15. 1 Standard Enthalpy Changes

15.1.1 Standard Enthalpies

The **standard enthalpy change of combustion**, $\Delta H^{\ominus}_{C}$ (kJ mol^{-1}) is defined as *the enthalpy change that takes place when one mole of a gaseous substance reacts with excess oxygen under standard conditions*. The products are carbon dioxide and water. Standard enthalpy of combustion values can be found in the Chemistry data booklet. All enthalpy of combustion reactions are exothermic and their enthalpy change is given a negative sign.

Standard conditions are: Pressure, P = 1.01×10^{5} Pa (or 1atm),
Temperature, T = 298 K (or 25˚C)
1 mole of the combusting substance in it gaseous state

For example the equation for the standard enthalpy of combustion of butane in a lighter can be written:

$C_4H_{10(g)}$ + 6 ½ $O_{2(g)}$ → 4 $CO_{2(g)}$ + 5 $H_2O_{(g)}$

$\Delta H^{\ominus}_{C}$ = - 2877 kJ mol^{-1}

Exercises

Write the enthalpy of combustion equations, for the following reactions. Use the data booklet to find the actual value for ΔH°_{C} for each reaction.

1. methane, CH_4

2. ethene, C_2H_4

3. carbon (diamond)

4. ethanol, C_2H_5OH

5. Sucrose, $C_{12}H_{22}O_{11}$

The standard enthalpy of formation, $\Delta H^{\ominus}_{f}$ (kJ mol^{-1}) is defined as the *enthalpy change that takes place when <u>one mole</u> of a <u>gaseous</u> substance is formed from its elements under standard conditions*. Standard enthalpy of formation values can be found in the Chemistry data booklet. They can be either exothermic or endothermic.

Standard conditions are: Pressure, P = 1.01 x 10^5 Pa (or 1atm),
Temperature, T = 298 K (or 25˚C)
1 mole of the substance formed in its gaseous state.

The standard enthalpy of formation of an element is zero e.g. $\Delta H^{\ominus}_{f}(N_2) = 0$ $kJmol^{-1}$
This is because an element is already in its stable state. The seven diatomic elements are H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2.

For example the equations for the enthalpy of formation of methane and its standard enthalpy of formation can be written:

$$C_{(s)} + 2\,H_{2(g)} + \rightarrow CH_{4(g)} \qquad \Delta H^{\ominus}_{f} = -\,75 \text{ kJ mol}^{-1}$$

<u>Exercises</u>
Write the enthalpy of formation equations, for the following reactions. Use the data booklet to find the actual value for ΔH°_{f} for each reaction.

1. cyclohexane, C_6H_{12}

2. methane, CH_4

3. methanal, HCHO

4. ethanol, C_2H_5OH

5. hydrogen, H_2

6. ethanoic acid, CH_3COOH

15.1.2 Calculating the Enthalpy Change of Combustion or Formation using Standard enthalpy of values

$$\Delta H = \sum \Delta H_f^{\ominus}{}_{(products)} - \sum \Delta H_f^{\ominus}{}_{(reactants)}$$

In these calculations multiply the $\Delta H^{\ominus}_f$ by the number of moles given in the equation because standard values are for one mole of the substance.

NOTE: The ΔH_f for all elements including the seven diatomic elements: H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2 is zero. This is because they are already elements in their standard state.

Example

Calculate the ΔH for the combustion of ethanol according to the equation:

$$C_2H_5OH\ (l) \quad + \quad 3\ O_2\ (g) \quad \rightarrow \quad 2\ CO_2\ (g) \quad + \quad 3\ H_2O(l)$$

Given the following $\Delta H^{\ominus}_f$ values in kJ mol^{-1}

$$CO_2\ (g) = -394 \quad ; \quad H_2O(l) = -286 \quad ; \quad C_2H_5OH\ (l) = -278$$

Solution

$$\Delta H = \sum \Delta H^{\ominus}_f (products) - \Delta H^{\ominus}_f (reactants)$$

$$= (2 \times -394 + 3 \times -286) - (-278 + 0)$$

$$= (-1646) - (-278)$$

$$= -1368 \text{ kJ mol}^{-1}$$

Problems

1. During the Apollo II project that landed the first man on the moon on July 21, 1969 it was decided that methyl hydrazine (CH_3NHNH_2) and dinitrogen tetroxide (N_2O) would be used as fuels. These two substances were chosen because they ignite spontaneously and are very exothermic when mixed:

$$4\ CH_3NHNH_2\ (l) + 5\ N_2O_4\ (l) \rightarrow 4\ CO_2\ (g) + 12\ H_2O\ (l) + 9\ N_2\ (g)$$

Calculate the enthalpy change for the reaction using the standard enthalpy change data provided.

Substance	**$\Delta H_f^\ominus$ / $kJmol^{-1}$**
CH_3NHNH_2 (l)	+53
N_2O_4 (l)	-20
CO_2 (g)	-393
H_2O (l)	-286

2. (N04Mod) The equation for the catalytic decomposition of hydrogen peroxide is given below.

$$H_2O_{2(l)} \rightarrow \frac{1}{2} O_{2(g)} + H_2O_{(l)}$$

At 500K, ΔH for the reaction is -196 $kJmol^{-1}$.

a) Explain why ΔH for the reaction cannot be described as $\Delta H_f^\ominus$. [2]

b) What is the $\Delta H_f^\ominus$ of elemental oxygen? [1]

3. Which one of the following is not a “standard state” condition?
   - A. Temperature = 298 K
   - B. Pressure = 101.3 kPa
   - C. All reactants and products are in their gaseous state
   - D. All solutions are 1 mol dm^{-3}

4. The standard enthalpy of formation for hydrogen iodide is the enthalpy change for:
   - A. $H_2\ (g) + I_2\ (g) \leftrightarrow 2\ HI\ (g)$
   - B. $\frac{1}{2} H_2\ (g) + \frac{1}{2} I_2\ (g) \leftrightarrow HI\ (g)$
   - C. $H\ (g) + I\ (g) \leftrightarrow HI\ (g)$
   - D. $H^+\ (g) + I^-\ (g) \leftrightarrow HI\ (g)$

5. Given the standard enthalpy of formation data the enthalpy change for the reaction below is:

$NaHCO_3$ = - 948 $kJmol^{-1}$; Na_2CO_3 = -1131 $kJmol^{-1}$; CO_2 = -395 $kJmol^{-1}$;
H_2O = - 286 $kJmol^{-1}$

$$2\ NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)$$

A. + 84 $kJmol^{-1}$
B. + 864 $kJmol^{-1}$
C. - 864 $kJmol^{-1}$
D. - 84 $kJmol^{-1}$

6. Write balanced equations for the following reactions and use standard enthalpy of formation data to calculate the enthalpy change associated with each:

a) zinc and chlorine reacting to form zinc chloride [3]
b) hydrogen sulfide and sulfur dioxide reacting to form sulfur and water. [3]
c) lead (II) nitrate decomposing to lead (II) oxide, nitrogen dioxide and oxygen. [3]
d) (HL) Draw a Lewis dot diagram for the nitrogen dioxide molecule and account for why the nitrogen-oxygen bond lengths are same [3]

[Standard enthalpy of formation data in $kJmol^{-1}$: $ZnCl_2$ = -416 ; H_2S = -21 ;
SO_2 = -297 ; H_2O = -286 ; $Pb(NO_3)_2$ = -449 ; PbO = -218 ; NO_2 = +34]

7. (M05) The standard enthalpy change for the combustion of phenol, $C_6H_5OH_{(s)}$ is - 3050 $kJmol^{-1}$ at 25ºC.

a) Write an equation for the combustion of phenol. [1]
b) The standard enthalpy changes of formation of carbon dioxide and water are -394 $Jmol^{-1}$ and -286 $kJmol^{-1}$ respectively. Calculate the enthalpy of formation of phenol. [3]

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ANSWERS

1. $\Delta H = \sum \Delta H^\circ_f(\text{products}) - \Delta H^\circ_f(\text{reactants})$ [1]

$= [\,4(-393) + 12(-286) + 9\,(0)\,] - [\,4(+53) + 5(-20)\,]$ [1]

$= -5004 - 112$

$= -5116$ kJ mol^{-1} [1]

2. cannot be a standard enthalpy change because 500K is not standard temperature; Cannot be enthalpy of formation as it is a decomposition reaction;
ΔH_f^o of elemental oxygen is zero because it is an element;

3. D

4. B $\frac{1}{2} H_2\,(g) + \frac{1}{2} I_2\,(g) \leftrightarrow HI\,(g)$

5. A $\Delta H = \sum \Delta H^\circ_f(\text{products}) - \Delta H^\circ_f(\text{reactants})$

$= [1(-1131) + 1(-395) + 1(-286)\,] - 2(-948)$

$= -1812 + -946$

$= -84$ kJ mol^{-1}

6.

a) $Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(aq)}$ [1]

$\Delta H = \sum \Delta H^\circ_f(\text{products}) - \Delta H^\circ_f(\text{reactants})$ [1]

$= 1(-416) - 0$ [1]

$= -416$ kJ mol^{-1} [1]

b) $2\,H_2S_{(g)} + SO_{2(g)} \rightarrow 3\,S_{(s)} + 2\,H_2O_{(l)}$

$\Delta H = \sum \Delta H^\circ_f(\text{products}) - \Delta H^\circ_f(\text{reactants})$ [1]

$= 0 + 2(-286) - 2(-21) + 1(-297)$ [1]

$= -572 - (-399)$

$= -233$ kJ mol^{-1} [1]

c) $2\ Pb(NO_3)_{2(aq)} \rightarrow 2\ PbO_{(s)} + 4\ NO_{2(l)} + O_{2(g)}$

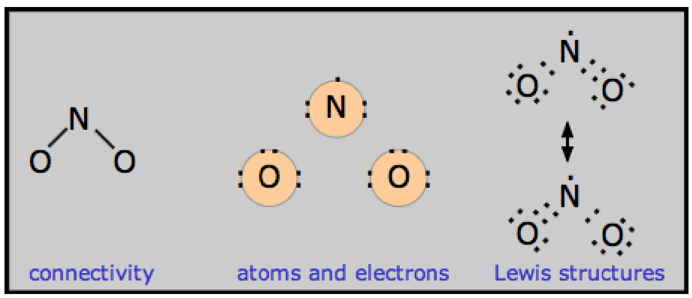
ΔH = $\sum \Delta H^{\circ}_f$(products) - ΔH°_f(reactants) [1]

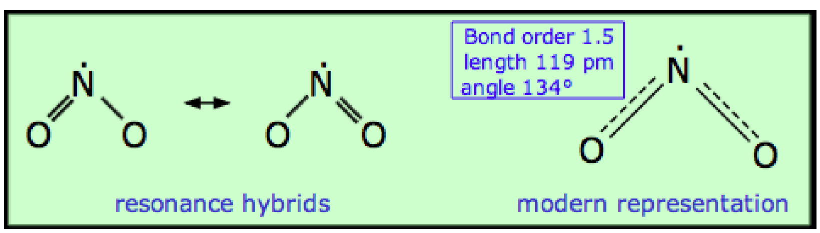
= 2(-218) + 4(+34) + 0 - 2(-449) [1]

= 598 kJ mol^{-1} for 2 mol

= 299 kJ mol^{-1} [1]

d) Lewis structure (1)
Bond lengths the same due to delocalized electrons (1)
Resonance hybrid diagram (1)





7. a)

C_6H_5OH (l) + $7\ O_2$ (g) $\rightarrow$ $6\ CO_2$ (g) + $3\ H_2O$(l) [1]

b) ΔH°_f (phenol) = $\sum \Delta H^{\circ}_f$(products) - ΔH°_f(reactants) [1]

= (6(-394) + 3(-286) - (ΔH°_f + 0) [1]

= -172 kJ mol^{-1} [1]

(-(U) if incorrect or missing, 2 max if +172)