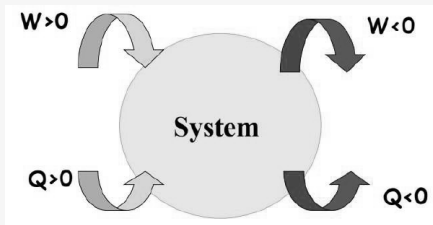


### Systems

A system can be open (freely exchanges energy and matter with the surroundings), closed (exchanges energy but not matter) or insulated (does not interact with the surroundings)

### Sign conventions



If the system gains heat, it is an endothermic process. If the system releases heat, it is an exothermic process.

### Heat

$$Q = m \cdot H_s \cdot \Delta T \quad \text{not a state function}$$

### Work

pressure-volume work  $W = P_{\text{ext}} \cdot V$  (if  $P = \text{constant}$ )

if carried out in a reversible way  $W = -nRT \cdot \ln(V_2/V_1)$

### Ideal gas law

$$P \cdot V = nRT \quad R = 0,082 \text{ atm} \cdot \text{L} / (\text{K} \cdot \text{mol})$$

### Calorimeter bomb

$$Q + W = 0 = \Delta E$$

$$W = 0 \quad Q = 0$$

$$Q_{\text{released}} + Q_{\text{absorbed}} = 0$$

$$Q_{\text{reaction}} + Q_{\text{water}} + Q_{\text{calorimeter}} = 0$$

$$Q_{\text{reaction}} + M_{\text{water}} \cdot (T_f - T_i) + K_{\text{calorimeter}} \cdot (T_f - T_i) = 0$$

$$Q_{\text{reaction}} = Q_v = \Delta E$$

### Laws of thermochemistry

#### Lavoisier and Laplace laws

The energy change accompanying any transformation is equal and opposite to energy change accompanying the reverse process.

#### Hess Law

The energy change accompanying any transformation is the same whether the process occurs in one step or many. The combination of chemical equations allows to determine unknown heats of reaction.

### Units

$$1 \text{ cal} = 4,184 \text{ J}$$

Specific heat: quantity of heat required to change the temperature of one gram of the substance by one degree celsius

Molar heat: quantity of heat required to change the temperature of one mol of the substance by one degree celsius

Heat capacity: quantity of heat required to change the temperature of a system by one degree celsius

### First law of thermodynamics

Internal energy is the total energy in a system  $E = \sum E_i$

Principle of conservation of energy  $\Delta E = Q + W$

For isolated system  $Q + W = 0 = \Delta E$

Heat and work are means by which a system exchanges energy with the surroundings

### Enthalpy (H)

It is the change in the internal energy when there is only pressure-volume work, and the pressure is constant

$$\Delta E = Q + W = Q_p - P \cdot \Delta V \quad Q_p = \Delta E + P \cdot \Delta V$$

$$H = E + P \cdot V \quad \Delta H = \Delta E + V \Delta P + P \Delta V + \Delta P \Delta V$$

$$\text{if } P = \text{constant} \quad \Delta H = Q_p = m \cdot H_s \cdot \Delta T = n \cdot H_s \cdot \Delta T$$

### Relation of Qv and Qp (gases)

$$\Delta H = \Delta E + P \Delta V$$

$$\text{if } P \text{ and } T \text{ are constant} \quad \Delta H = \Delta E + \Delta n RT$$

### Relation of Qv and Qp (solids and liquids)

$$\text{if } P = \text{constant} \rightarrow \text{change in volume really small} \quad Q_v \approx Q_p \rightarrow \Delta E \approx \Delta H$$

### Enthalpy and bond energy

$$\Delta H_r = \sum H_{\text{broken bonds}} - \sum H_{\text{formed bonds}}$$

### Standard States. Standard enthalpy of reaction

enthalpy change of a reaction in which all reactants and products are in their standard states

the standard enthalpy of formation of a pure element in its standard state is 0

$$\Delta H^\circ = \sum \nu_p \cdot \Delta H^\circ_f(\text{products}) - \sum \nu_r \cdot \Delta H^\circ_f(\text{reactants})$$