

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. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) \quad \Delta_r H = -570 \text{ kJ mol}^{-1}$
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 Δ means change, r stands for reaction and H is the symbol for enthalpy. $\Delta_r H$ is the **enthalpy change** of the reaction.

Enthalpy change: Symbol ΔH , 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. $\Delta_r H < 0$

Endothermic reaction: A reaction that absorbs energy from the surroundings. $\Delta_r H > 0$

$\Delta_r H$ 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 (mol^{-1}) in the units of $\Delta_r H$ refers to the stoichiometric coefficients in the equation as amounts in moles. Thus if the above equation were written as



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 mol^{-1} .

Latent heat: An old term for the enthalpy change of a change in state.

[e.g. $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l}) \Delta H = 6 \text{ kJ mol}^{-1}$. Ice has to be heated for it to melt, so ΔH is positive. This is called the enthalpy of fusion (or melting) and given the symbol $\Delta_{\text{fus}}H(\text{H}_2\text{O})$. The symbols for enthalpy of sublimation and vaporisation are $\Delta_{\text{sub}}H$ and $\Delta_{\text{vap}}H$ respectively.]

Note: The convention used here is to place the explanatory subscript between the Δ and H , as recommended by IUPAC, the International Union of Pure and Applied Chemistry. Until recently the subscript was placed after the H and r was omitted for enthalpy changes of chemical reactions.

Calorimetry: The measurement of enthalpy change using a **calorimeter**.

Calorimeter: An apparatus for measuring the heat absorbed or released in a chemical reaction.

Heat capacity: symbol C , the ratio of the heat supplied to the temperature rise produced. i.e. the energy required to raise the temperature of a substance or system by one degree ($^{\circ}\text{C}$ or K)

when no chemical or phase changes occur. (i.e. $C = \frac{q_p}{\Delta T}$; SI units, J K^{-1})

Heat capacity at constant pressure: symbol C_p , the heat capacity when the change occurs at constant pressure, the most common condition.

Specific heat capacity: Symbol c_p , the heat capacity of unit mass of a substance; common units, $\text{J K}^{-1} \text{g}^{-1}$.

Molar heat capacity: Symbol $C_{p,m}$, the heat capacity of one mole of a substance; common units, $\text{J K}^{-1} \text{mol}^{-1}$.

[e.g. The absorption of 390 J of heat by a 100 g block of copper caused its temperature to increase by 10°C . Calculate the heat capacity of the block and the specific and molar heats of copper.

$$C_p(\text{block}) = \frac{q_p}{\Delta T} = \frac{390 \text{ J}}{10 \text{ K}} = 39.0 \text{ J K}^{-1}$$

$$c_p(\text{Cu}) = \frac{C_p(\text{block})}{m(\text{Cu})} = \frac{39.0 \text{ J K}^{-1}}{100 \text{ g}} = 0.390 \text{ J K}^{-1} \text{g}^{-1}$$

$$C_{p,m}(\text{Cu}) = \frac{C_p(\text{block})}{n(\text{Cu})} = \frac{C_p(\text{block})M(\text{Cu})}{m(\text{Cu})} \quad \left(\text{as } n = \frac{m}{M}\right)$$

$$= \frac{39.0 \text{ J K}^{-1} \times 63.5 \text{ g mol}^{-1}}{100 \text{ g}} = 24.8 \text{ J K}^{-1} \text{mol}^{-1} \quad]$$

If the reaction of a known amount of substance X, $n(\text{X})$, is carried out in a calorimeter and the temperature change measured, the enthalpy change for that reaction (written with 1 mole of X in the equation) can be calculated as the actual energy transferred is given by $q = -C_p\Delta T$

and $\Delta_r H = \frac{q_p}{n(\text{X})} = \frac{-C_p\Delta T}{n(\text{X})}$. Note the negative sign because if the temperature of the

calorimeter rises (ΔT positive) energy has been transferred from the reaction system to the calorimeter (the surroundings) and the reaction is exothermic.

[e.g. When 16 g of sulfur is combusted to sulfur dioxide 149 kJ of energy is released.

Determine $\Delta_r H$ for the reaction $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$

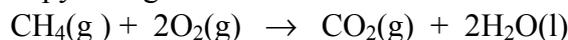
$$n(\text{S}) = \frac{m(\text{S})}{M(\text{S})} = \frac{16 \text{ g}}{32 \text{ g mol}^{-1}} = 0.50 \text{ mol}$$

$$\Delta_r H = \frac{q_p}{n} = \frac{-149 \text{ kJ}}{0.50 \text{ mol}} = -298 \text{ kJ mol}^{-1} \quad]$$

Heat of formation of a substance: Symbol $\Delta_f H$, the heat (enthalpy) change when one mole of that substance is formed from its elements in their standard states. By convention an element in its most stable form at 100 kPa pressure and 25 °C (298 K) is said to be in its standard state and to have an enthalpy of formation, $\Delta_f H$, of zero [e.g. from the reaction of hydrogen and oxygen above, it follows that $\Delta_f H(\text{H}_2\text{O}) = -285 \text{ kJ mol}^{-1}$].

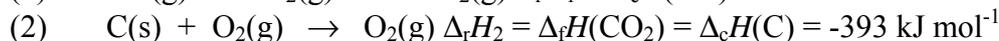
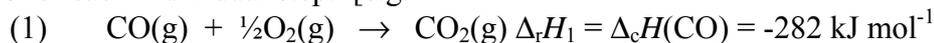
Heat of combustion of a substance: Symbol $\Delta_c H$, the heat given out when one mole of that substance reacts with dioxygen to give the most oxidised products.

[e.g. $\Delta_c H(\text{CH}_4)$ is the enthalpy change for the reaction

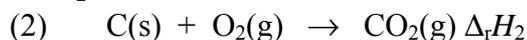


From the appropriate equation above it can be seen that $\Delta_c H(\text{H}_2) = \Delta_f H(\text{H}_2\text{O})$.]

Hess's law (of constant heat summation): The enthalpy change for a reaction is independent of the way the reaction is carried out (i.e. it depends only on the initial conditions of the reactants and the final conditions of the products). Put another way if a reaction is carried out in a number of steps the enthalpy change is the sum of the enthalpy changes for each individual step. [e.g.

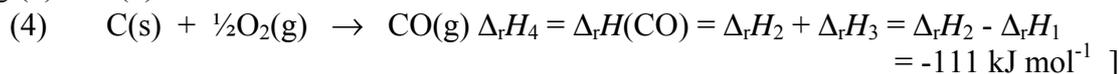


Imagine that we burn graphite (the most stable form of carbon) and then decompose the CO_2 to CO and O_2 :



changes when the reaction direction is reversed.

Adding (2) and (3):



It follows from Hess's law that for the general reaction $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$
 $\Delta_r H = c\Delta_f H(\text{C}) + d\Delta_f H(\text{D}) - a\Delta_f H(\text{A}) - b\Delta_f H(\text{B})$ or $\Delta_r H = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$

where \sum means "the sum of". This is a very useful expression because the enthalpy change for any reaction can be calculated from tables of heats of formation of the compounds involved.

[e.g. For the reaction $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{l})$

$$\Delta_r H = 3\Delta_f H\{\text{Fe}(\text{s})\} + 4\Delta_f H\{\text{H}_2\text{O}(\text{l})\} - \Delta_f H\{\text{Fe}_3\text{O}_4(\text{s})\} - 4\Delta_f H\{\text{H}_2(\text{g})\}$$

$$= 4\Delta_f H\{\text{H}_2\text{O}(\text{l})\} - \Delta_f H\{\text{Fe}_3\text{O}_4(\text{s})\} \quad \text{because } \Delta_f H \text{ for an element is zero. }]$$

Bond enthalpy (strength): The energy needed to break a chemical bond, with the bonding electrons being evenly divided between the fragments [e.g. The oxygen-oxygen bond strength of dimethyl peroxide, $\text{CH}_3\text{O}-\text{OCH}_3$, is $\Delta_r H$ for the reaction $\text{CH}_3\text{OOCH}_3 \rightarrow 2\text{CH}_3\text{O}\cdot$].

EXERCISES

1. The absorption of 62.76 kJ of heat by 500 g of liquid water caused its temperature to rise by 30 °C. Calculate the specific heat capacity of water in (i) $\text{J g}^{-1} \text{K}^{-1}$ and (ii) in $\text{cal g}^{-1} \text{K}^{-1}$ and the molar heat capacity of water in $\text{J mol}^{-1} \text{K}^{-1}$. (1 cal = 4.184 J)
2. It required 36.61 MJ of heat to distil 50 L of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, at its boiling point. Calculate $\Delta_{\text{vap}}H(\text{ethanol})$. ($\rho(\text{ethanol}) = 0.785 \text{ g cm}^{-3}$)
3. The combustion of exactly 1 kg of elemental sulfur to sulfur dioxide released 9.28 MJ of heat. Calculate $\Delta_fH(\text{SO}_2)$ in kJ mol^{-1} .
4. Carbon disulfide, CS_2 , has a boiling point of 46 °C. The products of combustion are CO_2 and SO_2 . (i) Write the equation for its combustion. (ii) Calculate $\Delta_fH(\text{CS}_2)$ given the following $\Delta_cH/\text{kJ mol}^{-1}$: $\text{CS}_2 = -1077$; $\text{C} = -393$; $\text{S} = -297$
5. Calculate the approximate Δ_rH for the reaction $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ from the following average bond strengths / kJ mol^{-1} : $\text{C-H} = 415$, $\text{C-Cl} = 327$, $\text{H-Cl} = 431$, $\text{Cl-Cl} = 242$ (Consider what bonds are broken and what bonds are made.)