General Chemistry II

Chem 102

Lecture 6

Thermochemistry

Ahmad Alakraa

Energy the capacity to do work or to produce heat

Law of energy's conservation: energy can be converted from one form to another but can neither be **created** nor **destroyed**.

Basic forms of Energy

Potential Energy

energy due to position or composition.

e.g., attractive and repulsive forces

Kinetic Energy

energy due motion of an object of a mass m and a velocity υ.

$$K.E. = \frac{1}{2} m \upsilon^2$$

Potential Energy

- Any type of stored energy: Chemical, nuclear, gravitational, mechanical.

Kinetic Energy

- is found in movement, e.g., a flying airplane; or vibrating atoms (if they are hot or transmitting sound waves).
- Electricity is the kinetic energy of flowing electrons between atoms.

Energy Conversion/Transformation

- Energy may transfer between systems in three basic forms:

Mass

Heat, q

Work, w

Mechanical work

- When a force acts upon an object to cause a displacement of the object, it is said that work was done upon the object

$W = F \,.\, d = m \,.\, g \,.\, h \quad (J)$

(force) . (distance) = (mass). (acceleration) .(height)

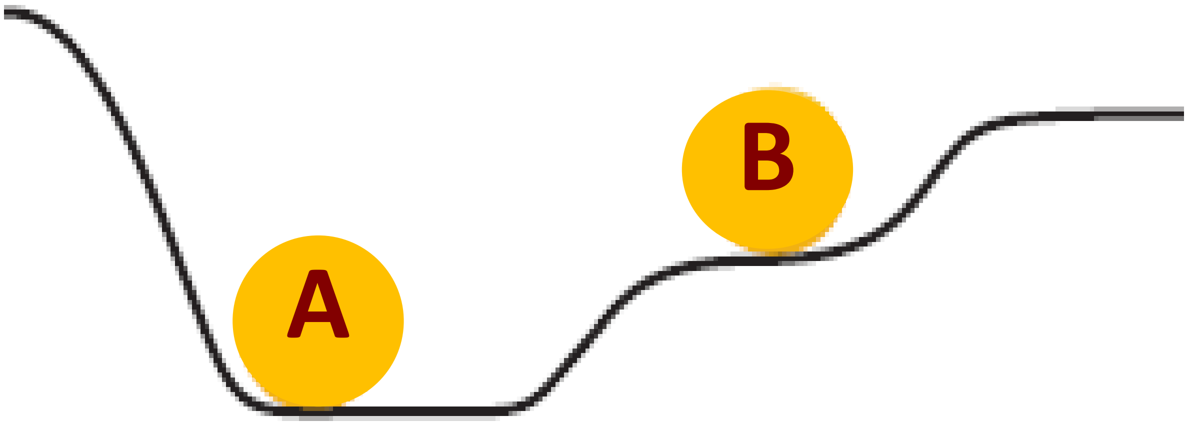
$= P \,.\, A \,.\, h = P \,.\, V$

(pressure) . (area).(height) (pressure) . (volume)

$PE_A > PE_B$

Initial

$PE,_{A\ lost} = PE,_{B\ gained}$ (work) + Frictional Energy (Heat)



$PE_A < PE_B$

Final

- If A rolls down, part of PE_A converts to KE_A.
- Part of KE_A is lost as frictional heating
- Upon collision with B, the other part transfers to B (PE_B increases) i.e. ,work was done by ball A on B.
- Ball A lost specific (fixed) amount of its potential energy $PE_{A,\ lost}$.
- The amount of energy transferred in the form of work or heat may vary based on the conditions (e.g., surface roughness),

$PE_{A,\ lost}$ (fixed)=

$PE_{B,\ gained}$ (work, variable) +

Frictional Energy (Heat, variable)

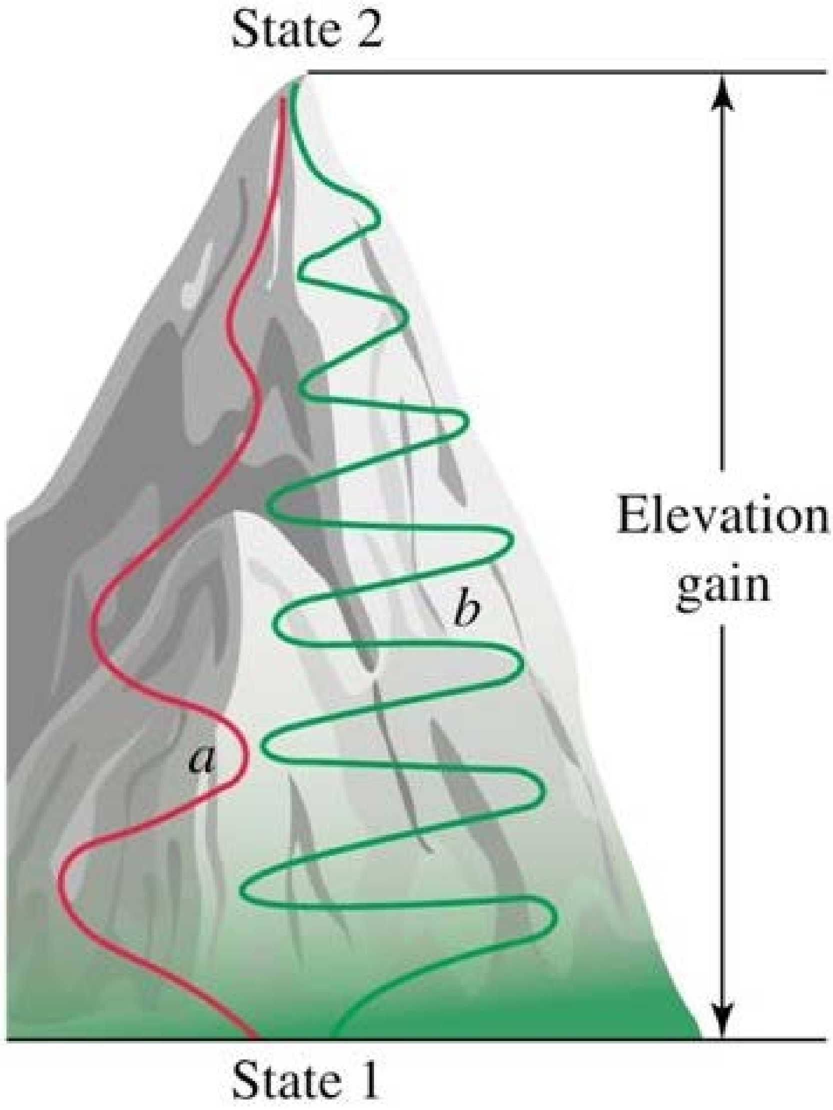
Temperature, Heat, and Work

- Temperature is a property reflecting the random motions of particles in a substance.
- Heat is a form of energy. It involves the energy transfer between two objects due to a temperature difference.
- Work is the force acting over a distance.

State (path-independent) functions

System's properties that depend only on the system's present (initial and final) state not on the system's past or future (pathway)

State (path-independent) functions



- ✓ A change in state functions is independent of the particular pathway taken between the two states.

- ✓ ΔE is a state function; however, work and heat are both non-state functions (depend on the pathway) .

State/Non-state functions

- **State property (Functions):** Functions which depend on the initial and final states of the system, not on the path it takes. (e.g., Internal energy, Temperature, Volume, Pressure).

- **Path or non-State property (Functions):** Functions which depend not only on the initial and final states of the system, but also on the path it takes. (e.g., **Heat** and **Work**; written dq or dw. Never written **Δq** or **Δw**).

Thermodynamics is largely concerned with relations between state functions which characterize systems.

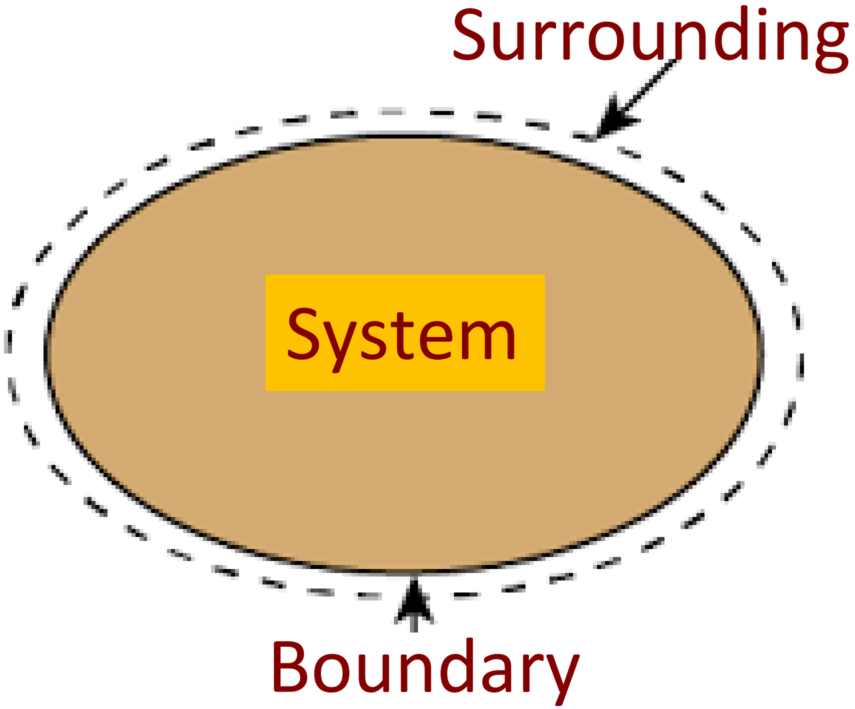
Extensive/Intensive Properties

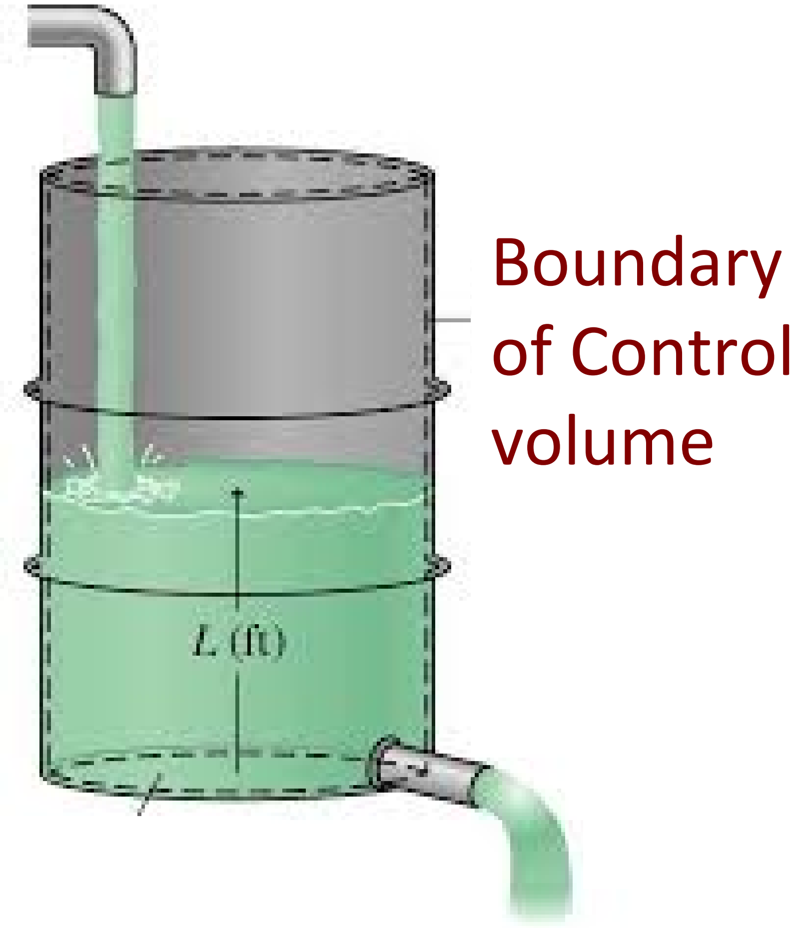
- **Extensive property (Functions):** Functions which depend on the mass of the material (e.g., Internal energy, Volume)

- **Intensive Property (Functions):** Functions which are independent of the mass of the material (e.g., Pressure, Temperature, Density, Molar quantities)

System/Surroundings

- **System**: volume of interest (reaction vessel, test tube, biological cell, atmosphere, etc.)
- **Surroundings**: volume outside a system

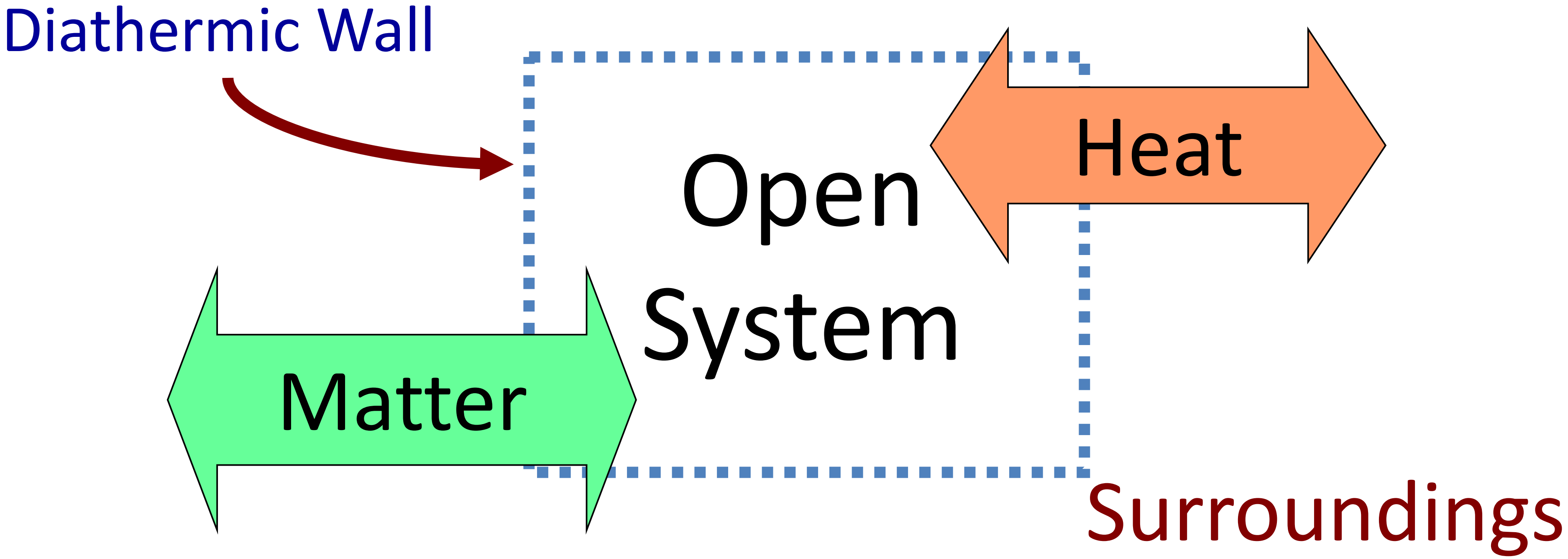




Open Systems

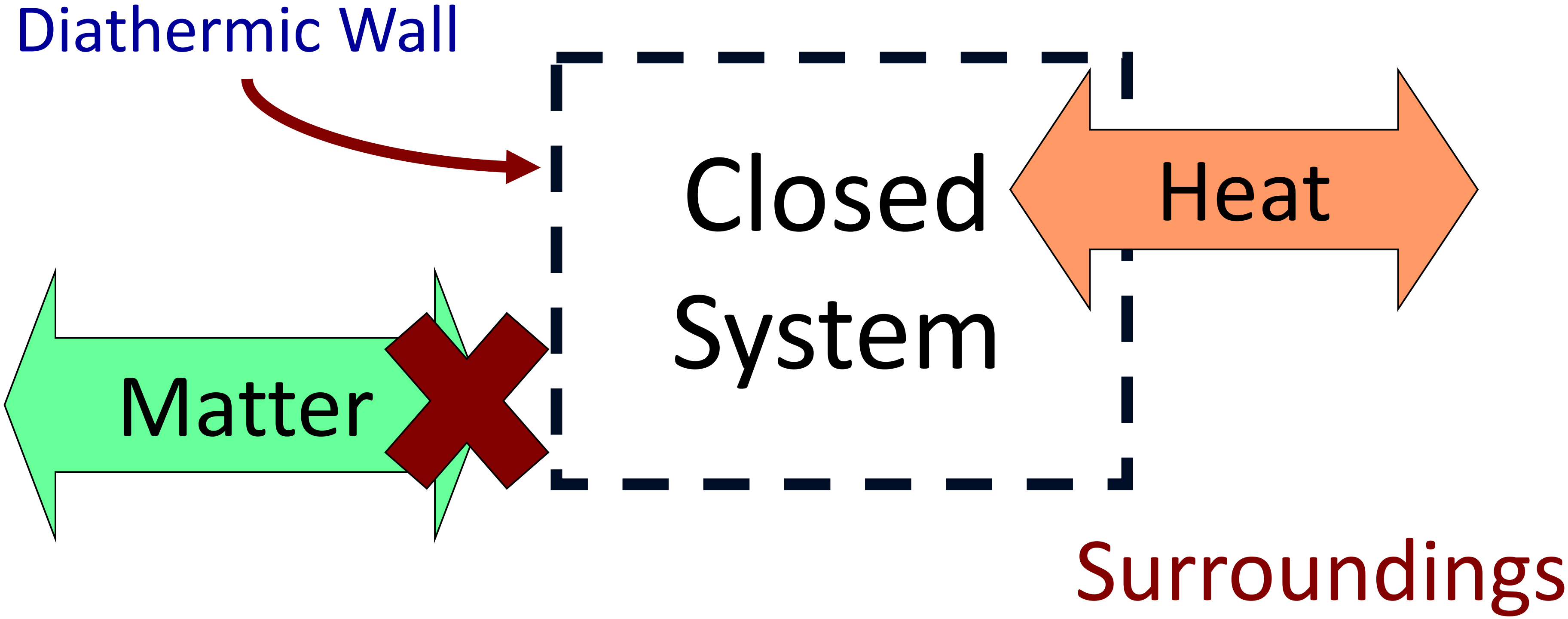
A system permitting the heat (Energy) and mass transfer between system & surroundings

- **Diathermic Walls:** Walls permitting energy transfer as heat (such as steel and glass) ('dia' is the Greek word for "through").



Closed Systems

A system permitting the heat (Energy) but not mass transfer between system & surroundings

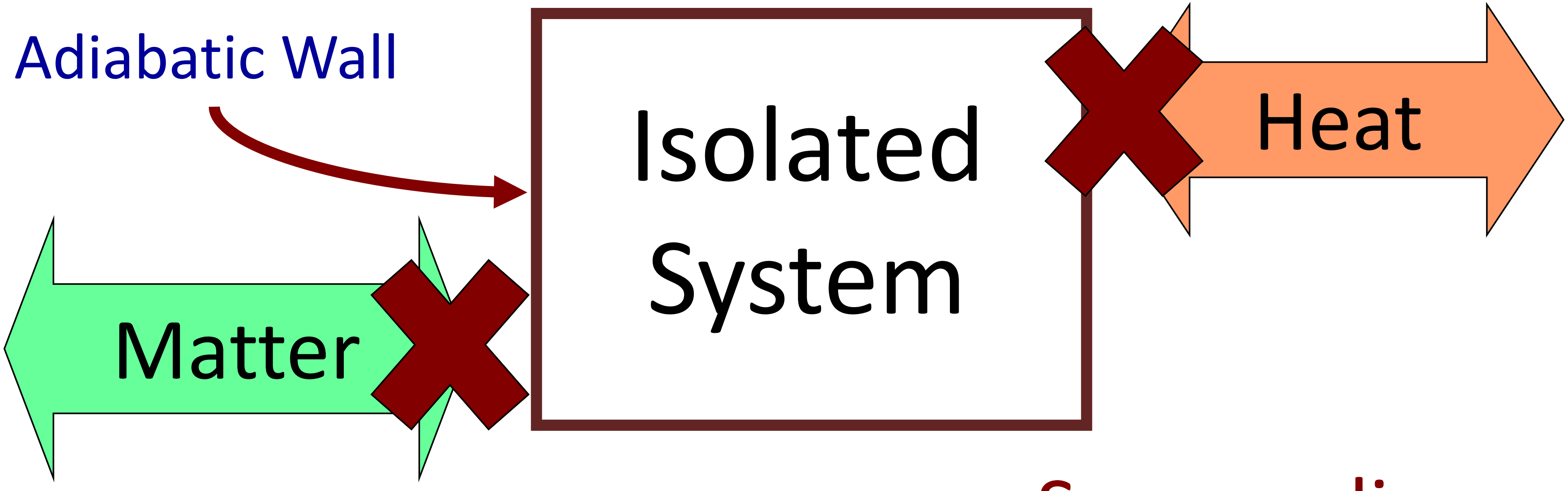


Isolated Systems

A system permitting neither the heat (Energy) nor mass transfer between system & surroundings

- **Adiabatic Walls**: Walls that DO NOT permit energy transfer as heat.

No change in internal energy (ΔE=0) if no work is done between system and surrounding



Adiabatic Wall

Isolated System

Heat

Matter

No thermal contact

Surroundings

General conventions

Work

- If the system does work on the surroundings, then work (w) is negative.
- If the surroundings does work on the system, then work (w) is positive.

Heat

- If the system loses heat to the surroundings, then heat (q) is negative.
- If the system gains heat from the surroundings, then heat (q) is positive.

Chemical-Heat Energy Transformations

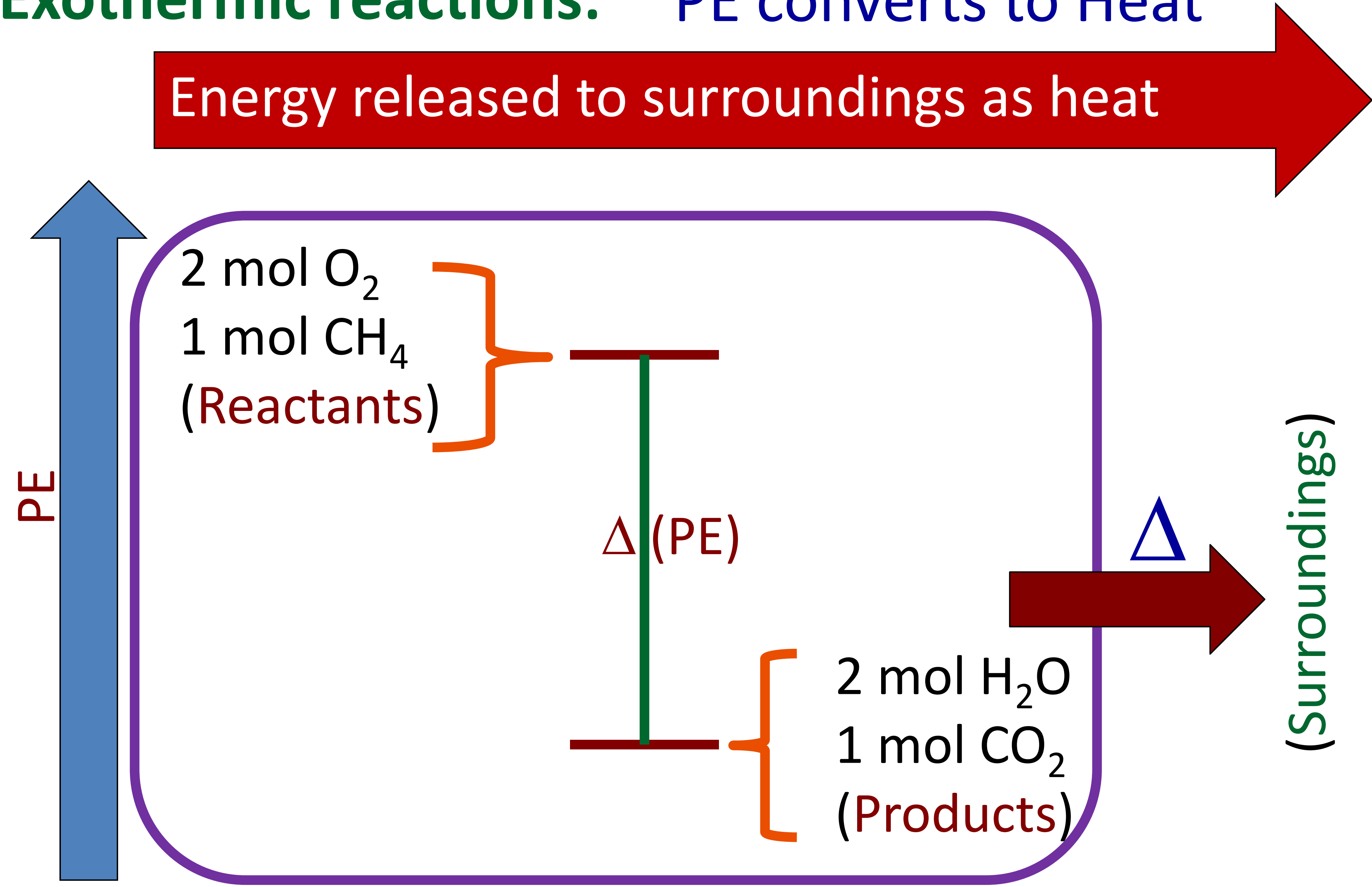
- The combustion of methane: heating homes

$$CH_4(g) + 2O_2(g)$$
$$\rightarrow\ CO_2(g) + 2H_2O\,(g) + \text{energy (heat)}$$

- Exothermic Reactions: reactions result in the evolution of heat.

- Endothermic Reactions: reactions that absorb energy from the surroundings.

Exothermic reactions: PE converts to Heat



Energy released to surroundings as heat

PE

2 mol O_2
1 mol CH_4
(Reactants)

Δ (PE)

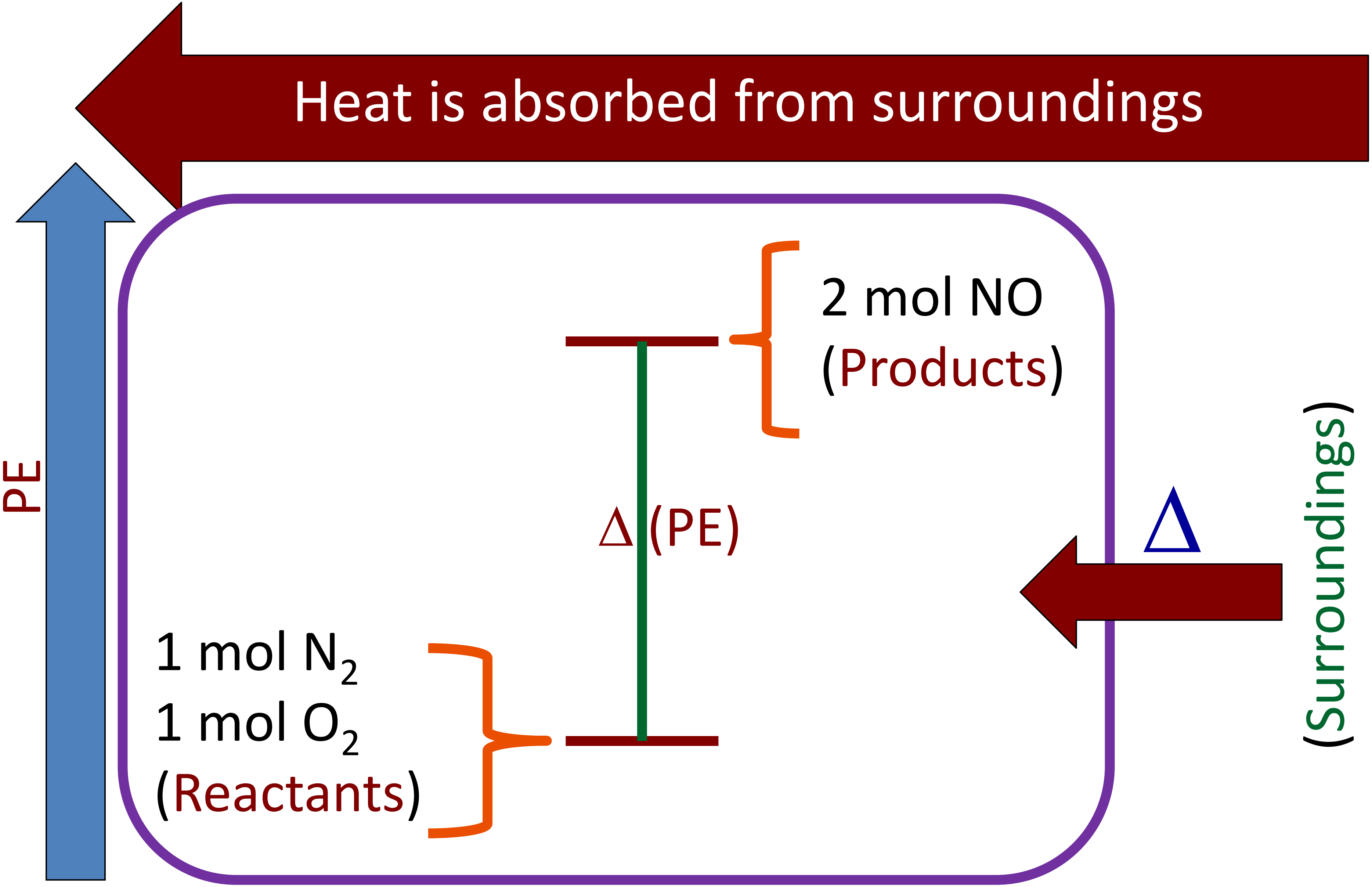
Δ

(Surroundings)

2 mol H_2O
1 mol CO_2
(Products)

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\ (g) + \textbf{energy}\ (\text{heat})$

Endothermic reactions: Heat converts to PE



Heat is absorbed from surroundings

PE

2 mol NO
(Products)

Δ (PE)

1 mol N_2
1 mol O_2
(Reactants)

Δ

(Surroundings)

$N_2(g) + O_2(g) +$ **energy (heat)** → $2NO\ (g)$

The First Law of Thermodynamics

Statements: (Energy is conserved)

- Energy can neither be created, nor destroyed.
- Energy can be converted from one form to another,
- Chemical and/or physical changes are accompanied by changes in energy.

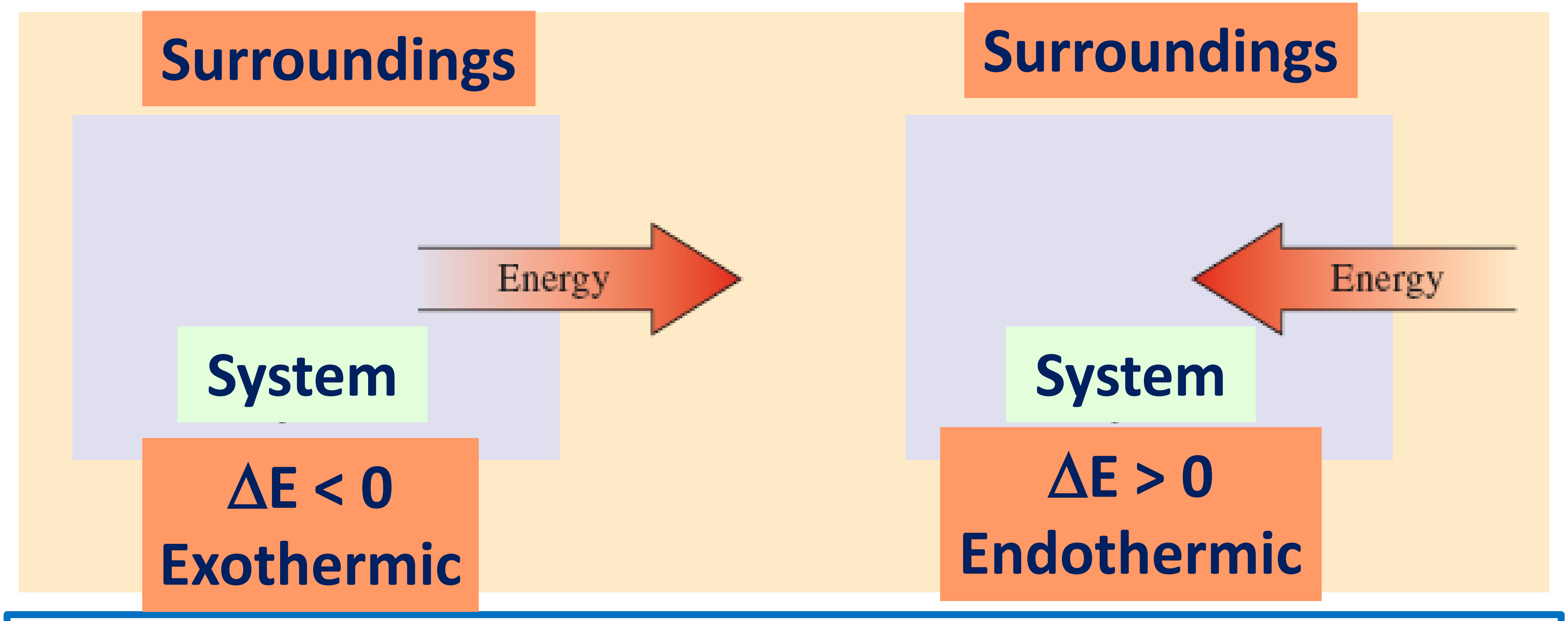
Internal Energy (E): (KE + PE)

- For infinitesimal متناهي الصغر changes in q and w:

$$dE = dq + dw$$

$$\Delta E = E_f - E_i = q + w$$ (closed system)

- For Isolated System: $\Delta E = 0$ if work is excluded



Surroundings

System

$\Delta E < 0$

Exothermic

Surroundings

System

$\Delta E > 0$

Endothermic

- ☐ Heat flows into system (**endothermic**), q is positive
- ☐ Heat flows out of system (**exothermic**), q is negative
- ☐ System does work on surroundings (energy flows out of system), w is negative.
- ☐ Surroundings do work on system (energy flows into system), w is positive.

Exercise

A certain electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings. What is the change in the internal energy of the motor each second?

Solution

Energy is lost from the system as work → w is negative

$w = -15\ \text{kJ}$

Energy is also lost as heat, so → $q = -2\ \text{kJ}$.

Total change in internal energy is therefore:

$$\Delta E = -2\ \text{kJ} - 15\ \text{kJ} = -17\ \text{kJ}$$

Work of compression and expansion

- **Work:** force applied over a distance.

$$w = -F\Delta h = -PA\Delta h = -P\Delta V$$

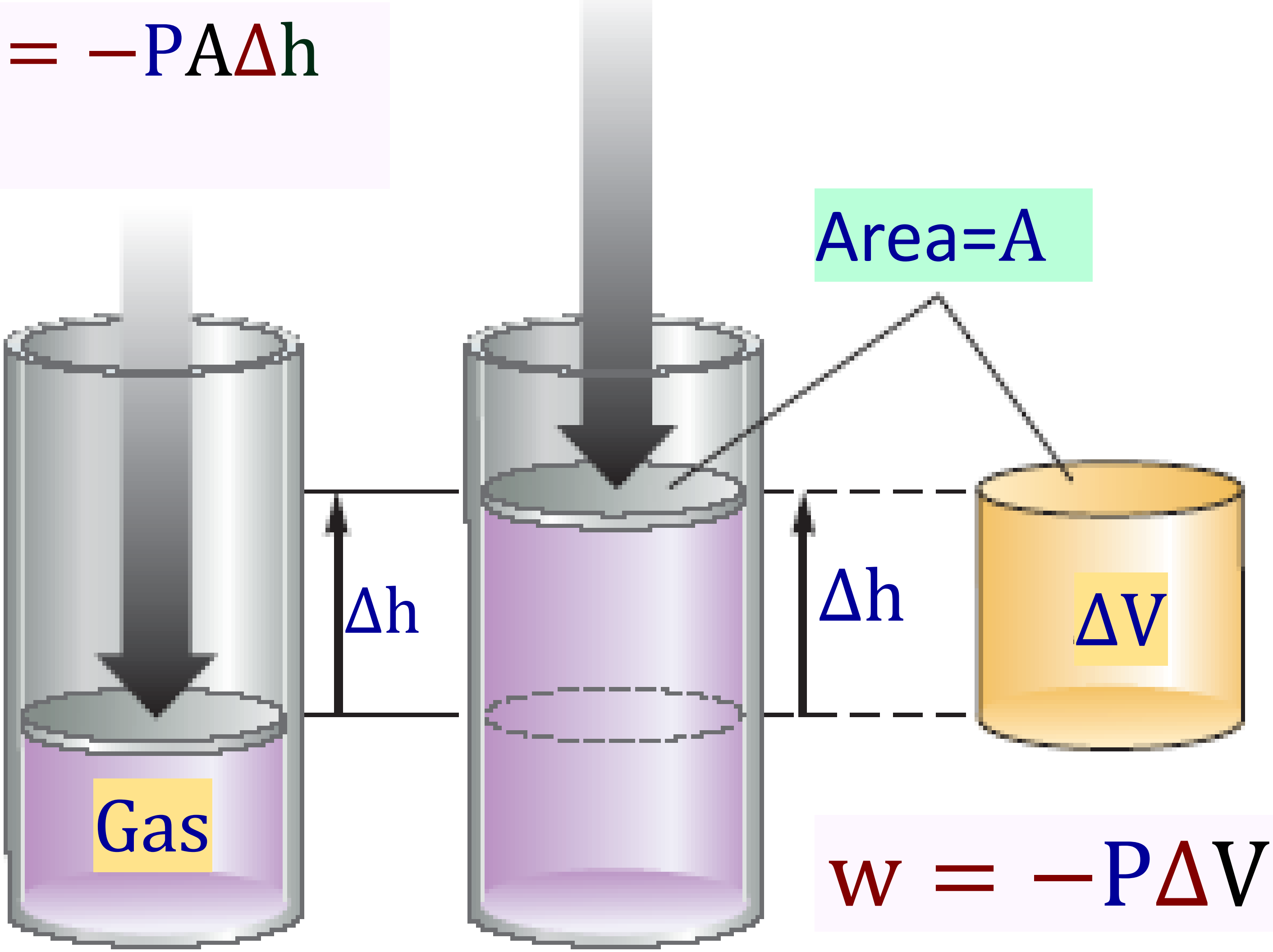
$$P = \frac{F}{A}$$

Expansion

w is $-$ ve,

ΔV is $+$ ve

ΔV and w must have opposite signs



$$w = -P\Delta V$$

Enthalpy (H): Heat change in a system at constant pressure

- For process taking place at constant volume,

$$w = -P\Delta V = 0 \qquad \Delta E = q_V + w = q_V$$

The increase or decrease in E of the system equals the heat absorbed or released, respectively, at constant volume.

- If a process is carried out at a constant pressure,

$$w = -P_{ex}\Delta V = -P\Delta V$$

$$\Delta E = q_P + w = q_P - P\Delta V$$

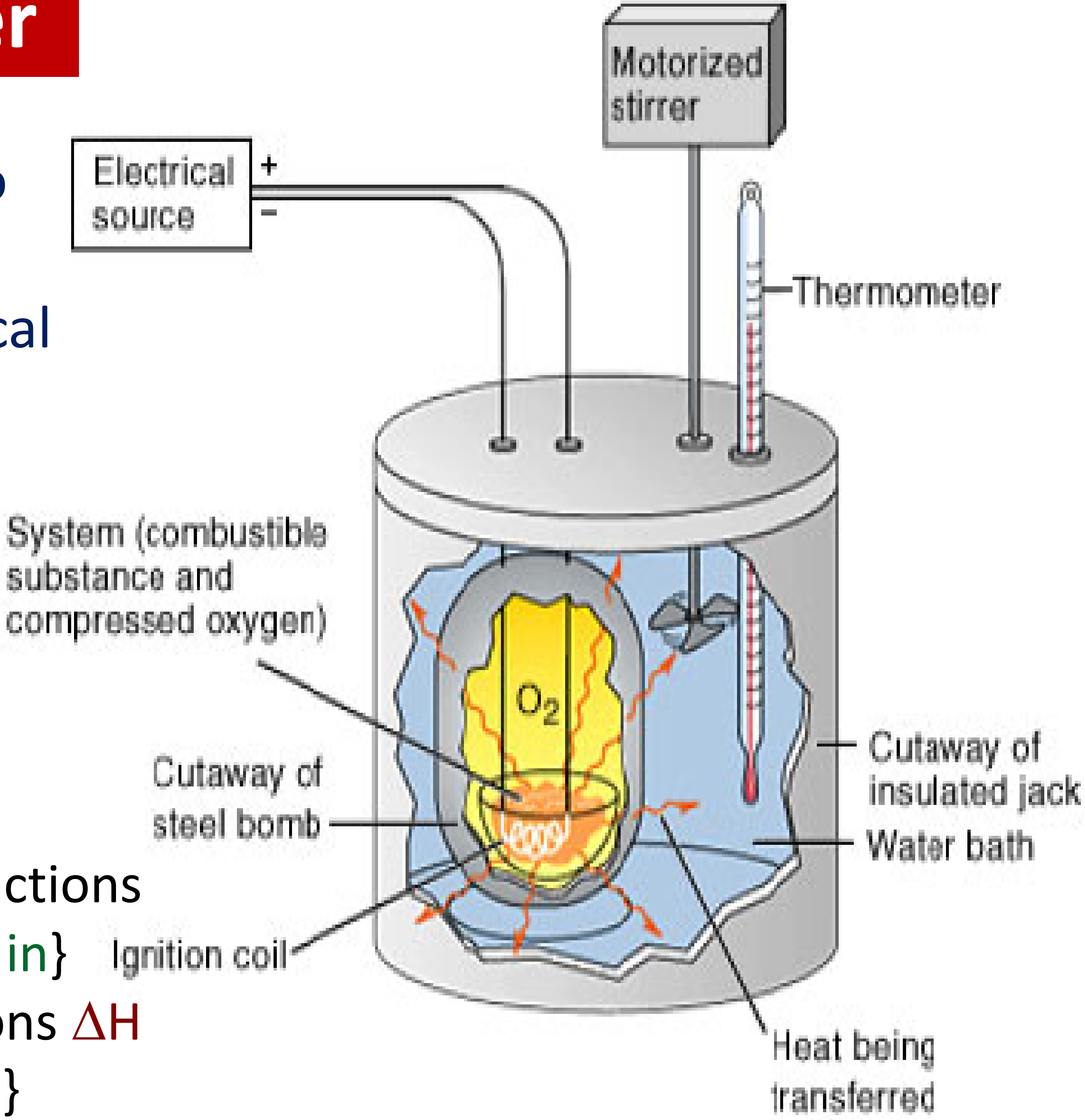
$$E_2 - E_1 = q_P - P\,(V_2 - V_1)$$

$$(E_2 + PV_2) - (E_1 + PV_1) = q_P$$

$$\boxed{\overset{\Delta H}{H_2 - H_1} = q_P}$$

Calorimeter

A device used to measure heat changes in chemical reactions.



Endothermic reactions $\Delta H > 0$ {heat flows in}
Exothermic reactions $\Delta H < 0$ {heat flows out}

Standard Enthalpy Change of reactions, $\Delta_r H^o$

- the change in enthalpy for substances in their standard state (1 bar ≈ 1 atm and 298 K)

Standard molar Enthalpy of formation, ΔH^o_f

- Enthalpy change of a reaction for the formation of one mole of a compound directly from its elements in their standard states (1 bar ≈ 1 atm and 298 K). ΔH^o_f for elements in their standard states are taken as zero

$$6C(s, gr) + 3H_2(g) \rightarrow C_6H_6(l)$$

$$\Delta H_f^0\ (C_6H_6(l)) = 49\ \mathrm{kJ\ mol^{-1}}$$

Enthalpies of Physical Change

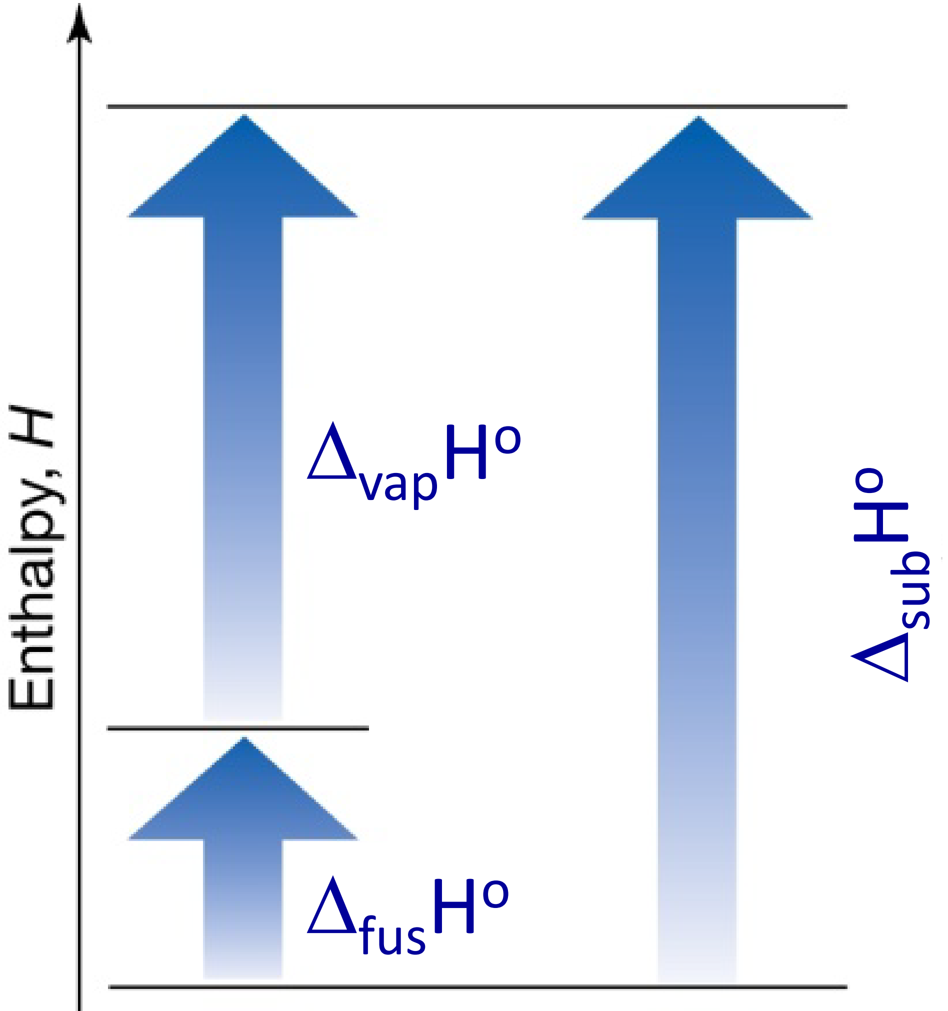
- Changes in state have enthalpies associated with the transition, $\Delta_{trans}H^o$

Liquid-to-Gas, $\Delta_{vap}H^o$

Solid-to-Liquid (fusion): $\Delta_{fus}H^o$

Solid-to-Gas, $\Delta_{sub}H^o$

Reverse of a process involves only change of the sign



Enthalpies of Chemical Change

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r H^o = \sum_{\text{products}} v\Delta H^o_m - \sum_{\text{reac tan ts}} v\Delta H^o_m$$

$$v = \text{stoichiometric coefficient of species}$$

$$\boxed{\Delta_r H^o = \sum_{\text{products}} v\Delta_f H^o_m - \sum_{\text{reac tan ts}} v\Delta_f H^o_m}$$

Exercise

Calculate $\Delta_r H^o$ for this reaction

$$2HN_3\,(l) + 2NO(g) \rightarrow H_2O_2\,(l) + 4\,N_2(g)$$

Knowing that

ΔH^o_f (kJ/mol) for H_2O_2 (l) = –187.78, HN_3 (l) = 264, NO(g) = 90.25.

Solution

ΔH^o_f for $N_2(g)$ =0 (it is an element)

$$\Delta_r H^o = \Delta H_f^0(H_2O_2) + 4\,\Delta H_f^0(N_2) - 2\Delta H_f^0(HN_3)$$
$$- 2\Delta H_f^0(NO) =$$
$$[(-187.78 + 0)] - [(2 \times 264) + (2 \times 90.25)]$$
$$= -896.28\ \mathrm{kJmol^{-1}}$$

Hess's Law

On going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2\,(g) \quad \boldsymbol{\Delta H_1 = ???\ kJ}$$

$$N_2(g) + O_2(g) \rightarrow 2NO\,(g) \quad \Delta H_2 = 180\ kJ$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2\,(g) \quad \Delta H_3 = -112\ kJ$$

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2\,(g) \quad \Delta H_1 = \Delta H_2 + \Delta H_3 = 68\ kJ$$

Factors affecting $\Delta_r H^o$

- quantities of reactants and products.
- physical state of reactants and products

$$H_2O(g) \rightarrow H_2(g) + {}^1/_2\, O_2(g) \quad \Delta H = 241.8\ \text{kJ}$$

$$H_2O(l) \rightarrow H_2(g) + {}^1/_2\, O_2(g) \quad \Delta H = 285.8\ \text{kJ}$$

- If a reaction is reversed, the sign of ΔH is also reversed.
- If the coefficients in a balanced reaction are multiplied by a factor, the value of ΔH is multiplied by the same factor.

Exercise

Consider the complete combustion of ethanol:

$$\mathbf{C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)} \qquad \mathbf{\Delta_rH^o} = ???$$

Knowing that

$$2C(graphite) + 3H_2(g) + {}^{1}/_{2}\,O_2(g) \rightarrow C_2H_5OH(l) \quad \Delta H_f^o = -277.7kJ$$

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_f^o = -282.8\ kJ$$

Reverse the first equation and the sign of ΔH

$$C_2H_5OH(l) \rightarrow 2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H_f^o = 277.7kJ$$

$$C_2H_5OH(l) \rightarrow 2C(\mathrm{graphite}) + 3H_2(g) + {}^{1}/_{2}\,O_2(g) \quad \Delta H_f^o = 277.7\mathrm{kJ}$$

$$C(\mathrm{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_f^o = -393.5\ \mathrm{kJ} \qquad \boxed{\times 2}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_f^o = -282.8\ \mathrm{kJ} \qquad \boxed{\times 3}$$

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta_r H^o = ????$$

$$\mathbf{\Delta_r H^o} = (1)277.7 - (2)393.5 - (3)282.8$$

$$= -21357.7\ \mathrm{kJ}$$

Exercise

How much heat is required to decompose calcium carbonate to calcium oxide and carbon dioxide?

Knowing that ΔH^o_f (kJ/mol) of $CaCO_3$ (s) = – 1207.1, CaO (s) = – 635.5, CO_2 (g) = – 393.5

Solution

$$\mathrm{Ca\,CO_3(s) \rightarrow CaO(s) + CO_2(g)} \quad \Delta_r H^o = ??\ \mathrm{kJ}$$

$$\boxed{\Delta_r H^o = \sum_{\text{products}} v\Delta_f H^o_m - \sum_{\text{reac tan ts}} v\Delta_f H^o_m}$$

$$\Delta_r H^o = (-635.5 - 393.5) - (-1207.1) = +178.1\ \mathrm{kJ}$$

Alternatively

$$\mathrm{Ca\,(s) + C\,(s) + {}^{3}\!/_{2}\,O_2\,(g) \rightarrow Ca\,CO_3(s)} \quad \Delta H_f^o = -1207.1\ \mathrm{kJ}$$

$$\mathrm{Ca\,(s) + {}^{1}\!/_{2}\,O_2(g) \rightarrow CaO(s)} \quad \Delta H_f^o = -635.5\ \mathrm{kJ}$$

$$\mathrm{C\,(s) + O_2(g) \rightarrow CO_2(g)} \quad \Delta H_f^o = -393.5\ \mathrm{kJ}$$

$$\mathrm{Ca\,CO_3(s) \rightarrow CaO(s) + CO_2(g)} \quad \Delta_r H^o = ??\ \mathrm{kJ}$$

$$\mathrm{Ca\,CO_3(s) \rightarrow \cancel{Ca\,(s)} + \cancel{C\,(s)} + \cancel{{}^{3}\!/_{2}\,O_2\,(g)}} \quad \Delta H_f^o = +1207.1\ \mathrm{kJ}$$

$$\mathrm{\cancel{Ca\,(s)} + \cancel{{}^{1}\!/_{2}\,O_2(g)} \rightarrow CaO(s)} \quad \Delta H_f^o = -635.5\ \mathrm{kJ}$$

$$\mathrm{\cancel{C\,(s)} + \cancel{O_2(g)} \rightarrow CO_2(g)} \quad \Delta H_f^o = -393.5\ \mathrm{kJ}$$

$$\Delta_r H^o = (1207.1) + (-635.5) + (-393.5) = +178.1\ \mathrm{kJ}$$

Exercise

Calculate the enthalpy change of formation of methane from solid carbon and hydrogen gas using

$$C\ (s) + O_2(g) \rightarrow CO_2(g)\ \ \Delta H_f^o = -393.5\ kJ$$

$$H_2(g) + {}^1/_2\, O_2\ (g) \rightarrow H_2O(l)\ \ \Delta H_f^o = -285.8\ kJ$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ \Delta H_r^o = -890.3\ kJ$$

Solution

$$C\ (s) + 2H_2(g) \rightarrow CH_4(g) \Delta_r H^o = ???\ kJ$$

$$\mathrm{C\,(s) + \cancel{O_2}(g) \rightarrow \cancel{CO_2}(g)} \quad \Delta H_f^o = -393.5\ \mathrm{kJ}$$

$$\mathrm{2H_2(g) + \cancel{O_2}\,(g) \rightarrow \cancel{2H_2O}(l)} \quad \Delta H_f^o = -571.6\ \mathrm{kJ}$$

$$\mathrm{\cancel{CO_2}(g) + \cancel{2H_2O}(l) \rightarrow CH_4(g) + \cancel{2O_2}(g)} \, \Delta H_r^o = 890.3\ \mathrm{kJ}$$

$$\mathrm{C\,(s) + 2H_2(g) \rightarrow CH_4(g)} \, \Delta_r H^o = ???\ \mathrm{kJ}$$

$$\Delta_r H^o = (-393.5) + (-571.6) + (890.3) = -74.8\ \mathrm{kJ}$$

Significance of knowing $\Delta_r H^o$

- Identifying the direction of heat transfer.
  - At room temperature, most exothermic reactions are product-favored.
- The heat of combustion of fuels can be calculated
- Taking precautions to prevent exothermic reactions from over-heating and possible damages when reactions are carried out on a large scale.