Enthalpy – lesson 2

Summary from lesson 1 : energy diagram, ΔH, standard conditions (⁰), definition of standard enthalpy of combusion & Hess's law (what goes in, must come out, $\Delta H_{reaction}^{\ominus} = \Delta H_{products}^{\ominus} + \Delta H_{reactants}^{\ominus}$).

Predicting the relative stabilities of compounds.

The greater the -ve, the greater the stability energetically. They have a lower energy level than the reactants.

Consider $H_2(g) + O_2(g) \rightarrow H_2O_2(l)$, $\Delta H = -188kJ$. However, this goes off when left in the light and air (photosensitive). Why? H_2O_2 decomposes to $H_2O + ½O_2(g)$ ($\Delta H = -98kJ$). It is stable with respect to the elements, but not to water and oxygen. It is therefore vital to say with respect to the substances a compound is stable or unstable to.

Consider the formation of ethyne – $2C\ (graphite) + H_2(g) \rightarrow C_2H_2(g)$, $\Delta H = +227kJ$. Ethyne, once formed can be stored quite happily without any problems. Why does it not decompose readily? It is kinetically unfavourable to do so (kinetically stable – think of a stone on a hill).

Will a reaction happen?

In general, if ΔH is -ve, it will happen, therefore exothermic reactions are more likely to occur than endothermic ones. However, some endothermic ones do occur.

Thing to bear in mind

1. ΔH is no guide to the rate a reaction occurs at. It only describes the relative energy stabilities, not the kinetic. A reaction may be massively exothermic, yet nothing happens ($H_2 + O_2$ at room temperature)
2. In order to say if a reaction will occur, the degree of disorder has to be taken into account. Take a solid + liquid. When they dissolve, the degree of disorder increases greatly with an increase in how energy can be distributed around the system. It explains why endothermic reactions occur. The name for the disorder is entropy.
3. Predictions for $\Delta H_f^{\ominus}$ are for only standard condition and vary greatly away from this.

Example – octane and air

Recall structure of octane from organic lessons. $\Delta H_c^{\ominus} = -5513\ kJ\ mol^{-1}$. Would this react with oxygen? Why is octane/oxygen mixtures stable at room temperature and why does a spark change everything?

Relationship between ΔHc and structure.

Take butane and 2-methylpropane. Both have 3 C-C bonds and 10 C-H bonds. $\Delta H_c^{\ominus}$ are -2877 kJ and -2869kJ respectively. Very similar molecules and very similar $\Delta H_c^{\ominus}$ values.

Alkane	Formula	$\Delta H_c^{\ominus}$ kJ mol-1	Difference kJ
Methane	CH_4	-890	
Ethane	C_2H_6	-1560	670

Propane	C_3H_8	-2220	660
Butane	C_4H_{10}	-2877	657
Propane	C_5H_{12}	-3520	643

From this the following can be observed

- each CH_2 group gives a fixed increment
- each bond makes a contribution to the overall energy content

Energy must be supplied to break a bond therefore it is an endothermic process.

When dealing with $\Delta H_c^{\ominus}$ for alkanes, the enthalpy changes by a constant amount as one more H_2O and CO_2 are produced for each reaction

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$C_2H_6 + 3\ ½\ O_2 \rightarrow 2CO_2 + 3H_2O$
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$