

Starter for Ten

6. Thermodynamics

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STARTER FOR 10!!!

6. THERMODYNAMICS

- 6.1. Definitions
- 6.2. Calorimetry
- 6.3. Hess's law
- 6.4. Using bond enthalpies

Thermodynamics answers



STARTER FOR 10!!!

6.1. Definitions

Complete the gaps in the boxes below;

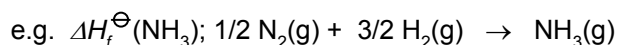
Standard enthalpy change, ΔH^\ominus

Definition; The heat energy change at under standard conditions (pressure ; temperature).

(2 marks)

Standard molar enthalpy change of formation, ΔH_f^\ominus

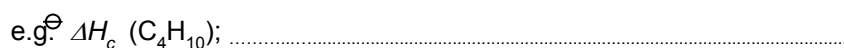
Definition; The enthalpy change when one mole
.....
.....



(3 marks)

Standard molar enthalpy change of combustion,

Definition; The enthalpy change when one mole of a compound is completely burned in excess oxygen under standard conditions, all reactants and products in their standard states.



(3 marks)

Mean bond energy

Definition; The
.....
.....

(2 marks)



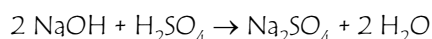
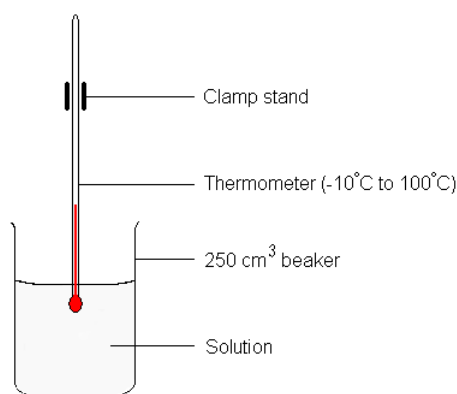
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6.2. Calorimetry

Below is a student's write up of the calorimetry practical he recently completed in class. There are 10 ways in which the teacher thinks he could have improved his experimental technique and analysis. Can you spot them?

Measuring the enthalpy change for the neutralisation of one mole of NaOH by H₂SO₄

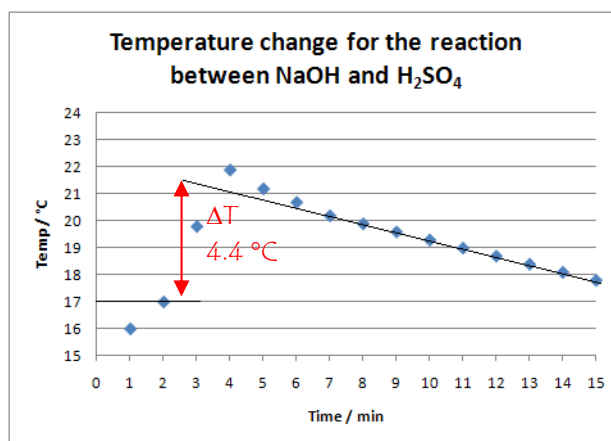
Method



100 cm³ of a 1 mol dm⁻³ solution of NaOH was placed in a 250 cm³ beaker and the temperature recorded every minute for two minutes using the equipment shown in the diagram. On the second minute, a solution of 1 mol dm⁻³ H₂SO₄ was removed from the fridge and 50 cm³ added to the beaker. The temperature of the mixture was recorded on the third minute and repeated every minute for a further 12 min.

Results

Time / min	Temp / °C
1	16
2	17
3	19.8
4	21.9
5	21.2
6	20.7
7	20.2
8	19.9
9	19.6
10	19.3
11	19
12	18.7
13	18.4
14	18.1
15	17.8



$$Q = mC\Delta T \quad m = 100 \text{ cm}^3 @ 1 \text{ g cm}^{-3} = 100 \text{ g} \quad \therefore Q = 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 4.4 \text{ }^\circ\text{C}$$

$$C = 4.18 \text{ J g}^{-1} \text{ K}^{-1} \quad = 1839.2 \text{ J}$$

$$\Delta T = 4.4 \text{ K}$$

$$\text{No. of moles of NaOH} = \frac{100 \text{ cm}^3}{1000 \text{ cm}^3 \text{ dm}^{-3}} \times 1 \text{ mol dm}^{-3} = 0.1 \text{ mole}$$

$$\therefore \text{Enthalpy change per mole of NaOH reacting} = \frac{1}{0.1 \text{ mole}} \times 1839.2 \text{ J} = 18392 \text{ J mol}^{-1} \\ = 18.4 \text{ kJ mol}^{-1}$$



STARTER FOR 10!!!

6.3. Hess's law

This question is all about the possible fuels you might come across when going camping. Use your knowledge of Hess's law to investigate the energetics of the processes involved.

- One form of camping stove runs on the fuel butane. Along with other isomers this contains the gas *iso*-butane or 2-methylpropane.
 - The enthalpy change of formation of *iso*-butane is $-134.5 \text{ kJ mol}^{-1}$. Write an equation, including state symbols, for the reaction to which this enthalpy change applies. (2 marks)
.....
 - In a camping stove, the *iso*-butane undergoes combustion. Write an equation to represent the enthalpy change of combustion of *iso*-butane in excess oxygen. (2 marks)
.....
 - Using the answers to part (i) and part (ii) together with the information in the table below, calculate ΔH_c^\ominus for *iso*-butane. (2 marks)

Compound	Standard enthalpy of formation / kJ mol^{-1}
$\text{CO}_2(\text{g})$	-394
$\text{H}_2\text{O}(\text{g})$	-242

- An alternative to a gas camping stove is a Trangia™. This burns methylated spirits which is predominantly ethanol with additives to make it more poisonous or unpalatable.
 - Write an equation to represent the enthalpy change of formation of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)
..... (2 marks)
 - Use the information in the table together with Hess's law to calculate ΔH_f^\ominus for ethanol. (2 marks)

Compound	Standard enthalpy of combustion / kJ mol^{-1}
$\text{C}(\text{s})$	-394
$\text{H}_2(\text{g})$	-242
$\text{CH}_3\text{CH}_2\text{OH}(\text{l})$	-1367



STARTER FOR 10!!!

6.4. Using bond enthalpies

1. A student is carrying out a project to compare the theoretical and experimental value for the enthalpy change of combustion of ethanol. Using the data in the table, calculate a theoretical value for ΔH_c^\ominus [$\text{CH}_3\text{CH}_2\text{OH}(\text{l})$].

(**HINT** Remember to fully balance any equations before starting your calculations) (4 marks)

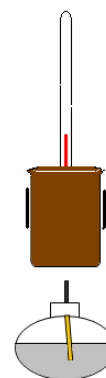
Bond	Mean bond enthalpy / kJ mol^{-1}
C—C	347
C—H	413
C—O	358
O—H	464
O=O	498
C=O	805

2. When the student shows his calculation to his teacher, she points out that mean bond enthalpies are only applicable for molecules in the gas state. Therefore the student must take into account the enthalpy change of vaporisation of ethanol [$\text{CH}_3\text{CH}_2\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{g})$, $\Delta H_{\text{vap}} +39 \text{ kJ mol}^{-1}$].

Use this value to correct your answer to Q1 (You may assume that the water formed from the combustion is in the gas state). (1 mark)

3. The student now wishes to determine an experimental value for the enthalpy of combustion of ethanol. He intends to burn approximately 1 g of fuel and measure the heat energy produced by heating up a known volume of water in a copper calorimeter (using the equipment shown).

Using your answer to question 2, suggest a suitable volume of water for the copper calorimeter if he is aiming for a temperature rise of no more than 40°C ? (Specific heat capacity of water = $4.2 \text{ J K}^{-1} \text{ g}^{-1}$) (4 marks)



4. The experimental value obtained by the student is considerably lower than the theoretical value calculated. Suggest one reason for this (other than experimental error). (1 mark)



STARTER FOR 10!!!

6. Thermodynamics answers

6.1. Definitions

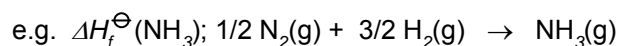
Standard enthalpy change, ΔH^\ominus

Definition; The heat energy change at constant pressure under standard conditions (pressure 100 kPa ; temperature 298 K). (one mark for both conditions)

(2 marks)

Standard molar enthalpy change of formation, ΔH_f^\ominus

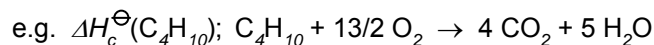
Definition; The enthalpy change when one mole of a compound is formed from its constituent elements under standard conditions, with all reactants and products in their standard states.



(3 marks)

Standard molar enthalpy change of combustion, ΔH_c^\ominus

Definition; The enthalpy change when one mole of a compound is completely burned in excess oxygen under standard conditions, all reactants and products in their standard states.



(one mark for symbols, one for balancing)

(3 marks)

Mean bond energy

Definition; The enthalpy change when 1 mole of a particular type of bond is broken or made (all species in the gas phase) averaged over many different molecules

(2 marks)

6.2. Calorimetry

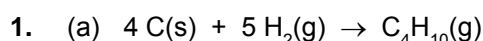
Possible improvements / corrections include (any 10 from);

1. The beaker needs some form of insulation (or a polystyrene beaker should be used)
2. An accurate thermometer is needed (not one that records -10 to 100 °C)
3. The thermometer is placed too near the surface of the mixture. It must be in the centre.

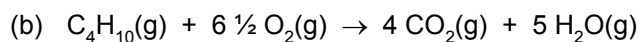
- The liquids are not allowed to equilibrate to similar temperatures before use; the H_2SO_4 is removed from the fridge!
- Only two readings were taken before the addition of the H_2SO_4 . It is therefore impossible to draw a line to indicate the average temperature of the NaOH before addition.
- It is more usual to mix the reagents on the 3rd minute say and take no measurement at this point then measure the temperature again on the 4th, 5th minutes etc.
- There is no mention of the mixture being stirred.
- Not all temperatures are recorded to 1 decimal point in the student's results table
- A straight line is drawn for the temperature of the solution after addition of the H_2SO_4 despite the fact that the temperature clearly drops more steeply initially – better extrapolation needed.
- A volume of 100 cm^3 is indicated in the student's calculation for the energy transferred. The volume is in fact 150 cm^3 (100 cm^3 of NaOH and 50 cm^3 of H_2SO_4).
- The calculation requested is per mole of NaOH reacting. This reaction involves two equivalents of NaOH so the final enthalpy change must be divided by 2.

NOTE The experimental data is made up and in no way represents the real enthalpy of neutralisation of NaOH.

6.3. Hess's law

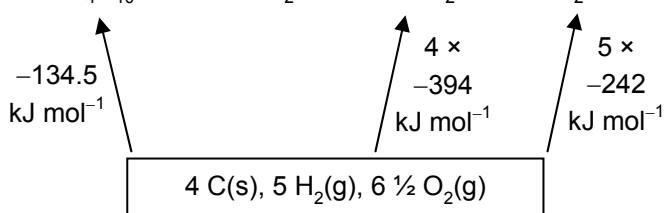
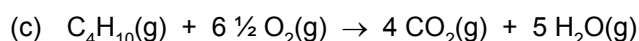


(1 mark equation + balancing; 1 mark state symbols)



(1 mark equation; 1 mark balancing)

(NOTE) Must be combustion of 1 mole of C_4H_{10}

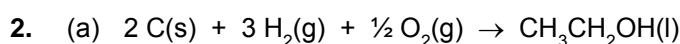


$$\Delta H_c^\ominus = [-(-134.5) + (4 \times -394) + (5 \times -242)]$$

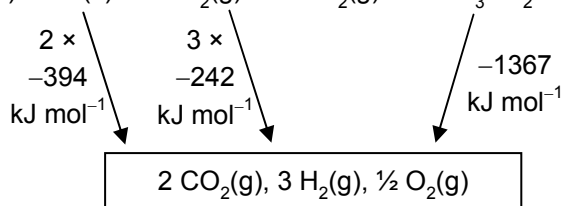
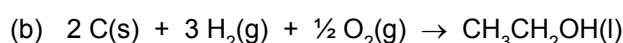
$$= -2651.5\text{ kJ mol}^{-1}$$

(1 mark for the cycle or equiv)

(1 mark answer)



(1 mark equation + balancing; 1 mark state symbols)



$$\Delta H_f^\ominus = [(2 \times -394) + (3 \times -242) - (-1367)]$$

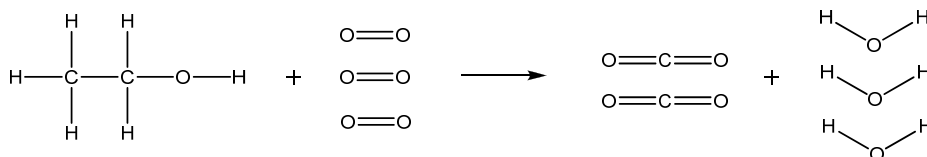
$$= -147\text{ kJ mol}^{-1}$$

(1 mark for the cycle or equiv)

(1 mark answer)

6.4. Using bond enthalpies

1.



Bonds broken / kJ mol ⁻¹		Bonds made / kJ mol ⁻¹	
1 × C—C	1 × 347	4 × C=O	4 × 805
5 × C—H	5 × 413	6 × O—H	6 × 464
1 × C—O	1 × 358		
1 × O—H	1 × 464		
3 × O=O	3 × 498		
Total energy in = 4728 kJ mol⁻¹		Total energy out = 6004 kJ mol⁻¹	

(1 mark balanced equation)

(2 marks bonds broken /made)

$$\begin{aligned}\Delta H_c^\ominus (\text{CH}_3\text{CH}_2\text{OH}) &= \text{Total energy in} - \text{total energy out} \\ &= 4728 \text{ kJ mol}^{-1} - 6004 \text{ kJ mol}^{-1} \\ &= \mathbf{-1276 \text{ kJ mol}^{-1}}\end{aligned}$$

(1 mark correct sum)

2. 39 kJ mol⁻¹ of energy must be put in to the reaction to initially convert the liquid ethanol into gaseous ethanol. Hence, the total energy in becomes 4728 kJ mol⁻¹ + 39 kJ mol⁻¹ = 4767 kJ mol⁻¹. Therefore the more correct $\Delta H_c^\ominus [\text{CH}_3\text{CH}_2\text{OH}(\text{l})] = 4767 \text{ kJ mol}^{-1} - 6004 \text{ kJ mol}^{-1} = \mathbf{-1237 \text{ kJ mol}^{-1}}$

(1 mark)

3. Number of moles in 1 g = 1 g ÷ $M_r(\text{CH}_3\text{CH}_2\text{OH}) = 1 \text{ g} \div 46 \text{ g mol}^{-1} = \mathbf{0.022 \text{ moles}}$ (1 mark)

Theoretical heat transferred by 1 g = 0.022 moles × 1237 kJ mol⁻¹ = **26.9 kJ** (1 mark)

26891 J = mass of water × 4.2 J K⁻¹ mol⁻¹ × 40 K

∴ mass of water = 26891 J / (4.2 J K⁻¹ g⁻¹ × 40 K)

= 160 g (1 mark)

Density of water = 1 g cm⁻³, therefore 160 g has a volume of **160 cm³** (1 mark)

4. *either* Mean bond enthalpies are averages of the bond enthalpies in many different compounds. Therefore they are not exact for the specific bonds in ethanol
- or* There is considerably loss of heat to the environment / copper calorimeter that is not included in the calculations for the experimental enthalpy of combustion of ethanol. This loss of heat would result in an experimental value that is lower than the actual value.
- or* The heat capacity of the copper calorimeter has not been taken into account meaning that the heat transferred into the copper is not included in the calculation.