Lecture 1: Thermodynamics

1.1 Thermodynamic functions

- **Internal energy (U)** — the total energy of all the individual particles in a sample of matter.
- **Enthalpy (H)** — a quantity related to the heat absorbed or released by a chemical system.
  - **ΔH > 0**: endothermic — heat is absorbed.
  - **ΔH < 0**: exothermic — heat is released.
- **Entropy (S)** — a measure of the number of ways energy can be distributed throughout a chemical system.
- **Gibbs energy (G)** — relates to the energy available to do useful work:

$$G = H - TS$$

- Gibbs energy helps predict spontaneity, indicating the direction in which a process will proceed towards equilibrium.
- We are usually interested in changes in U, H, S and G rather than their absolute values. For any thermodynamic quantity X:

$$\Delta X = X_{final} - X_{initial}$$

- Temperature change follows the same convention:

$$\Delta T = T_{final} - T_{initial}$$

1.2 Systems, heat and temperature

- Heat (q) is the transfer of energy caused by a temperature difference.
- Thermodynamic temperature (T) is measured in kelvin (K).
- Two bodies at the same temperature are in thermal equilibrium — there is no net heat flow between them when they are in direct thermal contact.
- A system is the part of the universe being studied. Everything outside it forms the surroundings.
- Systems differ in what can cross their boundaries:
  - **Open system**: can exchange both matter and energy with its surroundings.
  - **Closed system**: can exchange energy, but not matter.
  - **Isolated system**: cannot exchange matter or energy.
- The energy of an isolated system remains constant.

1.3 Gibbs energy and spontaneity

- Chemical reactions and physical changes have a spontaneous direction under particular conditions.
- At constant temperature and pressure, the sign of ΔG determines whether a process is spontaneous:

$$\Delta G = \Delta H - T\Delta S$$

- **ΔG < 0**: the process is spontaneous in the forward direction.
- **ΔG > 0**: the forward process is non-spontaneous.
- **ΔG = 0**: the system is at equilibrium.
- A spontaneous process proceeds towards equilibrium, but spontaneous does not necessarily mean fast.

1.4 Internal energy, heat and work

- The first law of thermodynamics states that energy cannot be created or destroyed — only transferred or transformed.
- A system's internal energy changes through the transfer of heat or work:

$$\Delta U = q + w$$

- Internal energy includes the kinetic and potential energies of the system's components:

$$U_{total} = U_{kinetic} + U_{potential}$$

- Heat (q):
  - Positive when heat is transferred into the system.
  - Negative when heat is transferred out of the system.
- Work (w):
  - Positive when work is done on the system by the surroundings.
  - Negative when work is done by the system on its surroundings.
- Work involves motion against an opposing force. In chemical reactions, gases may cause volume changes and therefore pressure–volume work.
- At constant external pressure:

$$w = -p_{ext}\Delta V$$

- **Expansion**: $\Delta V > 0$, so $w < 0$. The system does work on the surroundings, losing energy through work.
- **Compression**: $\Delta V < 0$, so $w > 0$. The surroundings do work on the system, transferring energy into it.
- **No volume change**: $\Delta V = 0$, so pressure–volume work is zero.

1.5 Heat capacity and measurement of reaction heat

- Heat transferred during a temperature change is calculated using:

$$q = C\Delta T$$

- q = heat transferred, measured in J.
- C = heat capacity, measured in J K^{-1}.
- ΔT = final temperature minus initial temperature.
- A bomb calorimeter measures reaction heat at constant volume. Because the volume does not change, pressure–volume work is zero.
- Assuming no other work, the first law simplifies to:

$$\Delta_r U = q_v$$

- q_v is the heat of reaction at constant volume.
- Heat absorbed by the calorimeter is equal and opposite to the heat released by the reaction:

$$q_{calorimeter} = -q_{reaction}$$

- Therefore, using the calorimeter's heat capacity and temperature change:

$$q_{calorimeter} = C_{calorimeter}\Delta T$$

$$\Delta_r U = q_{reaction} = -C_{calorimeter}\Delta T$$

Exam tips

- Distinguish open, closed and isolated systems by their exchange of matter and energy.
- Know the signs of ΔG for spontaneous, non-spontaneous and equilibrium conditions.
- Assign heat and work signs from the system's perspective.
- Remember why expansion gives negative work and compression gives positive work.
- **Explain why a bomb calorimeter measures ΔU**: constant volume means no pressure–volume work.
- **Keep calorimeter heat and reaction heat separate** — their signs are opposite.

Memory tips

- Change = final − initial.
- Energy in → positive; energy out → negative.
- Expansion → $w < 0$; compression → $w > 0$.
- Calorimeter warms → reaction releases heat.