

Energy & thermochemistry

13.1 Energy changes in chemistry: heat and work


- Chemical systems can be classified as:
 - isolated systems* that have no exchange of energy or matter with the surroundings;
 - open systems* that have both energy and matter exchange with the surroundings;
 - closed systems* that contain a fixed amount of matter but allow energy exchange.
- Heat is energy transferred as a result of a temperature difference.
- Work involves energy exchange as a result of motion against an opposing force.
- The heat capacity, C , relates the heat supplied to a substance to the resulting temperature rise.
 - Specific heat capacity, C_s , is the energy required to raise the temperature of 1 g of a substance by 1 K

$$C_s = \frac{q}{m \times \Delta T}$$

- Molar heat capacity, C_m , is the energy required to raise the temperature of 1 mol of a substance by 1 K


$$C_m = \frac{q}{n \times \Delta T}$$

- For gases, C_p and C_v are the molar heat capacities at constant pressure and constant volume, respectively.
- Extensive* properties depend on the quantity of substance that is present; *intensive* properties do not.

 For practice questions on these topics, see questions 1–3 at the end of this chapter (p.651).

13.2 Enthalpy and enthalpy changes

- The enthalpy change, ΔH , is the heat transferred at constant pressure by a chemical reaction or process.
- Enthalpy is a state function: $\Delta H = H(\text{final state}) - H(\text{initial state})$.
- Standard enthalpy change of fusion, $\Delta_{\text{fus}}H^\ominus$, is the enthalpy change when 1 mol of a substance melts at its melting point, T_m , and 1 bar pressure.
- Standard enthalpy change of vaporization, $\Delta_{\text{vap}}H^\ominus$, is the enthalpy change when 1 mol of a liquid vaporizes at its boiling point, T_b , and 1 bar pressure.
- For sublimation, $\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus$.

 For practice questions on these topics, see questions 4–6 at the end of this chapter (p.651).

13.3 Enthalpy changes in chemical reactions

- The standard enthalpy change of reaction, $\Delta_r H^\ominus$, is defined as the enthalpy change at 1 bar for a reaction with all components in their standard states. The value refers to the molar amounts given in the accompanying thermochemical equation.
- Values for standard enthalpy changes are often reported at 298 K (25°C).
- The standard enthalpy change of formation, $\Delta_f H^\ominus$, is the enthalpy change when 1 mol of a substance is formed under standard conditions from its constituent elements in their standard states.
- For elements in their standard states, $\Delta_f H^\ominus = 0$.
- Hess's law states that the total enthalpy change for a chemical reaction is independent of the path by which the reaction occurs, provided the starting and finishing states are the same for each reaction path.
- Enthalpy changes for reactions can be calculated from $\Delta_f H^\ominus$ values for the components

$$\Delta_r H_{298}^\ominus = \sum v_i \Delta_f H_{298}^\ominus (\text{products}) - \sum v_i \Delta_f H_{298}^\ominus (\text{reactants})$$

- The standard enthalpy change of combustion, $\Delta_c H^\ominus$, is the enthalpy change when 1 mol of a substance reacts completely with excess oxygen gas at 1 bar pressure.
- The bond dissociation enthalpy, $D_{(A-B)}$, is the enthalpy change per mole when a *particular* chemical bond, A–B, is broken under standard conditions in the gas phase.
- The mean bond enthalpy, $\bar{D}_{(A-B)}$, is the mean value of the bond dissociation enthalpy for the A–B bond, averaged across a range of related compounds.



For practice questions on these topics, see questions 7–10, 12, 13, 20, 22, and 29–31, 34 at the end of this chapter (pp.651–653).

13.4 Variation of enthalpy with temperature

- The change of enthalpy of a *substance* with temperature is given by

$$H_{T_2} = H_{T_1} + C_p(T_2 - T_1)$$

- The difference in heat capacity between products and reactants is

$$\Delta C_p = \sum v_i C_p (\text{products}) - \sum v_i C_p (\text{reactants})$$

where v_i is the stoichiometric coefficient in the balanced equation.

- Enthalpy change of reaction at temperatures other than 298 K can be found from the Kirchhoff equation

$$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta C_p(T_2 - T_1)$$



For practice questions on these topics, see questions 14, 23, 24, and 37 at the end of this chapter (pp.651–653).

13.5 Internal energy and the First Law of thermodynamics

- The sign convention used for values of energy changes is:
 - energy *gained* by a system is *positive* (heat absorbed by or work done on a system);
 - energy *lost* by a system is *negative* (heat released from or work done by a system).
- The sum of the kinetic and potential energies of molecules in a sample is the internal energy, U .
- First Law of thermodynamics: $\Delta U = q + w$ where q is the energy transferred as heat, and w is the energy transferred as work. This is also called the Law of Conservation of Energy.
- For an isothermal expansion of an ideal gas: $\Delta U = 0$; $q = -w$.
- $\Delta U = q_V$ (the heat change for a process at constant volume).
- Relation between enthalpy change and change of internal energy:

$$\Delta H = \Delta U + p\Delta V, \text{ or}$$

$$\Delta H = \Delta U + \Delta n_{\text{gas}}RT$$



For practice questions on these topics, see questions 15–19, 33 and 36 at the end of this chapter (p.651–653).

13.6 Measuring energy changes

- $\Delta_c U$ can be measured using a bomb calorimeter.
- Calorimeters can be calibrated by measuring the energy change for compounds with known $\Delta_c U^\ominus$.
- $\Delta_c H^\ominus$ can be calculated from measurements of $\Delta_c U^\ominus$, using

$$\Delta_c H^\ominus = \Delta_c U^\ominus + \Delta n_{\text{gas}}RT$$
- Solution calorimeters are used to study reactions that take place in solution.
- Solution calorimeters can be calibrated by the reaction of a strong acid and a strong base which has $\Delta_r H = -56.9 \text{ kJ mol}^{-1}$.



For practice questions on these topics, see questions 11, 21, 25–28, 32, and 35 at the end of this chapter (pp.651–653).



Concept review

By the end of this chapter you should be able to do the following.

- Give examples of the different ways that energy can be transferred in chemical systems.
- Understand what is meant by the terms *system* and *surroundings*.
- Explain the difference between *isolated*, *open*, and *closed* systems.
- Define, and perform calculations involving, heat and work.
- Understand the difference between *heat capacity*, *specific heat capacity*, and *molar heat capacity*, and carry out calculations using these properties.
- Explain the difference between *extensive* and *intensive* properties.
- Describe the characteristics of a state function.
- Define enthalpy change and calculate changes of enthalpy during phase changes and chemical reactions.
- Use Hess's law to calculate enthalpy changes.
- Define enthalpy changes of formation, $\Delta_f H_{298}^\ominus$, and use them to calculate enthalpy changes during reactions.
- Define and use enthalpy changes of combustion, $\Delta_c H_{298}^\ominus$, and enthalpy changes of solution, $\Delta_{\text{sol}} H_{298}^\ominus$.
- Explain and use bond dissociation enthalpy, D , and mean bond enthalpy, \bar{D} .
- Use the Kirchhoff equation to calculate enthalpy changes at temperatures other than 298 K.
- Define and calculate expansion work.
- Describe and explain the First Law of thermodynamics.
- Define internal energy, U .
- Calculate ΔU from ΔH and vice versa.
- Describe how to use a bomb calorimeter to measure energy changes of combustion.



Key equations

Specific heat capacity

$$C_s = \frac{q}{m \times \Delta T} \quad (13.1)$$

Molar heat capacity

$$C_s = \frac{q}{m \times \Delta T} \quad (13.2)$$

Hess's law and enthalpy change of formation

$$\Delta_r H_{298}^\ominus = \sum v_i \Delta_f H_{298}^\ominus (\text{products}) - \sum v_i \Delta_f H_{298}^\ominus (\text{reactants}) \quad (13.6)$$

The sum of all the standard enthalpy changes of formation of the products

The sum of all the standard enthalpy changes of formation of the reactants

Kirchhoff equation

$$\Delta_r H_{T_2}^\ominus = \Delta_r H_{T_1}^\ominus + \Delta_r C_p (T_2 - T_1) \quad (13.10)$$

Expansion work

$$w = -p_{\text{ext}} \Delta V \quad (13.14)$$

The First Law of thermodynamics

$$\Delta U = q + w \quad (13.15)$$

Enthalpy change and internal energy change

$$\Delta H = \Delta U + p \Delta V \quad (13.18)$$

$$\Delta H = \Delta U + \Delta n_{\text{gas}} RT \quad (13.19)$$