Chemical Energetics Tutorial

Definition of Standard Enthalpy Change

- 1 With the aid of thermochemical equations, define the following terms.
 - (a) standard enthalpy change of combustion of methane, $\Delta H_c^{e}(CH_4(g))$
 - **(b)** standard enthalpy change of atomisation of hydrogen, ΔH_{at}^{e} (H₂).
 - (c) standard enthalpy change of formation of liquid methanol, ΔH_{f}^{e} (CH₃OH(I))
 - (d) bond energy of H-H bond
 - (e) standard enthalpy change of neutralisation of reaction between H_2SO_4 and NaOH, ΔH_n^{e}
 - (f) lattice energy for sodium oxide
 - (g) 1st ionisation energy of sodium
 - (h) 2nd ionisation energy of sodium
 - (i) 1st electron affinity of fluorine
 - (j) standard enthalpy change of solution of sodium hydroxide NaOH(s), ΔH_{sol}^{e} (NaOH(s))
 - (k) standard enthalpy change of hydration of $Mg^{2+}(g)$, $\Delta H_{hyd}^{e}(Mg^{2+}(g))$
 - (I) standard enthalpy change of vaporisation of liquid bromine, ΔH_{vap}^{e} (Br₂(I))

Experimentally Determined Enthalpy Change

2 Concepts:

Experimentally Determined Enthalpy Change (Mixing 2 solutions) + Experimentally Determined Enthalpy Change (Cooling Curve)

Hydrogen carbonate ions react with acids as follows.

$$HCO_{3}^{-}(aq) + H^{+}(aq) \rightarrow H_{2}O(1) + CO_{2}(g)$$

Two different experiments are conducted to determine the standard enthalpy change of the above reaction.

(a) In experiment 1, known volumes of 0.150 mol dm⁻³ NaHCO₃(aq) and 0.150 mol dm⁻³ HC*l*(aq) are mixed and stirred in order to obtain the maximum change in temperature of the reaction mixture.

The following results were obtained:

Volume of NaHCO ₃ (aq) used	25.0 cm ³
Volume of HC <i>l</i> (aq) used	25.0 cm ³
Maximum change in temperature	–0.8 °C

Using the data given and assuming that the specific heat capacity of all solutions are 4.2 J K⁻¹ g⁻¹, calculate the standard enthalpy change for the reaction.

(+44.8 kJ mol⁻¹)

(b) In experiment 2, 25.0 cm³ of 0.150 mol dm⁻³ NaHCO₃(aq) and 25.0 cm³ of 0.150 mol dm⁻³ HC*l*(aq) are mixed at time = 2 min, and several temperature readings were taken at fixed intervals. The results are shown in the graph below.



- (i) Explain why method to obtain the standard enthalpy change for the reaction in experiment 2 is expected to be more accurate than that obtained in experiment 1 in (a).
- (ii) Using the information in the graph and assuming that the specific heat capacity of all solutions are 4.2 J K⁻¹ g⁻¹, calculate the standard enthalpy change for the reaction using experiment 2. (+56.0 kJ mol⁻¹)

3 Concepts:

Experimentally Determined Enthalpy Change (Combustion, including heat capacity of calorimeter) An experiment was conducted to determine the enthalpy change of combustion of ethanol (C_2H_5OH) using the apparatus setup below.



The following results were obtained when the ethanol is **burnt completely** in excess oxygen.

initial mass of burner with wick containing ethanol/ g	60.0
final mass of burner with wick containing ethanol/ g	57.6
initial temperature of water in calorimeter/ °C	25
final temperature of water in calorimeter/ °C	60
heat capacity of calorimeter/ J °C ⁻¹	883
<i>M</i> _r of ethanol	46.0

(a) Using the data given, calculate the standard enthalpy change for the reaction.

(−592 kJ mol⁻¹)

(b) The actual enthalpy change of combustion of ethanol is found to be $-1370 \text{ kJ mol}^{-1}$.

Suggest **two** reasons for the deviation of the enthalpy change of combustion of ethanol calculated in **(a)** from the actual value.

<u>Hess' Law</u>

4 Concept: Hess' Cycle (Given Enthalpy Change of Formation Data)

The chemical equation for the combustion of propene is as shown below.

$$C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(I)$$

Standard enthalpy change of formation of C ₃ H ₆ (g)/ kJ mol ⁻¹	+20
Standard enthalpy change of formation of CO ₂ (g)/ kJ mol ⁻¹	-394
Standard enthalpy change of formation of H ₂ O(I)/ kJ mol ⁻¹	-286

Using the data given in the table above, calculate the standard enthalpy change of combustion of propene. (-2060 kJ mol⁻¹)

5 Concept:

Hess' Cycle (Given Enthalpy Change of Combustion Data)

Using the following data, construct an energy cycle to calculate the enthalpy change of formation of liquid ethanol, $C_2H_5OH(I)$.

enthalpy change of combustion of carbon/ kJ mol ⁻¹	-393
enthalpy change of combustion of hydrogen/ kJ mol ⁻¹	-286
enthalpy change of combustion of ethanol/ kJ mol ⁻¹	-1368

(-276 kJ mol⁻¹)

6 Concept:

Experimentally Determined Enthalpy Change + % Efficiency + Hess' Cycle (Given Enthalpy Change of Combustion Data) + Hess' Cycle (Given Bond Energy Data)

Propan-2-ol is a colourless liquid usually used as a solvent and antiseptic. Like any other alcohol, it may be used as a fuel. The complete combustion of propan-2-ol is given in the equation below.

$$CH_3CH(OH)CH_3(I) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(I)$$

(a) When 1.00 g of propan-2-ol was burned, it was found that 100 g of water was heated from 30 °C to 89 °C. The process was known to be only 75 % efficient.

Calculate and show that the enthalpy change of combustion per mole of propan-2-ol is $-2030 \text{ kJ mol}^{-1}$. Assume the specific heat capacity of water to be 4.3 J g⁻¹ K⁻¹.

(−2030 kJ mol⁻¹)

(b) Using bond energy data given in the *Data Booklet*, calculate the enthalpy change of combustion of propan-2-ol.

(−1888 kJ mol⁻¹)

- (c) Suggest a reason for the difference between the values calculated in (a) and (b).
- (d) Using the value given in (a) and the following data, construct a suitable energy cycle and calculate the enthalpy change of formation of propan-2-ol from its elements.

enthalpy change of combustion of carbon/ kJ mol-1	-393.5
enthalpy change of combustion of hydrogen/ kJ mol-1	-285.8

(-294 kJ mol⁻¹)

7 Concept: Hess' Cycle (Given Bond Energy Data)

One of the most important uses of alkanes is for fuels. In some countries, where crude oil is either scarce or expensive, biofuels such as ethanol are increasingly being used for fuels instead of hydrocarbons.

- (a) Define the term *bond energy*.
- (b) (i) Write a chemical equation for the complete combustion of liquid octane, C₈H₁₈.
 - (ii) Use bond energies in the Data Booklet to calculate a value for the enthalpy change of combustion of octane.

(−5130 kJ mol⁻¹)

(c) The accurate experimental enthalpy changes of combustion of three liquid hydrocarbons are given in the table below.

alkane	formula	$\Delta H_c / kJ mol^{-1}$
heptane	C ₇ H ₁₆	-4817
octane	C ₈ H ₁₈	-5470
nonane	C ₉ H 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 in (c).
- (ii) Suggest what the regular increase in the values of ΔH_c in the table in (c) represents.

8 Concept: Hess' Cycle (Mix) (Challenging)

During the industrial manufacture of nitric acid, NO2 is hydrolysed by passing the gas through water.

$$3NO_2(g) + H_2O(I) \rightarrow 2HNO_3(aq) + NO(g) \qquad \Delta H_r$$

The following enthalpy changes are given:

	∆H / kJ mol ⁻¹
$N_2(g) + O_2(g) \rightarrow 2NO(g)$	+183
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	-116
$2N_2(g) + 5O_2(g) + 2H_2O(h) \rightarrow 4HNO_3(aq)$	-256

(a) Using relevant data from the table above, calculate the enthalpy change of formation of NO₂(g).
(+33.5 kJ mol⁻¹)

(b) Using your answer in (a) and any relevant data in the table, calculate ΔH_r , the enthalpy change of reaction for the hydrolysis reaction of NO₂.

(−137 kJ mol⁻¹)

9 Concept:

Experimentally Determined Enthalpy Change (Solid added to solution) + % Efficiency + Hess' Cycle (Mix) (Challenging)

The enthalpy change, $\Delta H_{reaction1}$, for the reaction of calcium metal with dilute hydrochloric acid is given below.

$Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$	$\Delta H_{\text{reaction 1}}$
$CaCO_{3}(s) + 2HCl(aq) \rightarrow CaCl_{2}(aq) + CO_{2}(g) + H_{2}O(I)$	$\Delta H_{\text{reaction 2}}$

(a) 1.00 g of calcium metal powder was added to 50 cm³ of 2.00 mol dm⁻³ of dilute hydrochloric acid in a polystyrene cup. The maximum rise in temperature of the mixture was found to be 10.0 °C. The efficiency of the reaction was found to be 90% efficient.

Given that the heat capacity of the water is 4.18 J g⁻¹ K⁻¹, calculate and show that the standard enthalpy change, $\Delta H_{\text{reaction 1}}$ is -93.1 kJ mol⁻¹.

(−93.1 kJ mol⁻¹)

(b) It is given that ΔH_f (H₂O(I)), ΔH_f (CO₂(g)) and $\Delta H_{reaction 2}$ are -286 kJ mol⁻¹, -394 kJ mol⁻¹ and -112 kJ mol⁻¹ respectively.

Using the data in (a), draw an energy cycle and hence find the enthalpy change of formation of solid calcium carbonate.

(-661 kJ mol⁻¹)

10 Concept:

FAIL + Hess' Cycle (Given Enthalpy Change of Formation Data)

The following data will be useful in this question.

enthalpy change of formation of $AlCl_3(s)/kJ$ mol ⁻¹	-704
enthalpy change of formation of $LiCl(s)/kJ$ mol ⁻¹	-408.5
enthalpy change of formation of LiH(s)/ kJ mol ⁻¹	-90.5
enthalpy change of atomisation of Li(s)/ kJ mol ⁻¹	+159.5
1 st electron affinity of hydrogen/ kJ mol ⁻¹	-73.0

Heating lithium in a stream of hydrogen gas produces white, crystalline, ionic lithium hydride, LiH.

(a) Calculate the lattice energy of LiH using relevant data from the above list, together with relevant data from the *Data Booklet*.

(-914 kJ mol⁻¹)

(b) When heated with anhydrous aluminium chloride, lithium hydride forms the solid complex metal hydride, lithium aluminium hydride, LiA/H₄. Lithium chloride is also produced. The enthalpy change for this reaction is −276 kJ per mole of LiA/H₄.

Write an equation for this reaction, and use it together with the relevant data above to calculate a value for the enthalpy change of formation of $LiAlH_4$.

(-117 kJ mol⁻¹)

11 Concept: FAIL + Factors affecting L.E.

(a) Draw a Born-Haber cycle for the formation of calcium oxide and use it to calculate the lattice energy of calcium oxide.

enthalpy change of atomisation of calcium/ kJ mol ⁻¹	+177
enthalpy change of formation of solid calcium oxide/ kJ mol ⁻¹	-636
1 st electron affinity of oxygen/ kJ mol ⁻¹	-141
2 nd electron affinity of oxygen/ kJ mol ⁻¹	+790

(-3450 kJ mol⁻¹)

- (b) Explain clearly why the magnitude of the lattice energy of magnesium oxide is larger than that of calcium oxide.
- (c) Theoretical lattice energy can differ from experimental lattice energy calculated using Born-Haber cycle like that calculated in (a).

	Experimental lattice energy/ kJ mol ⁻¹	Theoretical lattice energy/ kJ mol ⁻¹
magnesium oxide	answer in (a)	-3848
sodium oxide	-2566	-2564

Explain why the experimental lattice energy of magnesium oxide will deviate more from its theoretical value, compared to sodium oxide.

12 Nov 2021/P3 Q2f Ethyne can be prepared by the reaction of calcium carbide, CaC₂, and water.

$$CaC_2 + 2 H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

The bond energy of C=C in the carbide ion is different from the bond energy of C=C in other compounds.

Use the data in Table 2.1, together with the data from the Data Booklet, to calculate the C≡C bond energy in a carbide ion.

Show your working.

Table 2.1

	value / kJ mol ⁻¹
1 st electron affinity of C ₂ (g)	-315
2 nd electron affinity of C ₂ (g)	+410
Standard enthalpy change of sublimation of C(s)	+715
Standard enthalpy change of atomisation of Ca(s)	+178
Standard enthalpy change of formation of CaC ₂ (s)	-60
Standard lattice energy of CaC ₂ (s)	-2884

[4]

13 Concept:

Hess' Cycle (Given Enthalpy Change of Formation Data) + Hess' Cycle (Involving Dissolution)

(a) Meals-ready-to-eat (MRE) are military meals that can be heated on a flameless heater. The heat is produced by the following reaction.

$$Mg(s) + 2H_2O(I) \rightarrow Mg(OH)_2(s) + H_2(g)$$

(i) Use the data below to calculate the standard enthalpy change for this reaction.

Compound	$\Delta H_{f} / kJ mol^{-1}$
H ₂ O(I)	-286
Mg(OH) ₂ (s)	-925

(–353 kJ mol⁻¹)

- (ii) A MRE pack contains 2.4 g of magnesium which comes in contact with 100 g of water upon breaking a valve. Using your answer in (a)(i), determine whether this pack can be used to raise the temperature of the water from 25 °C to its boiling point.
- (b) The following data relate to the energy changes which occur when sodium hydroxide, NaOH, and magnesium hydroxide, Mg(OH)₂, dissolve in water.

	sodium	magnesium
Hydration energy of metal ion / kJ mol ⁻¹	-390	-1890
Lattice energy of metal hydroxide / kJ mol ⁻¹	-896	-2995
Enthalpy change of solution of metal hydroxide / kJ mol ⁻¹	-44	x

- (i) Identify the type of interaction formed between the ion and the water molecule. Hence explain why the hydration energy of Mg²⁺ ion is more exothermic than that of Na⁺ ion.
- (ii) Use the data above to calculate x, the enthalpy change of solution of Mg(OH)₂.

(+5 kJ mol⁻¹)