Thermochemistry

Thermodynamics

All physical and chemical changes are accompanied by changes in energy.

Thermodynamics: the study of energy and its interconversions

Energy

Energy is the capacity to do work or produce heat

Some fundamentals

Mass (m)   **Acceleration (a)**

Force (F) = ma

Units of force: kg-m-s^{-2}

(derived term in Sl is called a Newton)

Work

- the result of a force acting on a body and producing motion

Some fundamentals (Work)

Force (F)   **Distance (l)**

Units of force: kg-m-s^{-2}

Work = force x distance

Units of work: kg-m^2-s^{-2}

(derived term in SI is called a joule)

Some fundamentals (Heat)

symbol: *q*

the transfer of energy between two bodies that are at different temperatures

has same units (*J*) as work

Calorie

approximately 1 cal is required to increase the temperature of exactly 1 g of water by 1K or 1°C

1 cal = 4.184 J

Some terminology

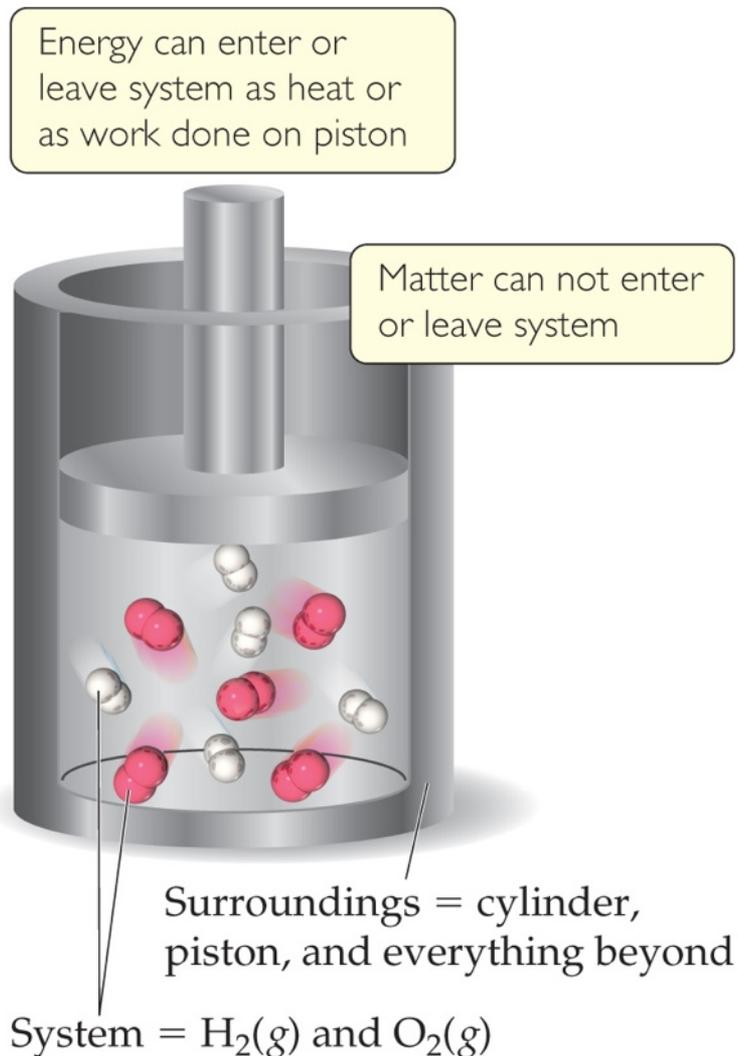**system + surroundings = universe**

what we study

chemical reactions: reactants and products

Definitions: System and Surroundings

Energy can enter or leave system as heat or as work done on piston

Matter can not enter or leave system

Surroundings = cylinder, piston, and everything beyond

System = $H_2(g)$ and $O_2(g)$

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- The **system** includes the molecules we want to study (here, the hydrogen and oxygen molecules).

- The **surroundings** are everything else (here, the cylinder and piston).
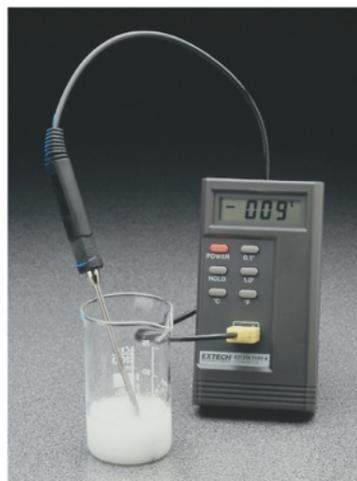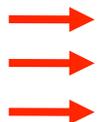
Thermochemistry

Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.

System: reactants + products

Surroundings: solvent, initially at room temperature

Heat

Heat flows from surroundings into system (endothermic reaction), temperature of surroundings drops, thermometer reads temperature well below room temperature

(a)

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Thermochemistry

Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.

- When heat is released by the system into the surroundings, the process is **exothermic**.

System: reactants

Surroundings:
air around reactants

Heat

Heat flows (violently) from system into surroundings (exothermic reaction), temperature of surroundings increases

(b)

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Thermochemistry

The heat released or absorbed during chemical reactions lies in the difference in potential energy between the products and the reactants
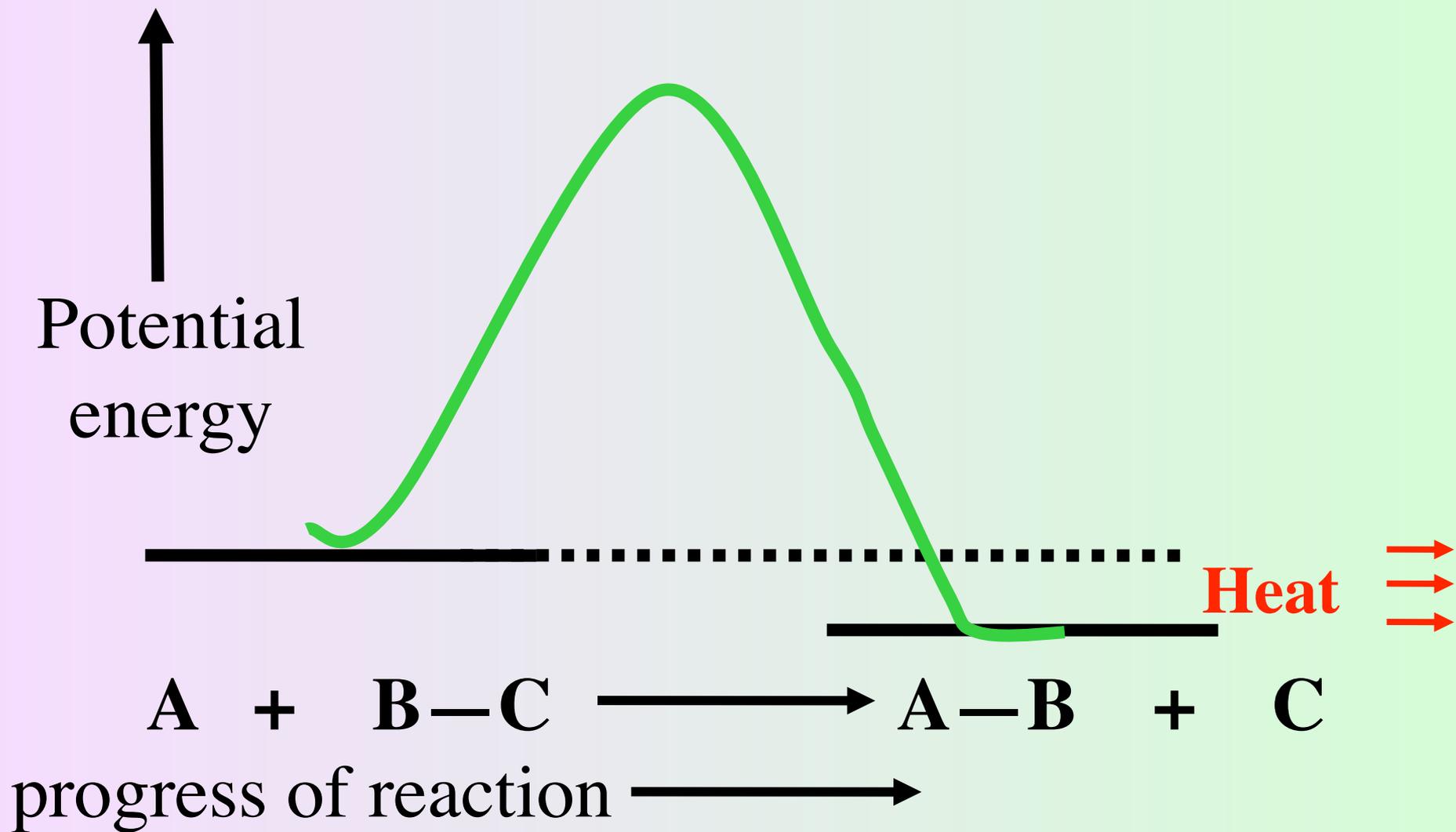
An exothermic reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) + energy$$

stronger chemical bonds in products than in reactants

less potential energy in products

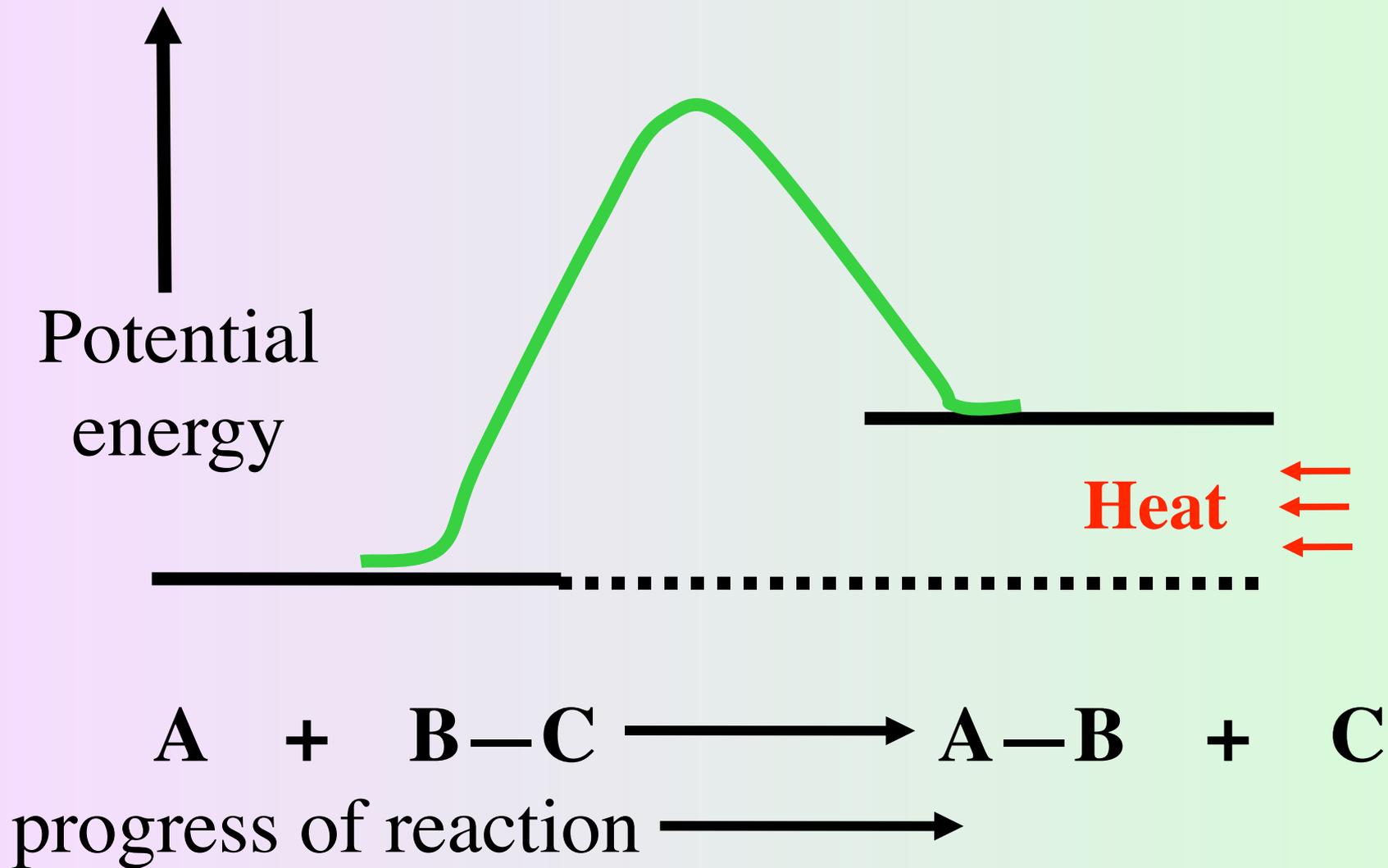**Consider a hypothetical one-step reaction (exothermic)**

Potential energy

Heat

A + B — C ⟶ A — B + C

progress of reaction

An endothermic reaction

$$2H_2O(l) + energy \longrightarrow 2H_2(g) + O_2(g)$$

weaker chemical bonds in products than in reactants

more potential energy in products

Consider a hypothetical one-step reaction (endothermic)

Potential energy

Heat

A + B—C ⟶ A—B + C

progress of reaction

First Law of Thermodynamics

energy can not be created or destroyed

types of energy

Kinetic (thermal) energy

energy associated with motion

Potential energy

energy available by an object by virtue of its position

Kinetic energy

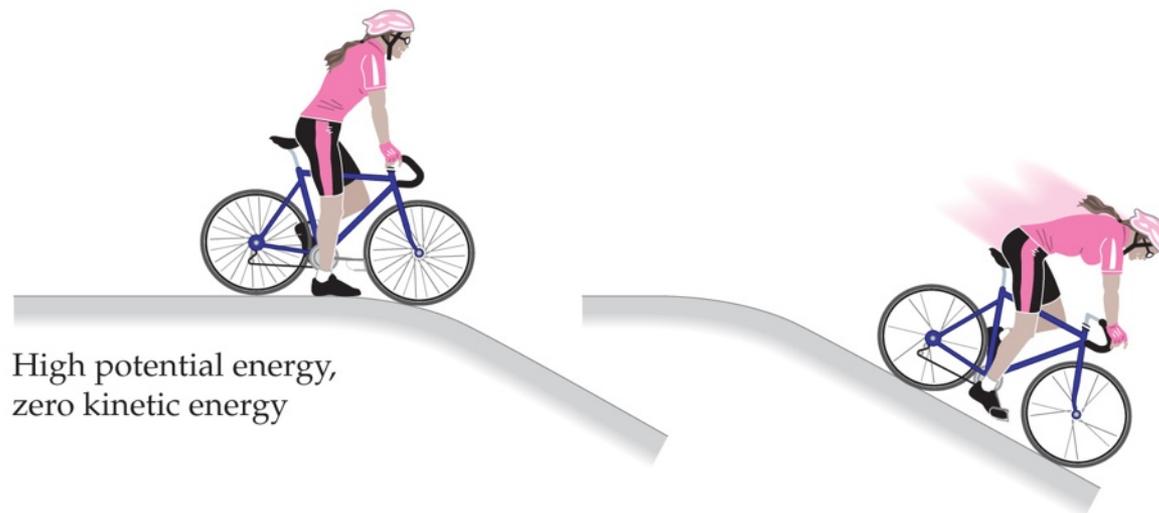**Energy an object possesses because of its motion**

$$\text{kinetic energy } = \frac{1}{2}\, mu^2$$

Units: kg-m^2-s^{-2} (joules)

Kinetic Energy

Kinetic energy is energy an object possesses by virtue of its motion:

$$E_k = \frac{1}{2} mv^2$$

High potential energy, zero kinetic energy

Decreasing potential energy, increasing kinetic energy

Thermochemistry

Potential energy

energy an object has because of position

an example is potential energy of an object with the potential to fall

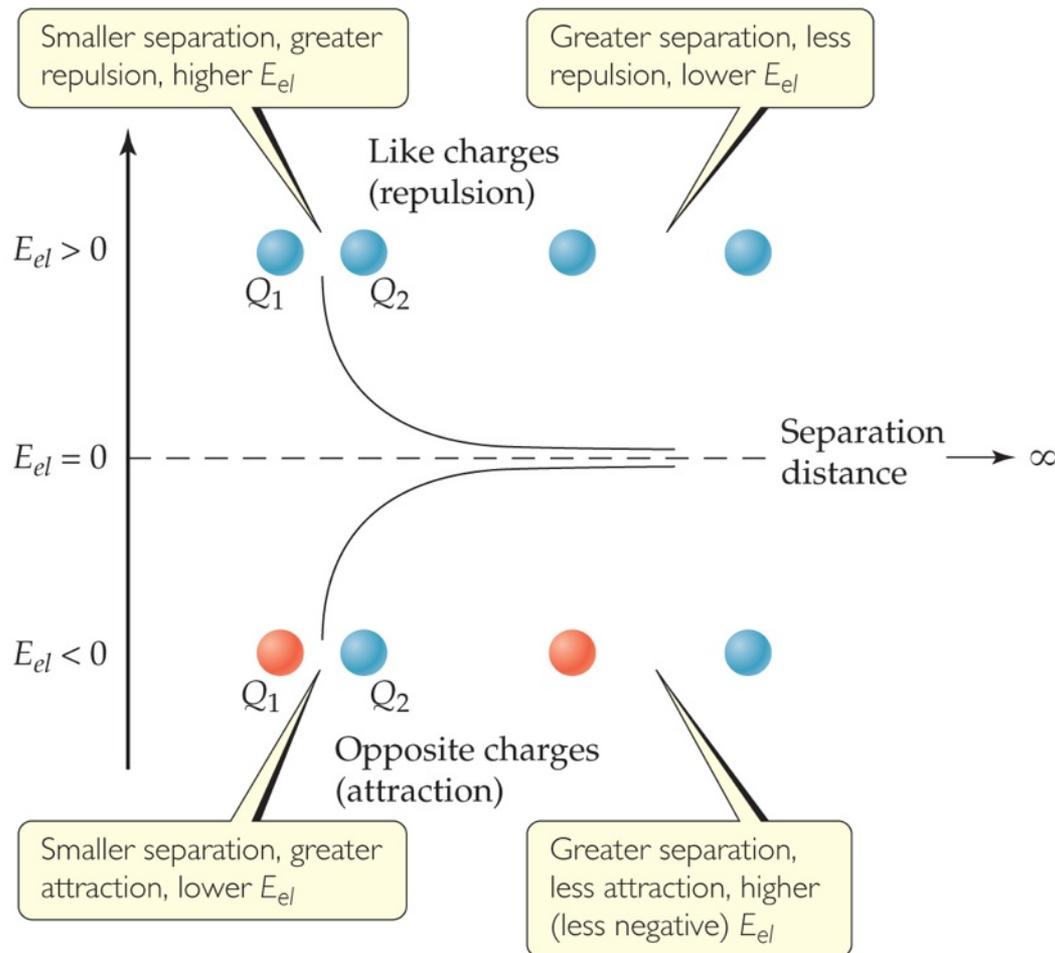gravitational potential energy = mass **x** height **x** gravitational constant

Units: kg-m^2-s^{-2} (joules)

Chemical Potential Energy

due to the attractive and repulsive forces between protons and electrons

Potential Energy

Smaller separation, greater repulsion, higher E_{el}

Greater separation, less repulsion, lower E_{el}

Like charges (repulsion)

$E_{el} > 0$

Q_1 Q_2

$E_{el} = 0$

Separation distance ∞

$E_{el} < 0$

Q_1 Q_2

Opposite charges (attraction)

Smaller separation, greater attraction, lower E_{el}

Greater separation, less attraction, higher (less negative) E_{el}

- **Potential energy** is energy an object possesses by virtue of its position or chemical composition.

- The most important form of potential energy in molecules is electrostatic potential

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

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Ionic Compounds

the potential energy between two ions in an ionic solid is directly proportional to the product of their charges and inversely proportional to the distance between them
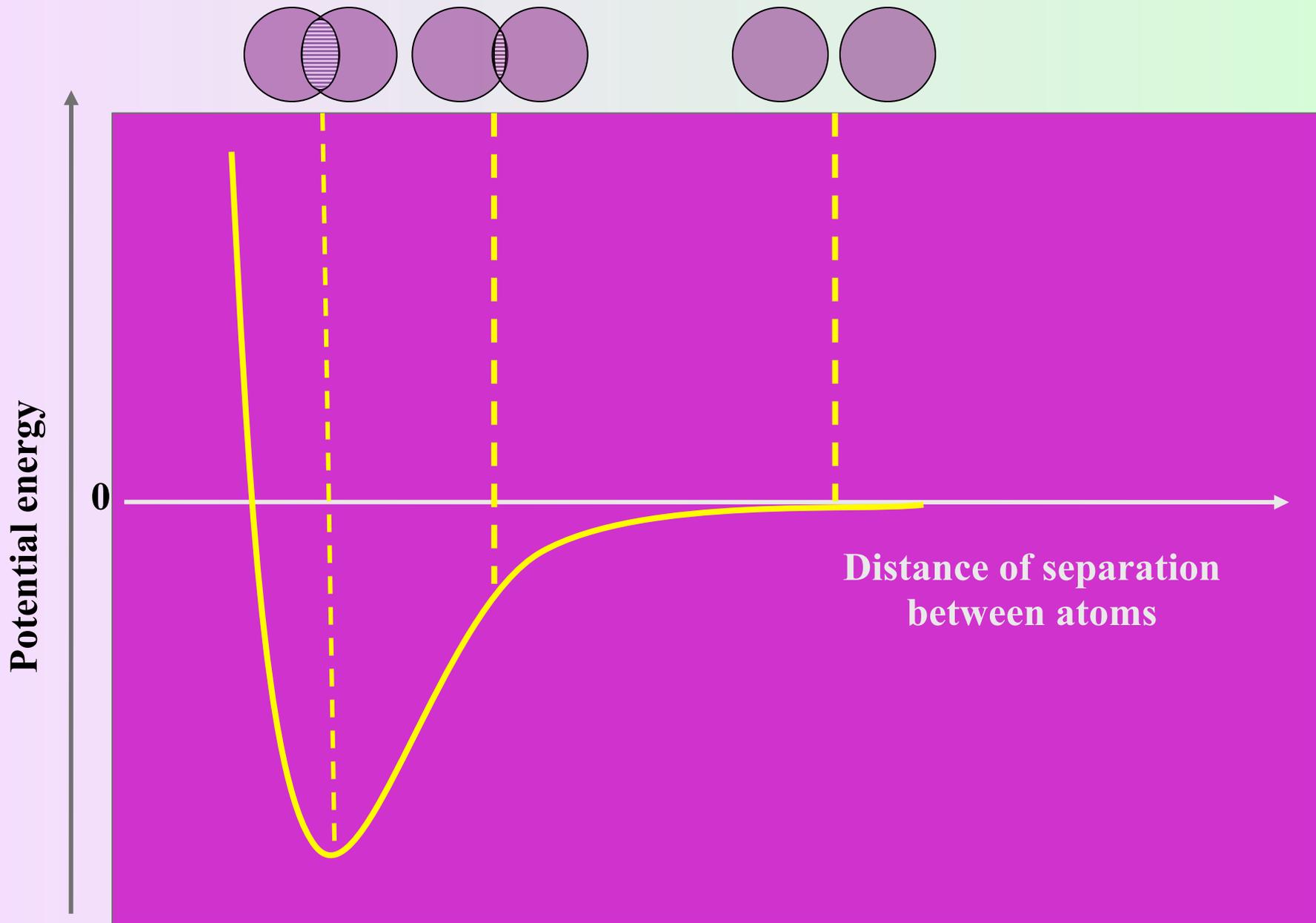
Charge on Li+   Charge on F -

$$E = k \; \frac{Q_{Li+} \, Q_{F-}}{r}$$

The distance between the ions

Covalent Compounds

Compounds containing covalent bonds

(electrons shared by two atoms)

First Law of Thermodynamics

Energy can be converted from one form to another but can neither be created nor destroyed

$$\text{Energy} = \text{Heat} + \text{Work}$$

$$E = q + w$$

Example : kinetic energy to potential energy

Internal Energy (E)

$$E = q + w$$

Internal Energy (E)

The sum of the kinetic and potential energies of all the particles in a system

$$E = q + w$$

Change Internal Energy (ΔE)

The energy entering or leaving the system

$$\Delta E = q + w$$

A common type of work associated with chemical processes is the expansion and compression of a gas.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$F = P\,A$$

$$\text{work} = F \text{ x } d$$

A common type of work associated with chemical processes is the expansion and compression of a gas.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$F = P A$$

$$\text{work} = \overset{m^2}{P A} \times \overset{m}{d}$$

the work done by an expanding gas against pressure P

W is negative because work is leaving the system during an expansion

$$\text{work} = -P\Delta V \quad {}^{m^3}$$

Example

A balloons volume changes from 4.0×10^6 L to 4.5×10^6 L by the addition of 1.3×10^8 J of heat energy. Assuming a constant pressure of 1.0atm, calculate ΔE for the process.

$$\Delta E = q + w$$

$$w = -P\Delta V = (-1.0\text{atm})(4.5 \times 10^6\text{L} - 4.0 \times 10^6\text{L})$$

$$= -5.0 \times 10^5 \text{ atmL} \quad \text{x} \quad \frac{101.3 \text{ J}}{\text{atmL}} = -5.1 \times 10^7 \text{ J}$$

$$\frac{R' \quad (8.314\text{J/mol}\cancel{K})}{R \quad (0.08206\text{atmL/mol}\cancel{K})} = \frac{101.3 \text{ J}}{\text{atmL}}$$

Example

A balloons volume changes from 4.0×10^6L to 4.5×10^6L by the addition of 1.3×10^8J of heat energy.Assuming a constant pressure of 1.0atm,calculate ΔE for the process.
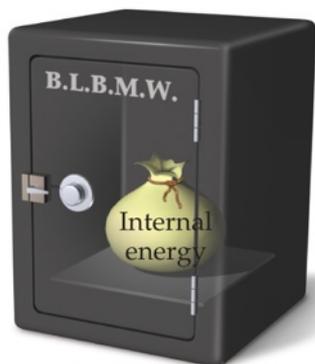
$$\Delta E = q + w$$

$$w = -5.1 \times 10^7 \text{ J}$$

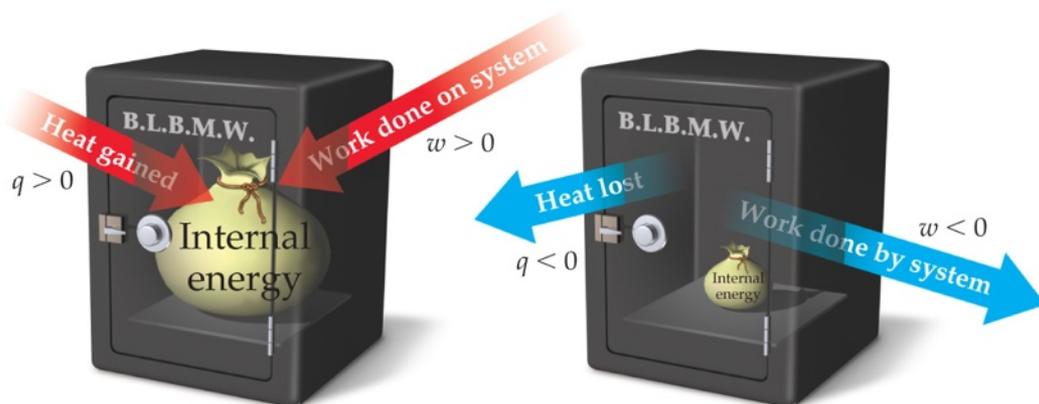$$\Delta E = q + w = 1.3 \times 10^8 \text{J} + (-5.1 \times 10^7 \text{ J})$$

$$\Delta E = 8 \times 10^7 \text{J}$$

Changes in Internal Energy

System is interior of vault

Energy deposited into system
$\Delta E > 0$

Energy withdrawn from system
$\Delta E < 0$

- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).
- That is, $\Delta E = q + w$.

Thermochemistry

Enthalpy

Enthalpy (H)

Used to describe heat changes taking place at a constant pressure (q_p)

$$\Delta E = q_p + w$$

$$\Delta E = q_p - P\,\Delta V$$

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

$$q_p = \Delta H$$

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

Enthalpy

- When the system changes at constant pressure, the change in enthalpy, ΔH, is

$$\Delta H = \Delta(E + PV)$$

- This can be written

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

Thermochemistry

Enthalpy

- Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

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

$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

- So, at constant pressure, the change in enthalpy *is* the heat gained or lost.