kJ mol}^{-1}$$

 $C(s) + 2 H_2(g) + \frac{1}{2} O_2(g) \longrightarrow CH_3OH(I) \quad \Delta H_f = ?$

 $\Delta H_{r^{\Theta}} = \sum n \Delta H_{c^{\Theta}}$ (reactants) $-\sum m \Delta H_{c^{\Theta}}$ (products)

 $\Delta H_{\rm f}(\rm CH_3OH) = -393.6 + 2(-285.9) - (-726.4)$ = -239 kJ mol⁻¹ 7 The chemical equation for the combustion of propene is as shown below.

$$C_{3}H_{6}(g) + 4\frac{1}{2}O_{2}(g) \rightarrow 3CO_{2}(g) + 3H_{2}O(I)$$

The table below shows the standard enthalpy changes of formation of the compounds involved in the reaction.

Compound	C ₃ H ₆ (g)	CO ₂ (g)	H ₂ O(I)	O ₂ (g)
∆ <i>H</i> ŧ / kJ mol⁻¹	+20	-394	-286	0

- (a) Explain why the standard enthalpy of formation, ΔH_{f}^{e} , of oxygen is zero. $O_{2}(g) \rightarrow O_{2}(g)$ Initial state = final state \therefore there is no change in the energy level, hence ΔH_{f}^{e} = zero. ΔH_{f}^{e} = zero for any elements in their standard states and most stable allotrope.
- (b) Use the data from the table above to calculate the standard enthalpy of combustion of propene. [-2060 kJ mol⁻¹] $\Delta H_c^{\circ} = 3(-394) + 3(-286) - (20) - 4\frac{1}{2} (0) = -2060 \text{ kJ mol}^{-1}$
- 8 The yellow chlorine dioxide gas, ClO₂, has been used for many years as a flour-improving agent in bread-making. It can be made in the laboratory by the following reaction:

 $2AgClO_3(s) + Cl_2(g) \longrightarrow 2AgCl(s) + 2ClO_2(g) + O_2(g) \Delta H_r^{e} = 0 \text{ kJ mol}^{-1}$

 $\begin{array}{ll} \mbox{Given that } \Delta H_{f^{e}} \mbox{ of } AgC/O_{3}(s) = -25 \ \mbox{kJ mol}^{-1} \mbox{ and } \Delta H_{f^{e}} \mbox{ of } AgC/(s) = -127 \ \mbox{kJ mol}^{-1}. \ \mbox{Calculate } \Delta H_{f^{e}} \mbox{ of } C/O_{2}(g). \mbox{ [+102 kJ mol}^{-1}] \mbox{ } \Delta H_{f^{e}} = 2(-127) + 2 \times \Delta H_{f^{e}} \mbox{ of } C/O_{2} - 2(-25) = 0 \mbox{ } 2 \times \Delta H_{f^{e}} \mbox{ of } C/O_{2} = 254 - 50 \mbox{ } \Delta H_{f^{e}} \mbox{ of } C/O_{2} = +102 \ \mbox{kJ mol}^{-1} \mbox{ } \end{array}$

- **9** One of the most important uses of alkanes is as fuels. In some countries, where crude oil is either scarce or expensive, biofuels such as ethanol are increasingly being used as fuels instead of hydrocarbons.
 - (a) Define the term "bond energy". Bond energy is the amount of energy absorbed to break <u>1 mole of covalent bonds</u> between atoms in a <u>gaseous molecule</u> to form <u>gaseous atoms</u>.
 - (b) (i) Write an equation that represents the standard enthalpy change of combustion of octane, $C_8H_{18}(I)$. $C_8H_{18}(I) + 25/2 O_2(g) \rightarrow 8CO_2(g) + 9H_2O(I)$
 - (ii) Use the bond energies given in the *Data Booklet* to calculate a value for the standard enthalpy change of combustion of octane. [-5130 kJ mol⁻¹] $\Delta H_c = \Sigma BE(reactants) - \Sigma BE(products)$ = [7BE(C-C) + 18 BE(C-H) + $\frac{25}{2}BE(O=O)$] - [8(2)(BE (C=O)) + 9(2)(BE (O-H)] = [7(350) + 18(410) + $\frac{25}{2}$ (496)] + [8(2)(805) + 9(2)(460)] = 16030 + (-21160) = $-5130 \text{ kJ mol}^{-1}$
 - (c) The standard enthalpy changes of combustion of three hydrocarbons are given in the table below.

Alkane	formula	∆ <i>H</i> c [⇔] / kJ mol ^{−1}
Heptane	C ₇ H ₁₆	- 4817
Octane	C ₈ H ₁₈	- 5470
Nonane	C_9H_{20}	- 6125

- (i) Suggest a reason for the discrepancy between the ΔH_c° for octane you calculated in (b)(ii) and that given in the table.
 - 1. The ΔH_c value given are for substances in their standard states i.e. <u>octane</u> <u>and water are liquids</u>. However, the bond energies in data booklet only applies to gaseous molecules. ΔH_{vap} of octane and H₂O not accounted for when bond energies are used for calculation.
 - 2. C-H and C-C bond energies given in the *Data Booklet* are only **average values** and they may deviate from the actual bond energy in the molecules of the reactants and products significantly.
- (ii) Suggest what the regular increase in the values of ΔH_c^e given in the table corresponds to.
 The regular increase (of about 650 kJ mol⁻¹) represents the ΔH_c value of a -CH₂ group.

10 Sulfur hexafluoride can be made by reacting sulfur tetrafluoride with fluorine in the gas phase: $SF_4(g) + F_2(g) \longrightarrow SF_6(g) \qquad \Delta H_r^{e} = -434 \text{ kJ mol}^{-1}$

Using relevant data from the Data Booklet, calculate an average value for the S-F bond energy.

 $\Delta H = \Sigma BE(bond broken) - \Sigma BE(bond formed)$ -434 = 4 × BE(S-F) + BE(F-F) - 6 × BE(S-F) BE(S-F) = ½(158 + 434) = +296 kJ mol⁻¹

11 (a) Define, with the aid of an equation and using magnesium nitride, Mg₃N₂ (s) as an example, what is meant by the term *lattice energy*.

 $Mg^{2+}(g) + N^{3-}(g) \longrightarrow Mg_3N_2(s)$

Lattice Energy is the heat evolved when 1 mole of solid Mg_3N_2 is formed from isolated gaseous Mg^{2+} and N^{3-} ions.

(b) How would you expect the magnitude of the lattice energy of Mg₃N₂ to compare with that of MgO? Explain your answer.

 Mg_3N_2 and MgO have the same cations, different anions. N^{3-} has a larger charge compared to $O^{2-}.$

$$|L.E| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$$

While N^{3-} has a larger ionic radius (0.171nm) than O^{2-} (0.140nm), product of charges is a more important factor than inter-ionic distance. hence magnitude of lattice energy of Mg₃N₂ will be larger than that of MgO.

12 [N99 P3 Q31]

The diagram illustrates the energy changes of a set of reactions.



Which statements are correct?

1 The enthalpy change for the transformation $U \rightarrow R$ is +42 kJ mol⁻¹.

2 The enthalpy change for the transformation $\mathbf{T} \rightarrow \mathbf{S}$ is endothermic.

3 The enthalpy change for the transformation $\mathbf{R} \rightarrow \mathbf{T}$ is -33 kJ mol⁻¹

A 1 only B 1 and 3 only C 2 and 3 only D 1, 2 and 3 (A) 1: $\Delta H(U \rightarrow R) = \Delta H(U \rightarrow S) + \Delta H(S \rightarrow R) = -(+92) - (-134) = +42 \text{ kJ mol}^{-1}$. (True)

2: $\Delta H(\mathbf{T} \rightarrow \mathbf{S}) = \Delta H(\mathbf{T} \rightarrow \mathbf{U}) + \Delta H(\mathbf{U} \rightarrow \mathbf{S})$ = -75 - (+92) = -167 kJ mol⁻¹. (EXOTHERMIC) (False)

3: $\Delta H(\mathbf{R} \rightarrow \mathbf{T}) = \Delta H(\mathbf{R} \rightarrow \mathbf{S}) + \Delta H(\mathbf{S} \rightarrow \mathbf{U}) + \Delta H(\mathbf{U} \rightarrow \mathbf{T})$ = -134 + 92 - (-75) = <u>+33 kJ mol⁻¹</u>. (False)