# *SECTION 11*

## THERMOCHEMISTRY

Most chemical reactions are accompanied by the release of energy to the surroundings or absorption of energy from the surroundings, or put more simply the reacting system gets hotter or cooler as the reaction proceeds. The most common form of energy transferred is heat. This section introduces the language used in measuring and representing the heat changes that occur, and how the amount of heat released or absorbed in a chemical reaction can be calculated from tabulated data for the reactants and products of the

**Thermochemistry**: Study of the **heat** released or absorbed by chemical reactions.

Rearrangements of atoms that occur during chemical reactions involve both bond breaking and bond formation. Bond breaking results in absorption of **heat** from the surroundings and bond formation in release of heat to the surroundings.

**Heat**: Energy transferred as a result of a temperature difference between a **system** and its **surroundings**. The quantity of energy transferred from the surroundings to the system is given the symbol $q$. The **system** means the substance, or reactants and products of a reaction, and the **surroundings** everything else. When energy is transferred from the system to the surroundings $q$ is negative. Chemists frequently make measurements at constant (atmospheric) pressure. Energy transferred at constant pressure is given the symbol $q_p$.

A chemical equation can be made more meaningful and informative by showing the states of the reactants and products and the quantity of heat released or absorbed.
[e.g. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta_rH = -570\ \text{kJ mol}^{-1}$
implies that when 2 moles of gaseous dihydrogen reacts with one mole of gaseous dioxygen to give two moles of liquid water 570 kilojoules of energy is released from the reacting system to its surroundings.] The $\Delta$ means change, r stands for reaction and $H$ is the symbol for enthalpy. $\Delta_rH$ is the **enthalpy change** of the reaction.

**Enthalpy change**: Symbol $\Delta H$, the change in energy of a system which undergoes a change at constant pressure. $\Delta H = q_p$

**Exothermic reaction**: A reaction that releases energy to the surroundings. $\Delta_rH < 0$

**Endothermic reaction**: A reaction that absorbs energy from the surroundings. $\Delta_rH > 0$

$\Delta_rH$ is negative for an exothermic reaction (the energy of the system, the reactants and products, is less after the reaction than before) and positive for an endothermic reaction (the energy of the system is greater than before).

Note that the per mole ($\text{mol}^{-1}$) in the units of $\Delta_rH$ refers to the stoichiometric coefficients in the equation as amounts in moles. Thus if the above equation were written as

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l), \text{ then } \Delta_rH = -285\ \text{kJ mol}^{-1}.$$

It is most important to understand the difference between the enthalpy change of a system, and
that of a reaction. The magnitude of the former depends on the amount present in the system and has units of energy, e.g. kJ, while the amount of the latter is defined by the chemical equation and has common units of kJ $\text{mol}^{-1}$.

**Latent heat**

$$n(\mathrm{S}) = \frac{m(\mathrm{S})}{M(\mathrm{S})} = \frac{16\ \mathrm{g}}{32\ \mathrm{g\ mol^{-1}}} = 0.50\ \mathrm{mol}$$

$$\Delta_{\mathrm{r}} H = \frac{q_p}{n} = \frac{-149\ \mathrm{kJ}}{0.50\ \mathrm{mol}} = -\ 298\ \mathrm{kJ\ mol^{-1}} \quad ]$$

**Heat of formation of a substance**: Symbol $\Delta_{\mathrm{f}}H$, the heat (enthalpy) change when one mole of that substance is formed from its elements in their standard states. By convention an

## EXERCISES

1. The absorption of 62.76 kJ of heat by 500 g of liquid water caused its temperature to rise by 30 $^{o}$C. Calculate the specific heat capacity of water in (i) J $g^{-1}$ $K^{-1}$ and (ii) in cal $g^{-1}$ $K^{-1}$and the molar heat capacity of water in J $mol^{-1}$ $K^{-1}$. (1 cal = 4.184 J)

2. It required 36.61 MJ of heat to distil 50 L of ethanol, $CH_3CH_2OH$, at its boiling point. Calculate $\Delta_{vap}H$(ethanol). ($\rho$(ethanol) = 0.785 g $cm^{-3}$)

3. The combustion of exactly 1 kg of elemental sulfur to sulfur dioxide released 9.28 MJ of heat. Calculate $\Delta_f H(SO_2)$ in kJ $mol^{-1}$.

4. Carbon disulfide, $CS_2$, has a boiling point of 46 $^{o}$C. The products of combustion are $CO_2$ and $SO_2$. (i) Write the equation for its combustion. (ii) Calculate $\Delta_f H(CS_2)$ given the following $\Delta_c H$/kJ $mol^{-1}$: $CS_2$ = -1077; C = -393; S = -297

5. Calculate the approximate $\Delta_r H$ for the reaction $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ from the following average bond strengths / kJ $mol^{-1}$: C-H = 415, C-Cl = 327, H-Cl = 431, Cl-Cl = 242 (Consider what bonds are broken and what bonds are made.)