

# Thermodynamics

## Chem1B, General Chemistry II

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- **System:** What you are studying (usually the reaction)
- **Surroundings:** Everything else (outside solution, beaker, air, etc.)
- **Universe** = system + surroundings

The **system** and **surroundings** always work opposite each other.

If the **system** gains, the **surroundings** lose

If the **system** loses, the **surroundings** gain

**State Functions** are path-independent and always capitalized (i.e., elevation)

**Path-dependent** functions change based on distance and are lower case (i.e., work done)

- **Energy (E):** the ability to do work
- **Kinetic Energy (KE):** related to movement or motion
- **Potential Energy (PE):** related to position or composition
- **Total Energy** = kinetic energy (KE) + potential energy (PE)

**Internal Energy ( $\Delta E/U$ ):** sum of kinetic and potential energy in a **system**

Always measured as the *change* ( $\Delta E = E_{\text{final}} - E_{\text{initial}}$ )

In a system,  $\Delta E = q + w$

- **Heat (q):** transfer of thermal energy
- **Work (w):** energy used to move an object against a force

For a system, the signs matter.

If q is **absorbed**, the sign is **positive**. If q is **released**, the sign is **negative**.

If w is done **on** a system, the sign is **positive**. If w is done **by** a system, the sign is **negative**.

For gases, work is specifically **pressure-volume (PV) work**,  $w = -P\Delta V$

If a gas **expands** ( $+\Delta V$ ) against an external pressure, the system is **doing work**.

If a gas **compresses** ( $-\Delta V$ ) by an external pressure, the system is **being worked on**.

**Enthalpy ( $\Delta H$ ):** heat flow in a constant-pressure (**isobaric**) system

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

In a system,  $\Delta H = \Delta E + P\Delta V$

With constant pressure,  $\Delta E = q + w$  and  $w = -P\Delta V$

so that  $\Delta H = (q + w) + (-w) = q_p$

The sign on q determines the sign on  $\Delta H$ .

If the system absorbs heat,  $\Delta H$  is **positive (endothermic)**.

If the system releases heat,  $\Delta H$  is **negative (exothermic)**.

Four ways to determine the enthalpy of a reaction:

- 1.) Calorimetry (coffee-cup or bomb, using  $q = mC_s\Delta T$ )
- 2.) Hess's Law (known heats of reactions summed together)
- 3.) Enthalpies of Formation ( $\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$ )
- 4.) Bond Enthalpies ( $\Delta H_{\text{rxn}} = \sum \Delta H_{\text{bonds broken}} - \sum \Delta H_{\text{bonds formed}}$ )

**Standard Conditions ( $^\circ$ ):** P = 1 atm, T = 298 K, concentrations = 1 M