Thermochemistry

– studies the energy aspects of chemical reactions

– chemical reactions either produce or consume energy

$$\mathbf{2CO(g) + O_2(g) \rightarrow 2CO_2(g) + \textcolor{red}{energy}}$$

$$\mathbf{2H_2O(g) + \textcolor{red}{energy} \rightarrow 2H_2(g) + O_2(g)}$$

6.1 Forms of Energy

- **Kinetic energy** (E_k) – due to motion (for an object with mass m and velocity u: $E_k = (1/2)mu^2$)
- **Potential energy** (E_p) – due to position or interactions (formulas for E_p depend on the type of interactions)

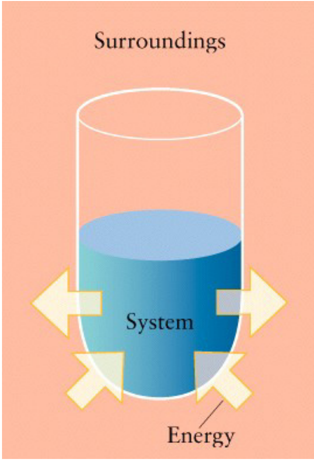
- The **total energy** (E_{tot}) is the sum of kinetic and potential energies

$$E_{tot} = E_k + E_p$$

- **Internal energy** (E) – the total energy of all atoms, molecules and other particles in a sample of matter
- **Law of conservation of energy** - the total energy of an isolated object (or a system of objects) is constant
  - E_k and E_p can change, but $E_k + E_p$ = constant

Systems and Surroundings

- **System** – part of the universe under investigation
- **Surroundings** – the rest of the universe outside the system
  - In practice, only the nearest surroundings relevant to the system are considered



- Energy transfer between the system and its surroundings results in a change of the system's internal energy
- **Internal energy change (ΔE)**

$$\Delta E = E_{final} - E_{initial}$$

  - If the system gains energy, $E_{final} > E_{initial}$ and $\Delta E > 0$
  - If the system loses energy, $E_{final} < E_{initial}$ and $\Delta E < 0$
- The energy gained by the system must be lost by the surroundings and vice versa (conservation of energy)

- **Open systems** – can exchange both matter and energy with the surroundings
  - open flask, fire, rocket engine, ...
- **Closed systems** – can exchange energy, but not matter with the surroundings
  - sealed flask, weather balloon, battery, ...
- **Isolated systems** – can exchange neither energy nor matter with the surroundings
  - sealed and thermally isolated container

Heat and Work

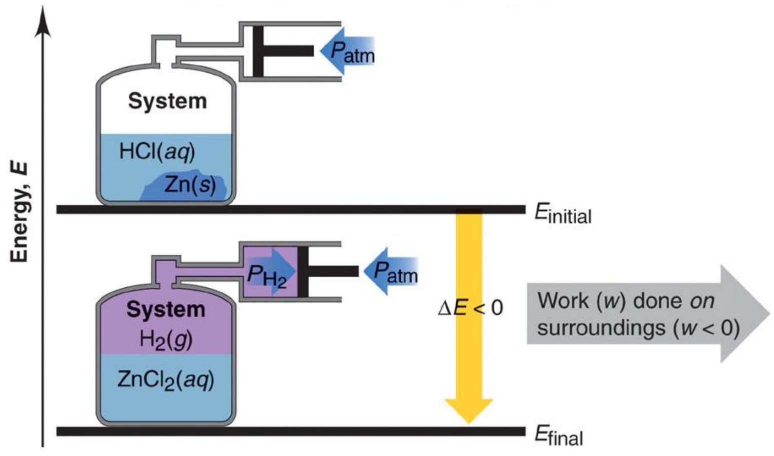
- **Thermal energy** – the energy of the random (thermal) motion of particles in a sample of matter (a part of the internal energy)
- **Heat (*q*)** – thermal energy transferred as a result of a temperature difference
  - thermal energy flows from places with high to places with low temperatures
  - heating changes the internal energy of a system
  - heating can change the temperature or the physical state of a system

- **Work (*w*)** – transfer of energy in the form of a motion against an opposing force (mechanical)
  - causes an uniform molecular motion
  - changes the internal energy of the system
- Energy can be transferred by heat and/or work

$$\Rightarrow \Delta E = q + w$$

- Heat and work are considered positive ($q > 0$ and $w > 0$), if they increase the internal energy of the system
  - Heat flowing into the system is positive
  - Work done on the system is positive

- Energy diagrams



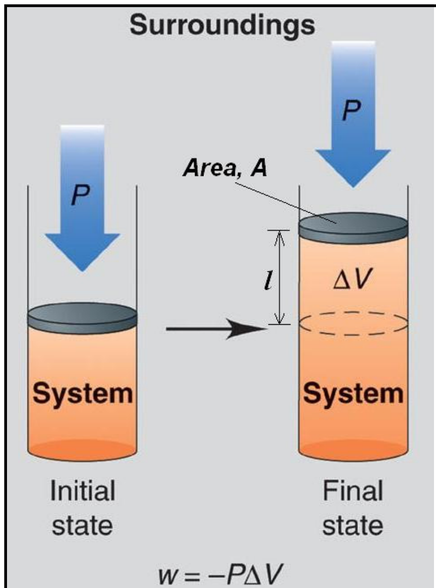
$$2Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

- **Expansion (*PV*) work** – due to changes in the volume of the system (important for reactions involving gases)
- If an object is moved over a distance (***l***) against an opposing force (***F***), the work is:

$$w = F \times l$$

- If a system expands against an external pressure (P_{ext}) applied over an area (A), the opposing force (F) is:

$$F = P_{ext} \times A \quad \Rightarrow \quad w = P_{ext} \times A \times l$$



$$w = P_{ext} \times A \times l$$
$$A \times l = \Delta V$$
$$\Rightarrow \quad w = P_{ext}\,\Delta V$$

$$\Delta V = V_f - V_i$$

– when the system expands $\Delta V > 0$, but ***w*** must be negative because the system does work

$$\Rightarrow \quad w = -P_{ext}\,\Delta V$$

The First Law of Thermodynamics

- **1st Law – The total energy of the universe is constant** (energy can't be created or destroyed, it can only be converted from one form to another)

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$$

- An **isolated system** can be viewed as a "small universe" ($q = 0$ and $w = 0$)

$$\Delta E = q + w = 0 \quad \Rightarrow \quad E = \text{constant}$$

- **1st Law** – The internal energy of an isolated system is constant (energy can not be created or destroyed within an isolated system)

- Energy units (same units are used for $\boldsymbol{E}$, $\boldsymbol{q}$ and $\boldsymbol{w}$)
  - SI unit → **joule, J (1 J = 1 kg·m²/s²)**
  - Other units → **calorie, cal (1 cal = 4.184 J)**
    → **1 cal** – the energy needed to increase the temperature of 1g of water by 1ºC

Example: Calculate the change of the internal energy of a system that gains 200 kJ as heat while doing 300 kJ of work.

q **= +200 kJ** $\qquad$ w **= -300 kJ**

$\Delta E = q + w$ **= 200 kJ + (-300 kJ) = -100 kJ**

- Units of $\boldsymbol{PV}$ work
  - If P_{ext} is in **Pa** and ΔV is in **m³**, than w is in **J**

1 Pa·m³ = 1 (kg/m·s²)×1 m³ = 1 kg·m²/s² = 1 J

  - If P_{ext} is in **atm** and ΔV is in **L**, than w is in **L·atm**

1 L·atm = 10^{-3} m³×101325 Pa = 101.325 J

Example: Calculate the work done when a gas is compressed from **12.0 L** to **5.0 L** by an external pressure of **2.6 atm.**

$w = -P_{ext}\Delta V = -2.6\ \text{atm}\times(5.0\ \text{L} - 12.0\ \text{L})$

$= -2.6\times(-7.0)\ \text{L·atm} = 18\ \text{L·atm}$

$18\ \text{L·atm}\times(101.325\ \text{J}/1\ \text{L·atm}) = 1.8\times10^{3}\ \text{J} = 1.8\ \text{kJ}$

- **State function** – a property that depends on the present state of the system (P, V, T, n), but not on the way it arrived in that state
  - $\boldsymbol{E}$ is a state function ⇒ ΔE depends only on the initial and final states of the system, but not on the path between these states → $\Delta E = E_{final} - E_{initial}$
  - $\boldsymbol{q}$ and $\boldsymbol{w}$ are not state functions because they depend on the path the system takes between two states