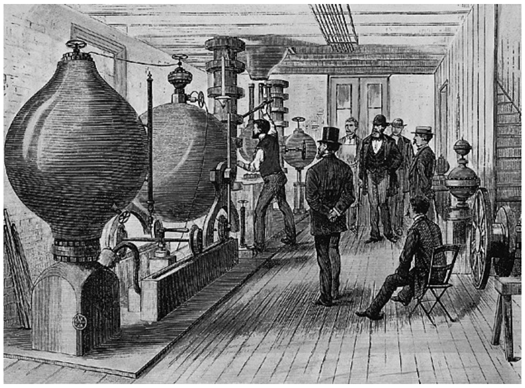


Thermochemistry

– studies the energy aspects of chemical reactions

Energy, Heat and Enthalpy

– chemical reactions either produce or consume energy

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ + energy

$2H_2O(g)$ + energy $\rightarrow 2H_2(g) + O_2(g)$

– energy is treated quantitatively just like the reactants and products in a reaction

6.1 The Conservation of Energy

- Types of energy
  - **kinetic energy** (E_k) - due to motion
    - for an object with mass m and velocity v:

$$E_k = (1/2)mv^2$$

  - **potential energy** (E_p) - due to position or interactions (formulas for E_p depend on the type of the interactions)
    - for an object with mass m at a height h above the Earth's surface:

$$E_p = mgh$$

- The **total energy** (E) is the sum of kinetic and potential energies

$$E = E_k + E_p$$

- **Internal energy** (U) - the total energy of all atoms, molecules and other particles in a sample of matter
  - U can be converted to useful work or heat
- **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

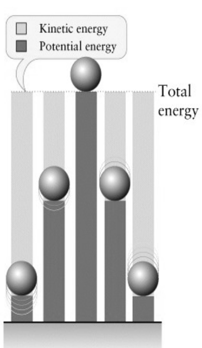


Fig. 6.2

- **Thermodynamics** - studies the transformations of energy in macroscopic samples of matter
- **Thermochemistry** - a part of thermodynamics dealing with the heats of chemical reactions

6.2 Systems and Surroundings

- **System** - part of the universe under investigation
- **Surroundings** - the rest of the universe outside the system

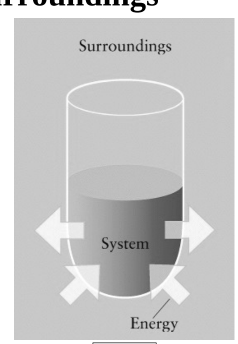


Fig. 6.3

- **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
- **Law of conservation of energy** - the total energy of the universe is constant

6.3 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*)** - transfer of thermal energy 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

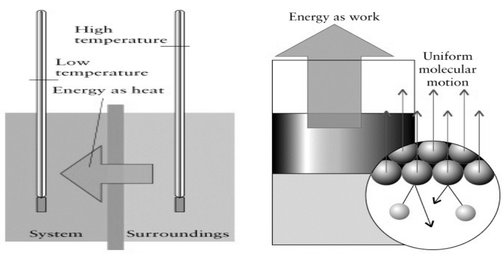


Fig. 6.6, 6.9

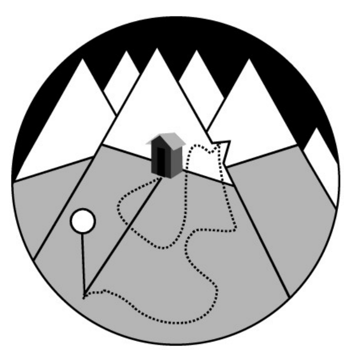
6.4 The First Law of Thermodynamics

- The internal energy depends on the size of the system (extensive property)
  - ⇒the internal energy of a system can be changed by heating, doing work or changing the system size
- Energy units (same units are used for ***q*** and ***w***)
  - SI unit → **joule**, **J** **(1 J = 1 kg·m^2/s^2)**
  - other units → **calorie, cal (1 cal = 4.184 J)**
    → 1 cal - the energy needed to increase the temperature of 1g of water by 1ºC

- Internal energy change (***DU***)

$$DU = U_{final} - U_{initial}$$

  DU > 0 → system gains energy
  DU < 0 → system losses energy
- **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
- ***U*** and ***DU*** are state functions (***DU*** depends only on the initial and final states of the system, but not on the path between these states)



- Work and heat are considered positive (***q, w*** > 0), if they increase the internal energy of the system

$$DU = q + w$$

q → energy supplied to the system as heat
w → energy supplied to the system as work

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 **w = -300 kJ**

$DU = q + w$ = 200 kJ + (-300 kJ) = -100 kJ

- Heat and work are equivalent ways of changing the internal energy
- For an isolated system

$$q = 0 \quad \text{and} \quad w = 0$$

$$DU = 0 \;\Rightarrow\; U = \text{constant}$$

- **The first law -** the internal energy of an isolated system is constant
  - energy can not be created or destroyed within an isolated system
  - a restatement of the law of conservation of energy