THERMOCHEMISTRY

Introduction….

- This section explores the relationship between chemistry and energy.

Thermochemistry is a branch of Thermodynamics, a scientific field that comprises the relationships between heat, work, and other forms of energy resulting from different chemical and physical processes. Thermochemistry itself is defined as energy changes when a chemical reaction takes place.

Energy is the capacity to supply heat or do work. Thermochemistry is concerned with the energy (usually in terms of heat) absorbed or released during the chemical or physical changes.

- **Energy** is the ability to do work or transfer heat.
- **Thermodynamics** is the study of energy and its transformations.
- **Thermochemistry** is the study of chemical reactions and the energy changes that involve heat.

Energy Units

- **Joule**: SI unit for energy, $1J = kgm^2/s^2$
- **Calorie**: abbreviated cal, originally defined as the amount of energy required to raise the temperature of 1 g of water by 1°C. 1 cal = 4.184 J

Heat is a form of energy (which cannot be created or destroyed). A chemical reaction cannot create or destroy energy, it just changes it from one form to another.

All substances have a type of chemical potential energy stored in them. This is called **enthalpy**.
The actual definition of enthalpy is *the total energy contained in a system*.

it's   easiest to think of enthalpy as mainly **chemical potential energy** stored in a substance.
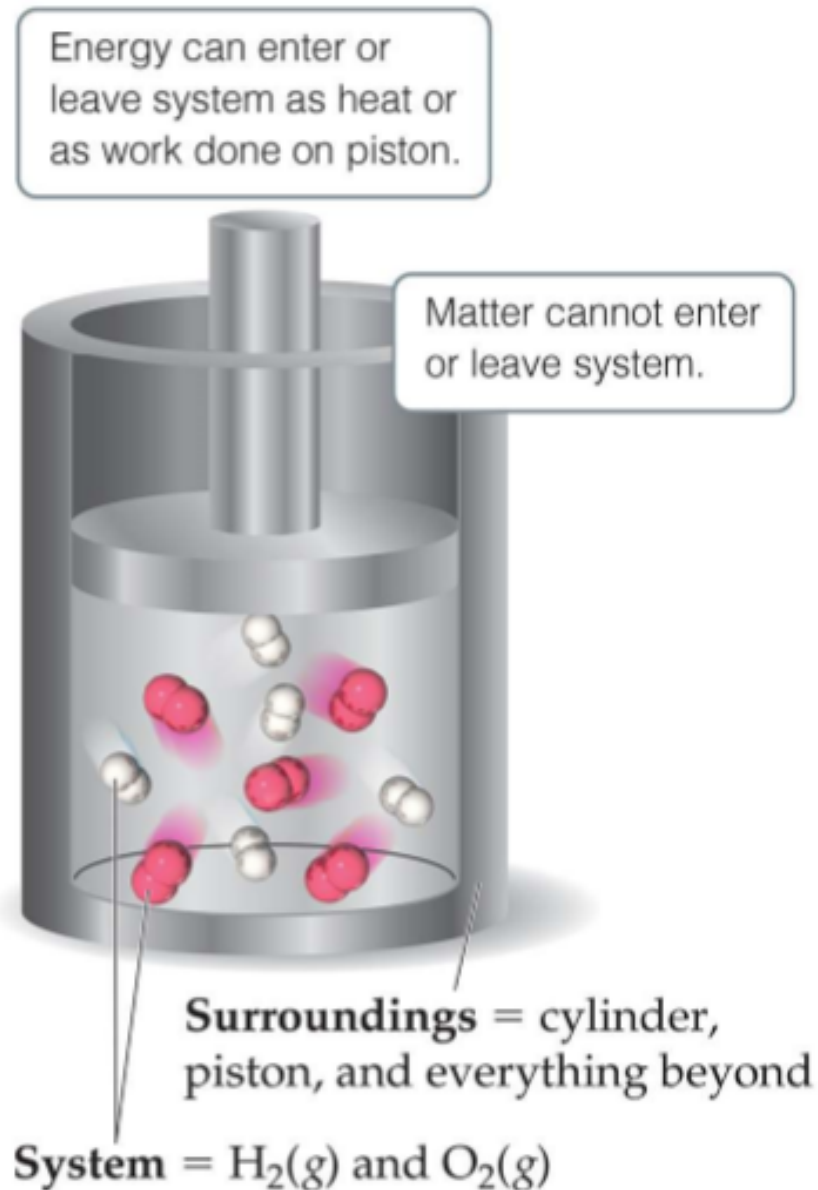
The symbol for **enthalpy** is "H" (historically, enthalpy used to be called "Heat Content")
The **change in enthalpy** during a reaction is called ΔH. (The symbol Δ (*delta*) means "change in")

There are 3 general types of systems which are the following:

1. **Open System** – involves the exchange of mass and energy/heat with its surroundings;
2. **Closed System** – involves the transfer of energy/hear but not mass;
3. **Isolated System** – does not allow the transfer of either energy/heat or mass.

System and Surroundings

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

Matter cannot enter or leave system.

Surroundings = cylinder, piston, and everything beyond

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

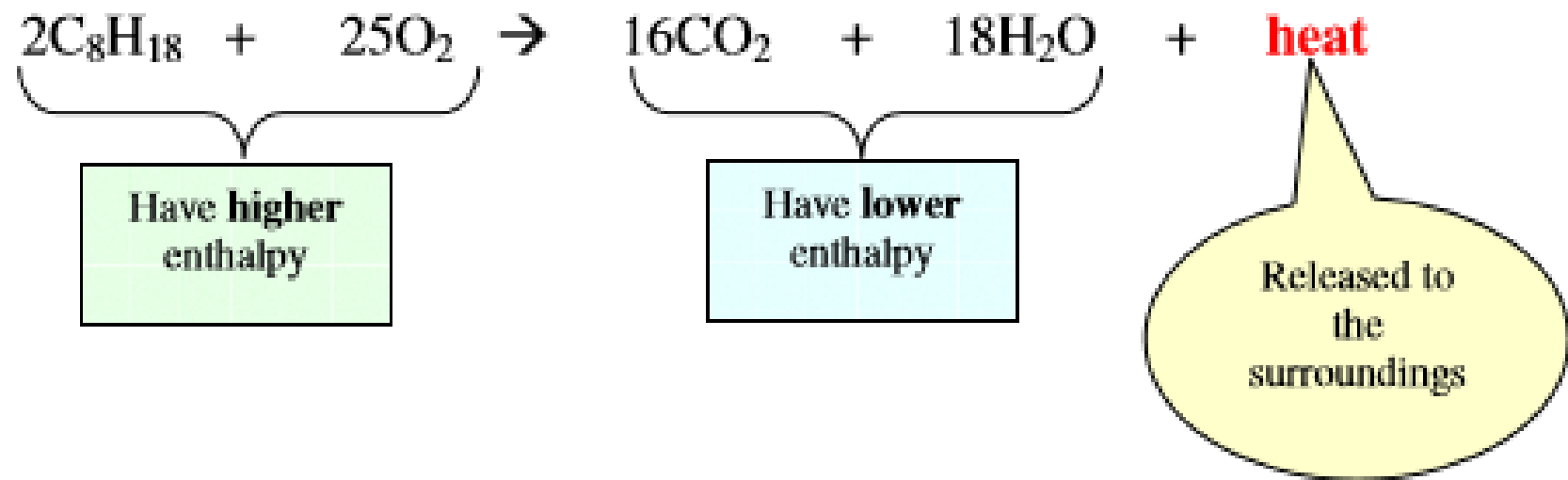- The **system** includes the molecules of interest.
- The **surroundings** are everything else.
- In thermochemistry we study the exchange of energy between the system and surroundings.
- *open system* – matter and energy can be exchanged with the surroundings
- *closed system* - exchange energy--but not matter--with the surroundings.
- *isolated system* - neither matter nor energy may be exchanged with surroundings.
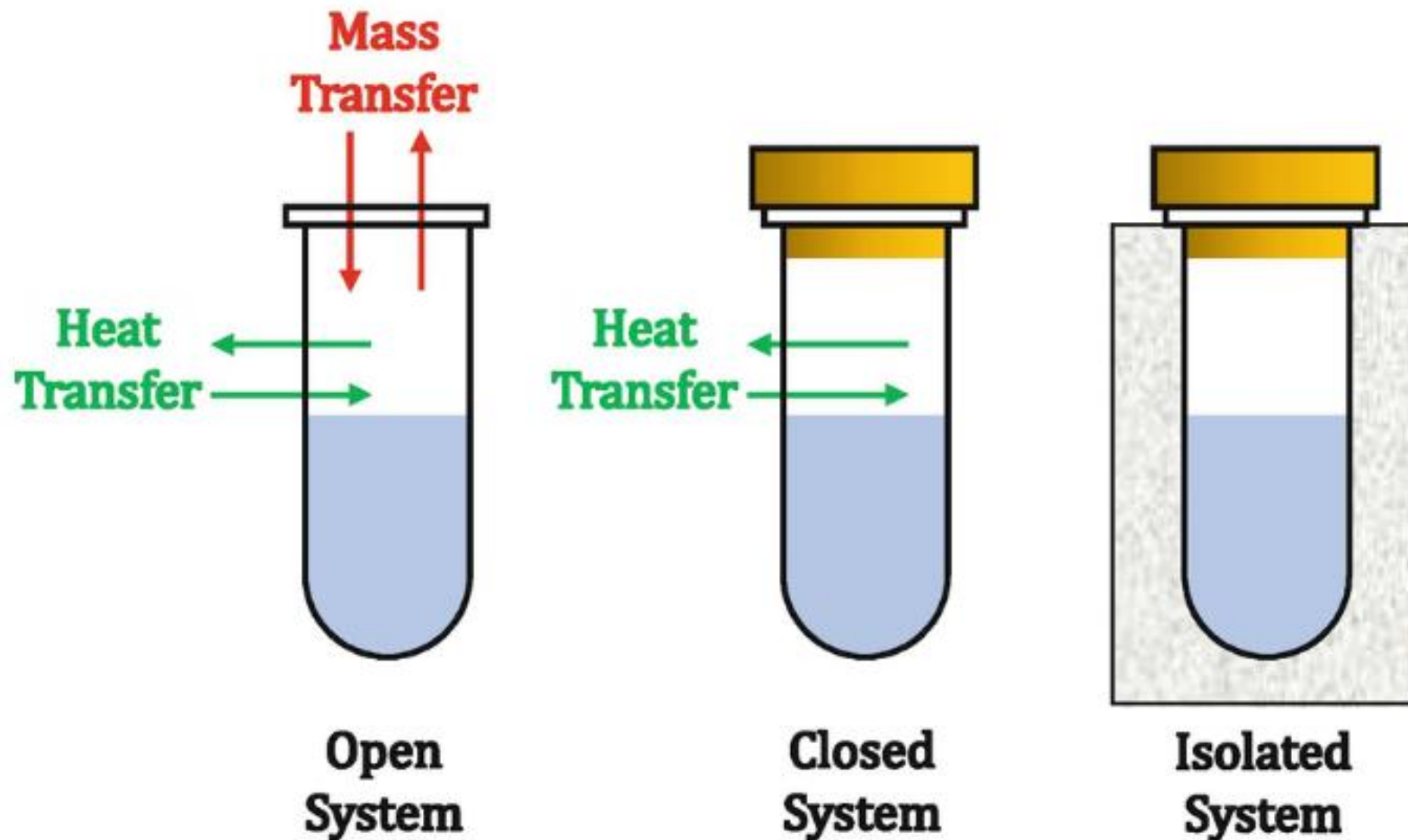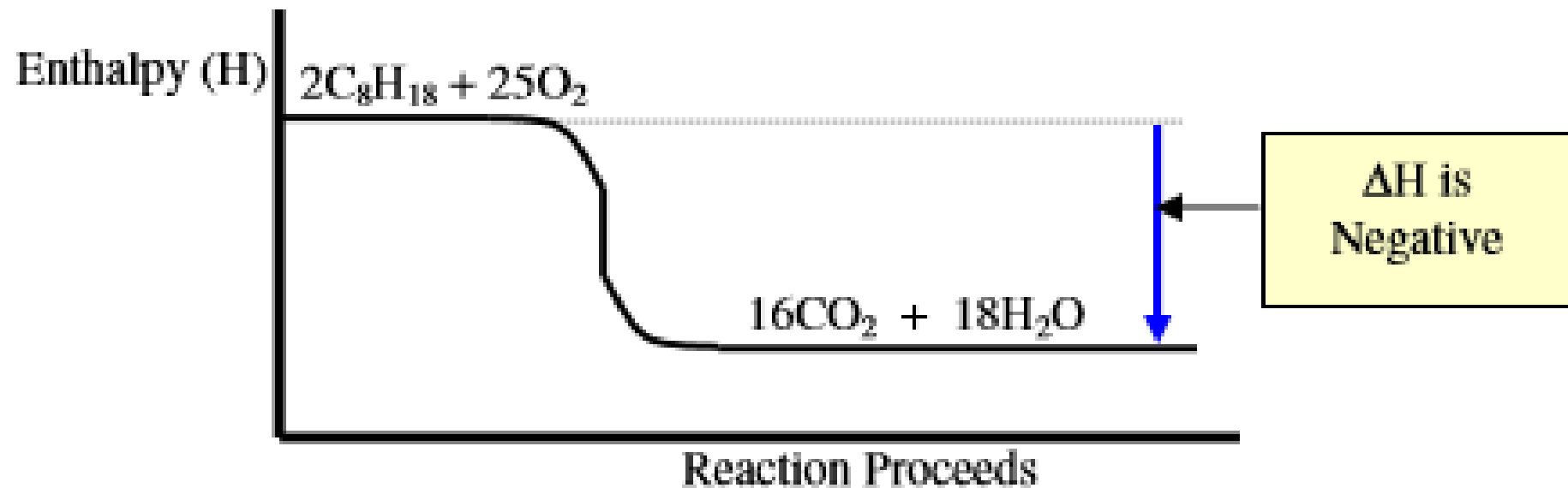
Thermochemistry for A-Level Chemistry focuses on the closed system, so we assume that there is no mass loss during the reaction.

An **exothermic** chemical reaction converts the **enthalpy** stored in a substance into **heat**, which is released to the surroundings. For example, when gasoline burns, the enthalpy in the gasoline (mainly C_8H_{18}) is converted into heat:

$$2C_8H_{18} \;+\; 25O_2 \;\rightarrow\; 16CO_2 \;+\; 18H_2O \;+\; \textbf{heat}$$

Have **higher** enthalpy

Have **lower** enthalpy

Released to the surroundings

An enthalpy diagram for an **exothermic** reaction:

So, to summarize, in an **exothermic** reaction:

> ➤ ΔH is negative
> ➤ Products are **lower** than Reactants on the Enthalpy Diagram
> ➤ Heat is released to the surroundings

There are **two ways** to show that a reaction is **exothermic**:

1. A "heat term" is written on the right side of a chemical equation to show that heat is given off or produced. This can be the word "heat" or an actual amount of heat in kJ:

   eg.) $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O + $ **5076 kJ**

   Heat term is on the **right** side of the equation.

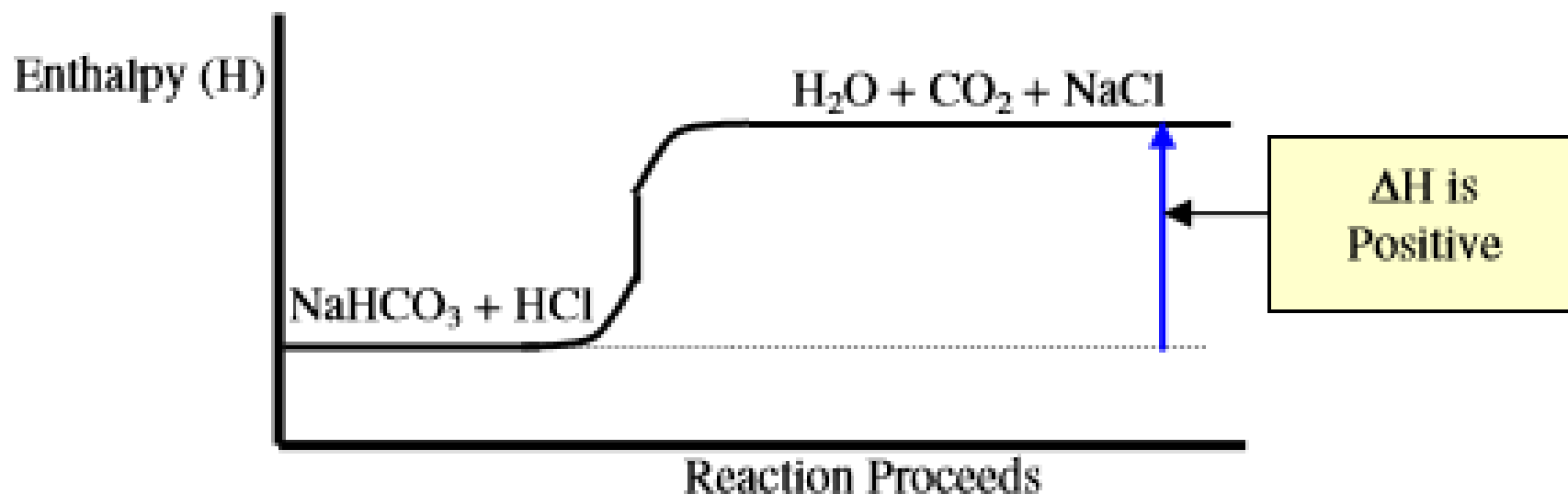2. An equation is written and the **ΔH** is written **beside** it (no "+" sign between):

   eg.) $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$ **ΔH = -5076 kJ**

   Notice that for an **exothermic** reaction, the ΔH is NEGATIVE!

For an **endothermic** reaction:

Eg.) $NaHCO_3$ + HCl + heat → H_2O + CO_2 + NaCl

Heat is **absorbed** from the surroundings and converted into **enthalpy**.

Here is an enthalpy graph for an **endothermic** reaction:

In an **endothermic** reaction, the "heat term" would be written on the LEFT side, or the ΔH written beside the equation would be **Positive**:

$$2C + 2H_2 + 52.3\ kJ \rightarrow C_2H_4$$

Heat term is on the **left** side of the equation.

$$2C + 2H_2 \rightarrow C_2H_4 \qquad \Delta H = +52.3\ kJ$$

Notice that for an **endothermic** reaction, the ΔH is POSITIVE!

ΔH and Moles

In a chemical equation, the coefficients can stand for "molecules" or for "moles".

1 mole = 6.02×10^{23}

The mole is a conversion to count a substance by weighing it. 1 mole is equal to 6.02×10^{23} representative particles of a substance. Depending on the substance the representative particles may be atoms, molecules, formula unit.

For an Element: 1 mole = 6.02×10^{23}
      Ionic Compound: 1 mole = 6.02×10^{23} formula units
      Covalent Compound: 1 mole = 6.02×10^{23} molecules

Molar mass

The molar mass of a substance is the mass of one mole of that substance. To calculate the molar mass of a substance you must add the individual atomic mass of all the elements that make up that compound. The unit for a molar mass is in grams/mole.

Example:

$C_6H_{12}O_6$

      Carbon: 6 x 12 = 72

      Hydrogen: 12 x 1 = 12

      Oxygen: 6 x 16 = 86

72+12+96= 180 grams/mole

$Fe_3(PO_4)_2$

      Iron: 3 x 55.85 = 167.55

      Phosphorus: 2 x 31 = 62

      Oxygen: 8 x 16 = 128

167.55 + 62 + 128 = 357.55 grams/ mole

The Elements, sorted by Atomic Mass

Atomic Number	Symbol	Name	Atomic Weight (amu, g/mol)
1	H	Hydrogen	1.00797
2	He	Helium	4.00260
3	Li	Lithium	6.941
4	Be	Beryllium	9.01218
5	B	Boron	10.81
6	C	Carbon	12.011
7	N	Nitrogen	14.0067
8	O	Oxygen	15.9994
9	F	Fluorine	18.998403
10	Ne	Neon	20.179
11	Na	Sodium	22.98977
12	Mg	Magnesium	24.305
13	Al	Aluminum	26.98154
14	Si	Silicon	28.0855
15	P	Phosphorus	30.97376
16	S	Sulfur	32.06

17	Cl	Chlorine	35.453
19	K	Potassium	39.0983
18	Ar	Argon	39.948
20	Ca	Calcium	40.08
21	Sc	Scandium	44.9559
22	Ti	Titanium	47.90
23	V	Vanadium	50.9415
24	Cr	Chromium	51.996
25	Mn	Manganese	54.9380
26	Fe	Iron	55.847
28	Ni	Nickel	58.70
27	Co	Cobalt	58.9332
29	Cu	Copper	63.546
30	Zn	Zinc	65.38
31	Ga	Gallium	69.72
32	Ge	Germanium	72.59
33	As	Arsenic	74.9216
34	Se	Selenium	78.96
35	Br	Bromine	79.904

If an equation contains a heat term or ΔH is shown, coefficients ALWAYS stand for moles.

For example, given the equation:

$$N_2 \; + \; 3H_2 \; \rightarrow \; 2NH_3 \; + \; 46.2 \text{ kJ}$$

It means that:
- If **1 mole** of N_2 is used up, 46.2 kJ of heat are released
- If **3 moles** of H_2 are used up, 46.2 kJ of heat are released
- If **2 moles** of NH_3 are produced, 46.2 kJ of heat are released

Example Question:
Find the amount of heat released if 5.0 moles of H_2 are consumed when making ammonia, given the reaction: $N_2 + 3H_2 \rightarrow 2NH_3 + 46.2$ kJ

Solution:

$$5.0 \text{ mol } H_2 \ \times \ \frac{46.2 kJ}{3 mol H_2} \ = \ 77 \text{ kJ}$$

Another Example:
Find the amount of heat released during the formation of 14.6 moles of NH_3, given the reaction:
$N_2 + 3H_2 \rightarrow 2NH_3 + 46.2$ kJ

Solution:

$$14.6 \text{ mol } NH_3 \ \times \ \frac{46.2 kJ}{2 mol NH_3} \ = \ 337 \text{ kJ}$$

Internal Energy

The internal energy of a system is the sum of all kinetic and potential energies of all components of the system; we call it *E*.

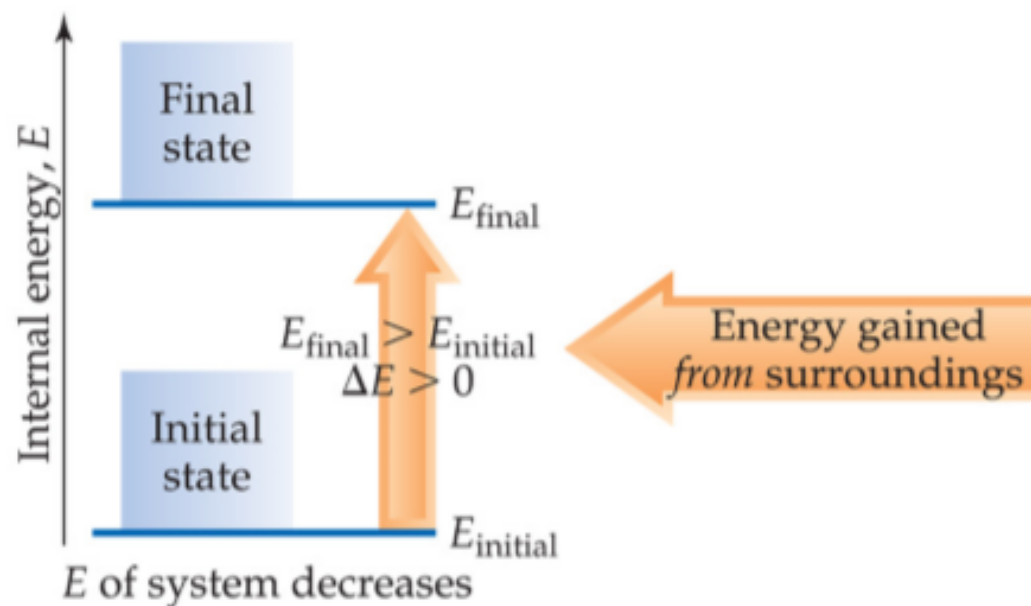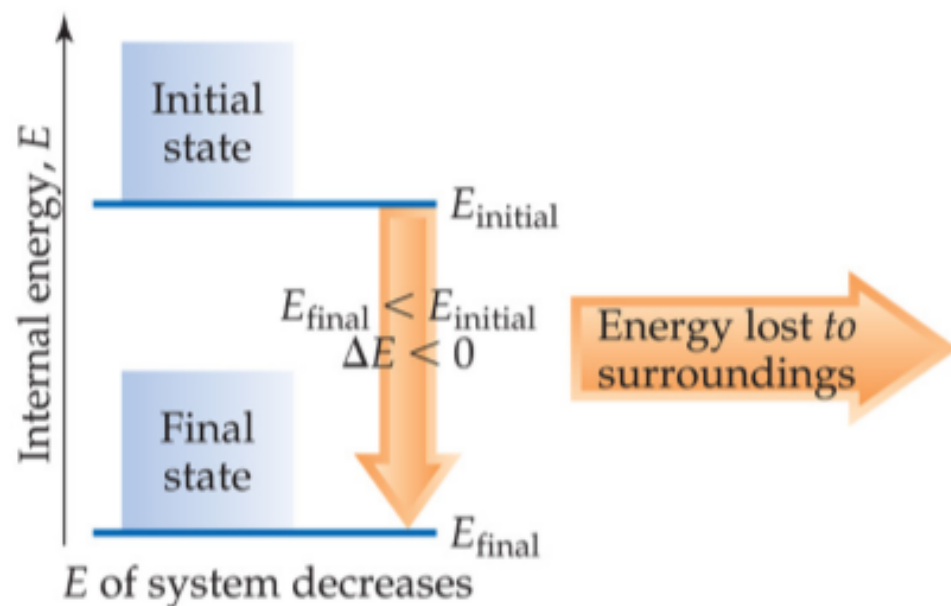$$E_{internal,total} = E_{KE} + E_{PE} + E_{electrons} + E_{nuclei} + \ldots\ldots$$

Almost impossible to calculate total internal energy
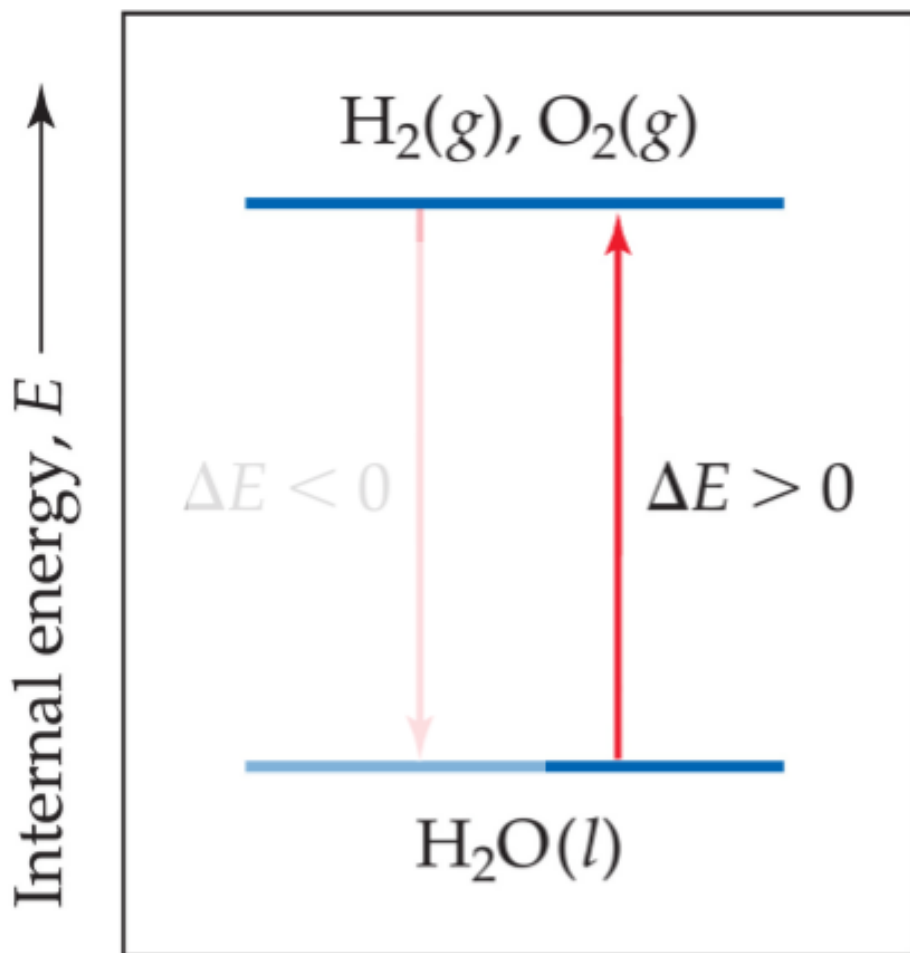
Instead we always look at the **change** in energy (ΔE).

Internal Energy

By definition, the change in internal energy, ΔE, is the final energy of the system minus the initial energy of the system:
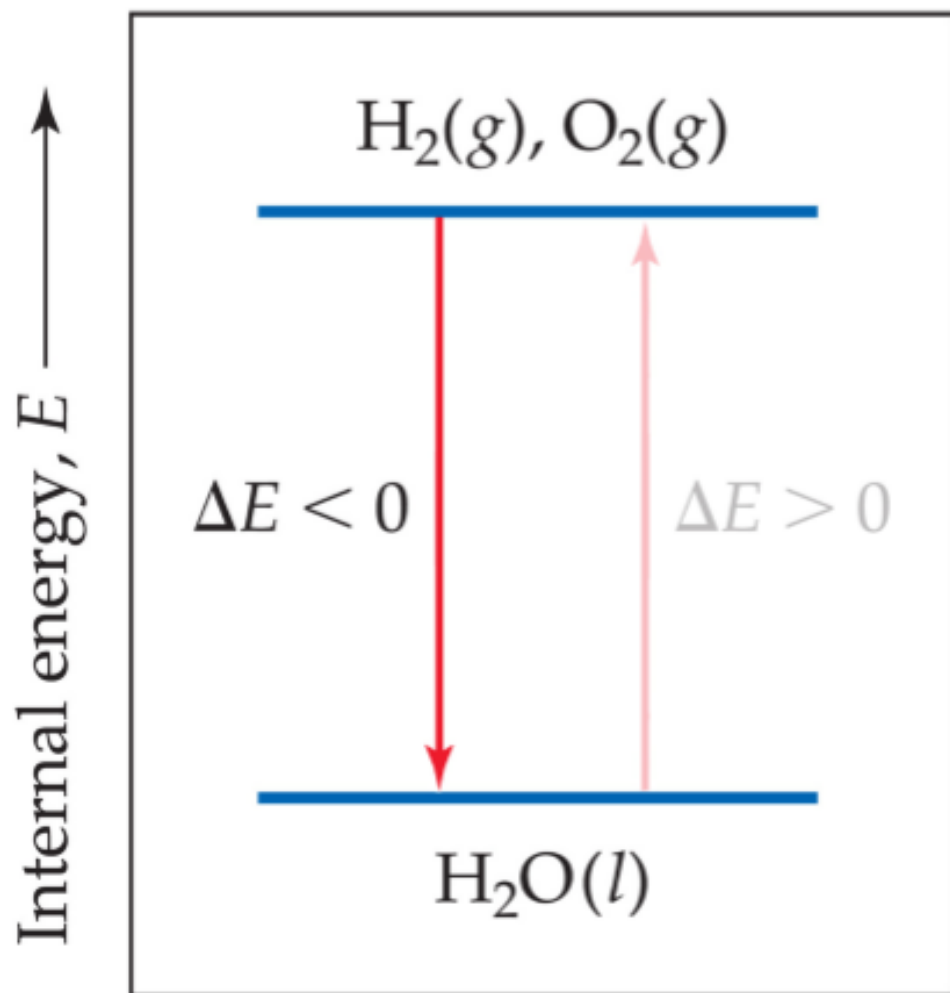
$$\Delta E = E_{final} - E_{initial}$$

Changes in Internal Energy

$$H_2(g), O_2(g)$$

$$\Delta E < 0 \qquad \Delta E > 0$$

$$H_2O(l)$$

Internal energy, E

- If $\Delta E > 0$, $E_{final} > E_{initial}$
  - ➤ Therefore, the system *absorbed* energy from the surroundings.
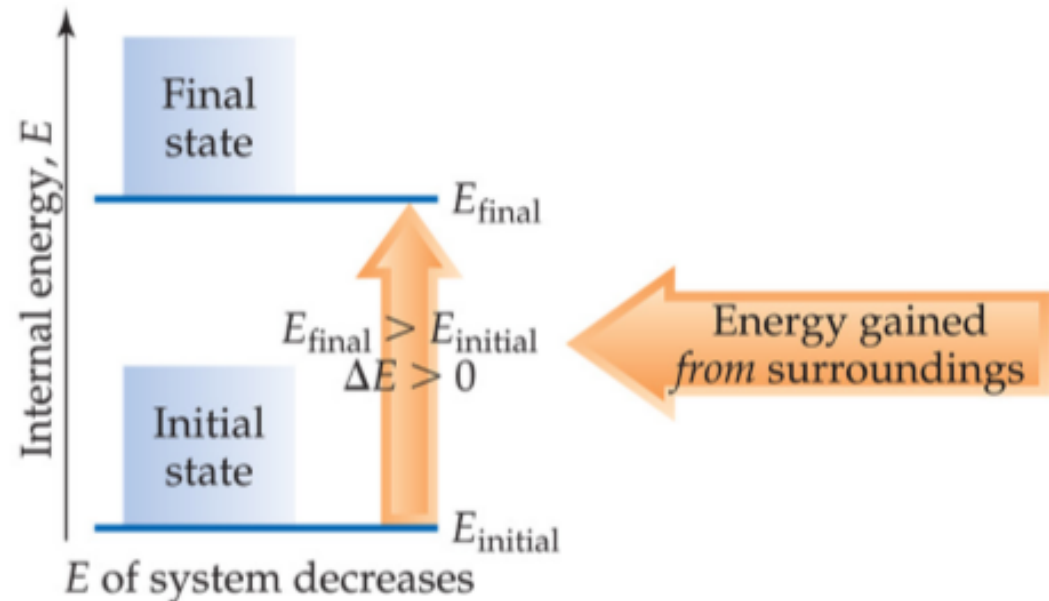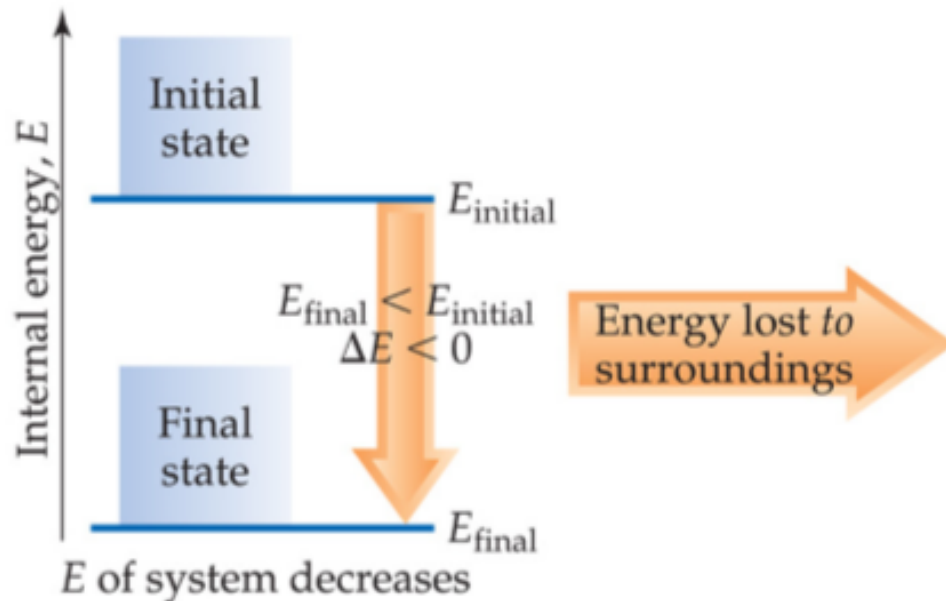
Changes in Internal Energy

- If $\Delta E < 0$, $E_{final} < E_{initial}$
  - ➢ Therefore, the system *released* energy to the surroundings.

First Law of Thermodynamics

- Energy is conserved.
- In other words, the total energy of the universe is a constant; $\Delta E_{System} = -\Lambda E_{surroundings}$

Internal energy, E

Initial state

$E_{initial}$

$E_{final} < E_{initial}$
$\Delta E < 0$

Energy lost *to* surroundings

Final state

E_{final}

E of system decreases

Internal energy, E

Final state

E_{final}

$E_{final} > E_{initial}$
$\Delta E > 0$

Energy gained *from* surroundings

Initial state

$E_{initial}$

E of system decreases

Internal Energy of a system = the sum of the kinetic and potential energies of all the "particles" in the system (the reaction).

↳ this internal energy (E) can be <u>changed</u> by a flow of work (w), heat (q), or both:

$$\Delta E = q + w$$

(a) if the reaction is endothermic, heat flows into the system and thus heat (q) is (+) $\Rightarrow$ $\boxed{q > 0}$.

(b) if the reaction is exothermic, heat flows out of the system and thus heat (q) is (-) $\Rightarrow$ $\boxed{q < 0}$.

(c) if the reaction (system) does work (w) on the surroundings, energy flows out of the system, so work (w) is (-) $\Rightarrow$ $\boxed{w < 0}$.

(d) if the surroundings do work (w) on the system, energy flows into the system, so work (w) is (+) $\Rightarrow$ $\boxed{w > 0}$.

Changes in Internal Energy

System

Heat $q > 0$

Surroundings

Work $w > 0$

$\Delta E > 0$
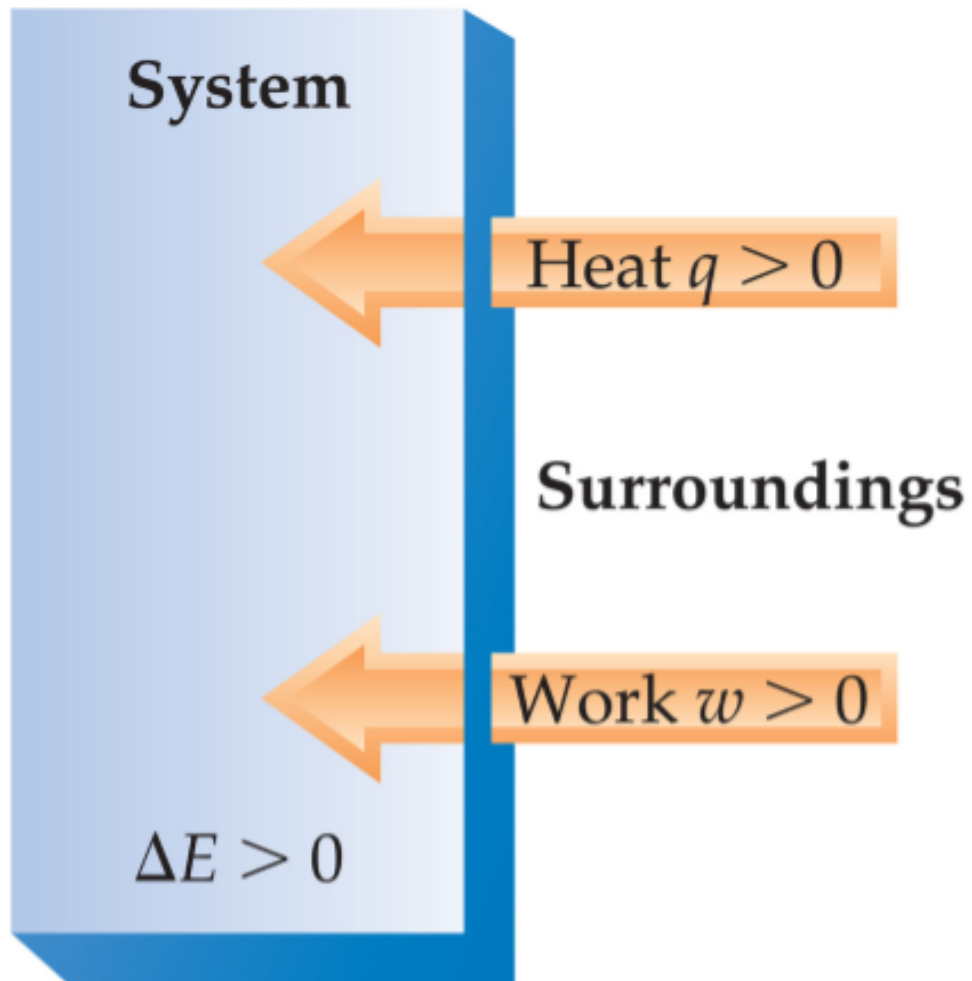
- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).

- **That is, $\Delta E = q + w$.**

ΔE, q, w, and Their Signs
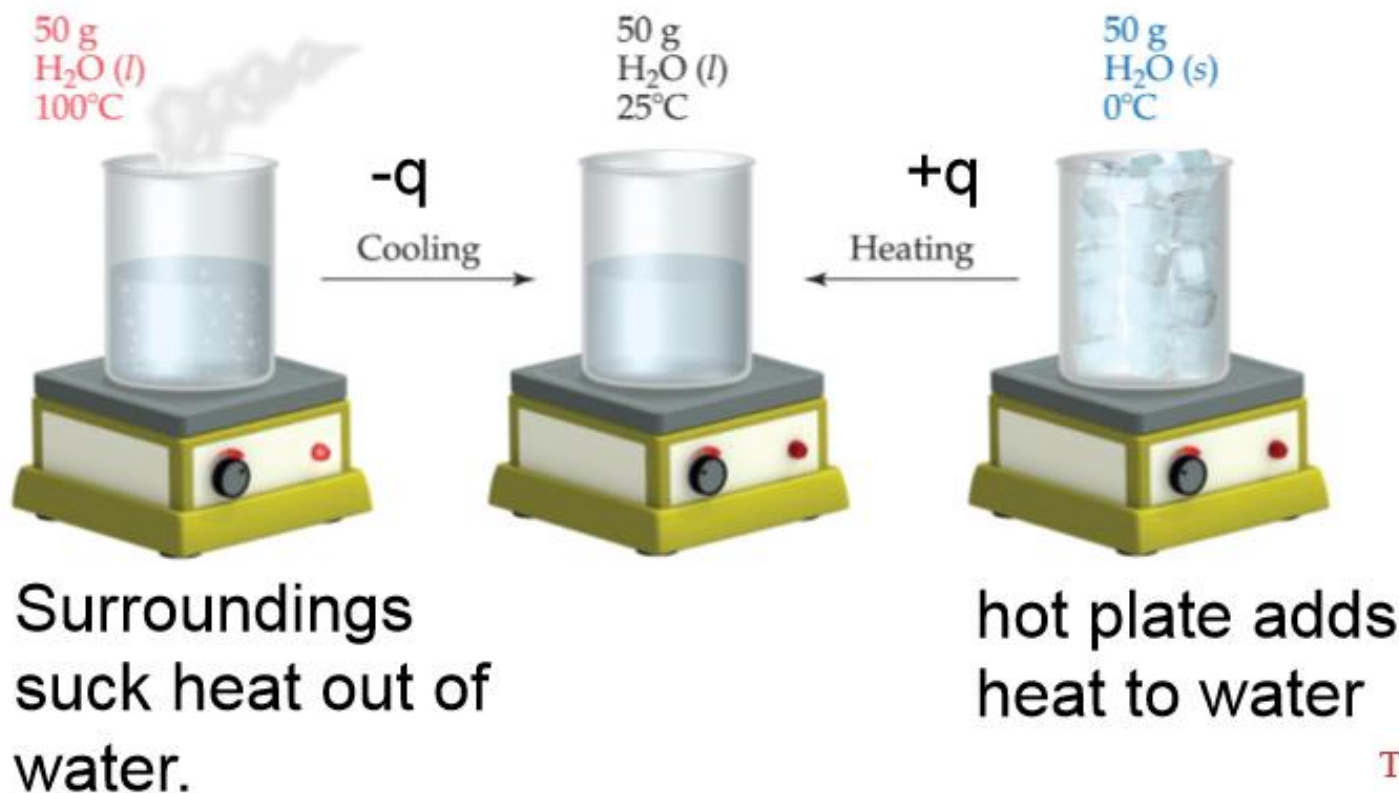
For q + means system *gains* heat   − means system *loses* heat
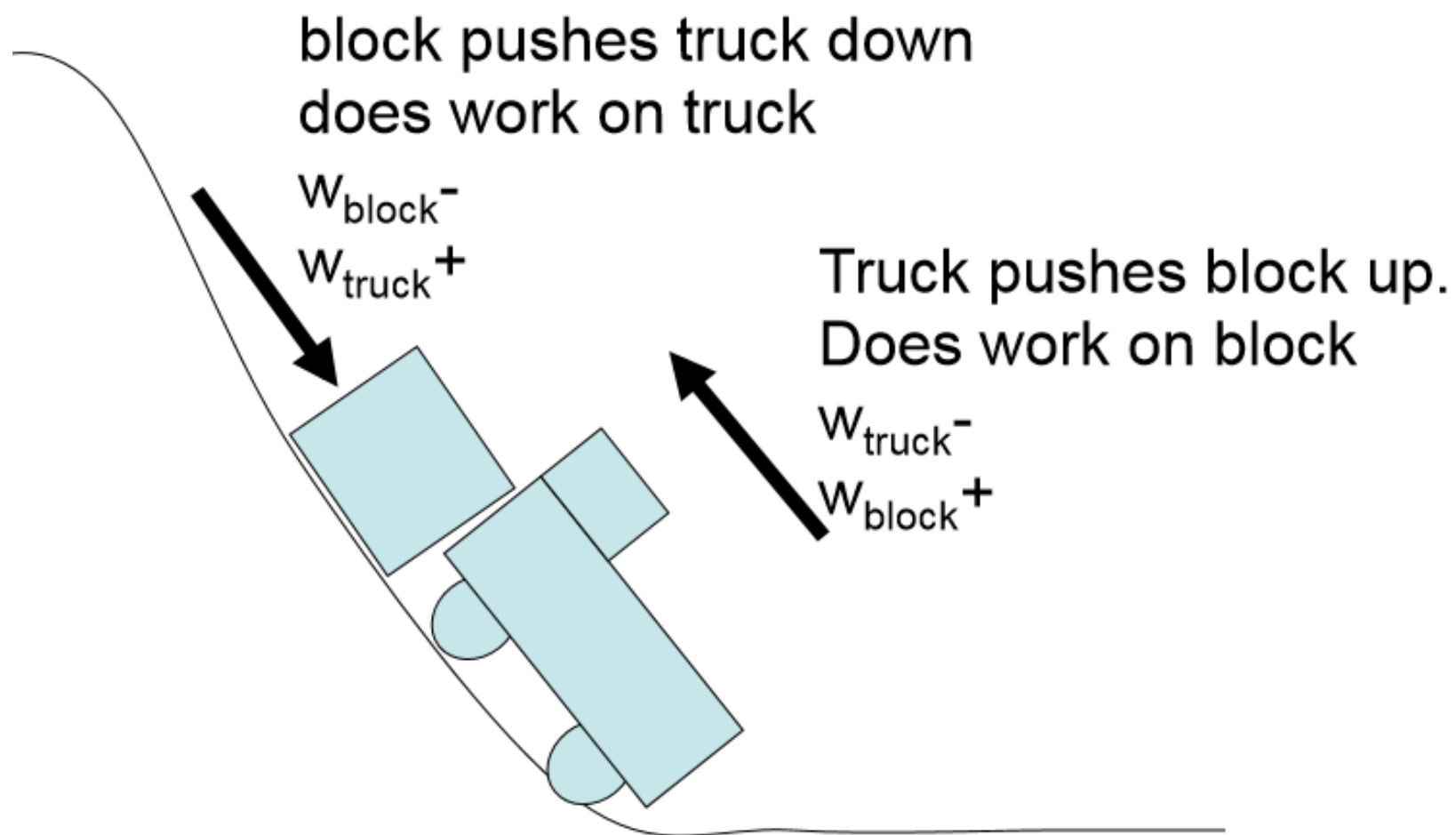
For w + means work done *on* system   − means work done *by* system

For ΔE + means *net gain* of energy by system − means *net loss* of energy by system

50 g
H_2O (*l*)
100°C

50 g
H_2O (*l*)
25°C

50 g
H_2O (*s*)
0°C

-q

Cooling

+q

Heating

Surroundings
suck heat out of
water.

hot plate adds
heat to water

Thermochemistry

Sign of work

block pushes truck down
does work on truck

$W_{block}-$
$W_{truck}+$

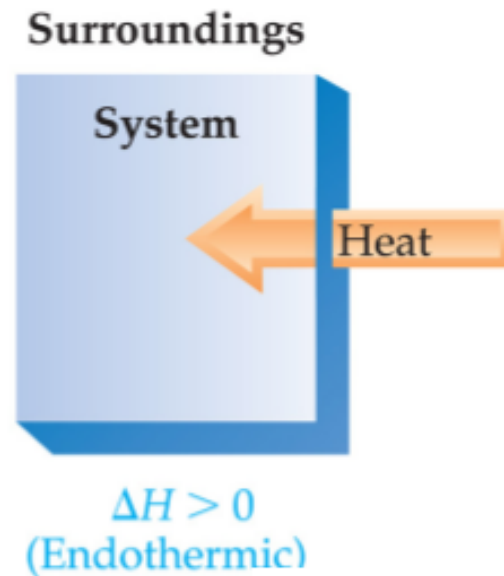Truck pushes block up.
Does work on block

$W_{truck}-$
$W_{block}+$

Exchange of Heat between System and Surroundings

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

Surroundings

System

Heat

$\Delta H > 0$
(Endothermic)

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 to the surroundings, the process is **exothermic.**

Surroundings

System

Heat

$\Delta H < 0$
(Exothermic)
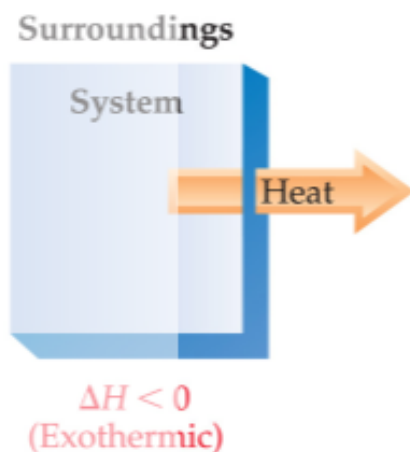
ex: Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1400 J of work is done on the system.

$$\Delta E = q + w \implies \Delta E = +15.6 \text{ kJ} + (+1400 \text{ J})$$

$$\Delta E = +15.6 \text{ kJ} + (1.400 \text{ kJ})$$

$$\boxed{\Delta E = +17.0 \text{ kJ}}$$

"the system (the reaction) is <u>gaining</u> 17.0 kJ of energy."

Calorimetry

- This is the science of measuring heat.

calorimetry is based on observing the temperature change (ΔT) when a substance absorbs or gives off heat (q).

— some substances require <u>a lot</u> of <u>heat energy (q)</u>
to raise their temperature | by $1°C$ or $1K$.

          └→ these substances make
             good <u>coolants</u> (<u>ex</u>: H_2O)

— other substances <u>don't</u> require very much <u>heat energy</u>
to raise their temperature by $1°C$ or $1K$.

        └→ <u>ex</u>: metals (Cu, Fe)

          └→ <u>metal</u> pan on a stove gets
            hotter much faster than <u>H_2O</u>
            in the pan!!

In order for the amount of heat to be measured in a chemical or physical change, **three** things have to be known.

1. The **temperature change** (Δt) (measured with a thermometer)
2. The **mass** of the substance (**m**) (measured with a balance)
3. The "**Heat Capacity**" of the substance (**C**) (this means the heat needed to raise the temperature of 1 kg of the substance by 1 °C)

   Heat Capacity (C) will **always be given** in a problem. The Heat Capacity for water is:

   $$C_{H_2O} = 4180 \text{ J/kg} \cdot {}^{\circ}\text{C}$$

<u>Heat Capacity (c)</u> = the amount of energy (as heat) required to raise the temperature of a substance by 1°C or 1K

 ↳ the <u>higher</u> the "heat capacity", the <u>smaller</u> the change in temperature for a given amount of absorbed heat.

   → H_2O has a high heat capacity (good coolant)

   ↳ metals have low heat capacities

** the term <u>heat capacity (c)</u> does <u>not</u> mention the <u>amount</u> of the substance being considered...

Heat Capacity and Specific Heat

- The amount of energy required to raise the temperature of a substance by 1 K (1°C) is its heat capacity (C in units of J/K).

$$C = \frac{q}{\Delta T}$$

- We define specific heat capacity (or simply specific heat; C_s or s in units of J/g·K) as the amount of energy required to raise the temperature of 1 g of a substance by 1 K.

- If the amount is one mole, it is the molar heat capacity.

$$C_s = s = \frac{q}{m \times \Delta T}$$

Measurement of Heat Flow: Calorimetry

- A calorimeter is a device used to measure the heat flow of a reaction
  - The walls of the calorimeter are insulated to block heat flow between the reaction and the surroundings
  - The heat flow for the system is equal in magnitude and opposite in sign from the heat flow of the calorimeter
    - $q_{reaction} = - q_{calorimeter}$
    - $q_{reaction} = - C_{cal} \, \Delta t$

Example: Given that the heat capacity of water: C_{H_2O} = 4180 J/kg · °C

Calculate the heat required to warm 400.0 g of water from 20 °C to 50 °C.

Solution:

First we have to change 400.0 g to 0.4000 kg and calculate the temperature change (Δt)
50 °C - 20 °C = 30 °C

Next, we write the equation:

$$\text{Heat} = m \cdot C \cdot \Delta t$$

Then we plug in the data:

Heat (J) = 0.4000 kg x 4180 J/kg · °C x 30 °C = **50 160 J**

Notice how the "kg" will cancel and the "°C" will cancel, leaving "J" as the unit for the answer. If you want to, you can convert the 50 160 J into 50.16 kJ.

Example: 75.0 kJ of heat are added to 850.0 g of water initially at 25.0 °C. Calculate the final temperature of the water. $C_{H_2O} = 4180$ J/kg·°C

Solution: First, the 75.0 kJ **must** be changed to 75,000 J and the 850.0 g of water must be changed to 0.8500 kg.

Now the use the equation to solve to Δt:

$$Heat = m \cdot C \cdot \Delta t$$

$$\Delta t = \frac{Heat}{m \cdot C} = \frac{75,000 J}{0.8500 kg \cdot 4180 \dfrac{J}{kg \cdot °C}} = 21.1 \,°C$$

Since the **initial** temperature was 25 °C, the **final** temperature will be:

$$t_{final} = t_{initial} + \Delta t = 25.0\,°C + 21.1\,°C = 46.1\,°C$$

State Changes

THE SIX CHANGES OF STATE

MELTING: change from a solid to a liquid.

VAPOURIZATION: change from a liquid to a gas. Slow vapourization is called **EVAPOURATION**.
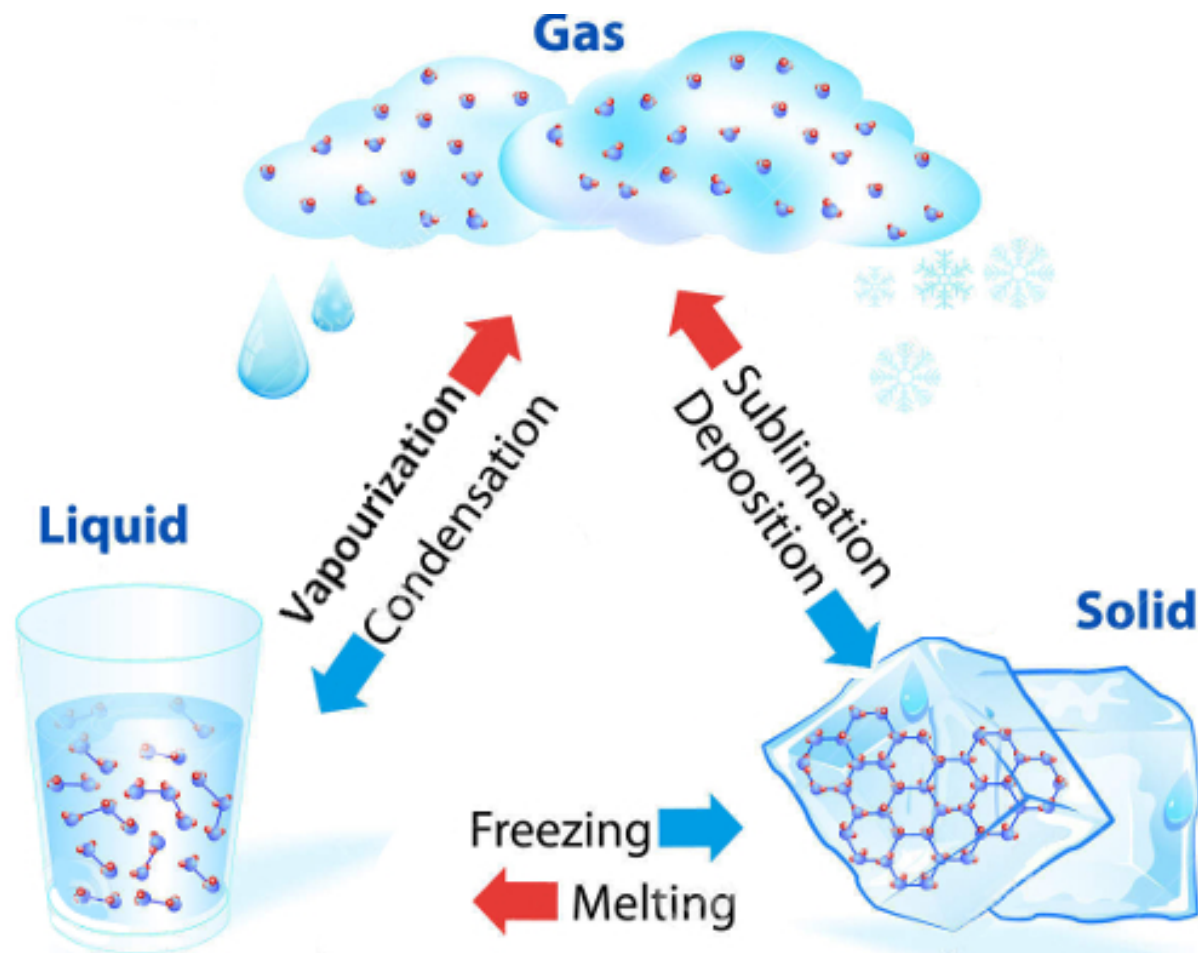Fast vapourization is called **BOILING**.

CONDENSATION: change from a gas to a liquid.

SOLIDIFICATION / FREEZING: change from a liquid to a solid.

SUBLIMATION: change from a solid directly to a gas

DEPOSITION: change from a gas directly to a solid

Change of State	From	To	Heat *Added* or *Removed*
Melting	Solid	Liquid	Added
Freezing	Liquid	Solid	Removed
Vapourization	Liquid	Gas	Added
Condensation	Gas	Liquid	Removed
Sublimation	Solid	Gas	Added
Deposition	Gas	Solid	Removed

A. Solid to Liquid

When you add heat to ice at 0°C, the temperature does not rise:

- The heat added is used to free the water particles from their set places in the solid.
- The particles set free are now in the liquid state.
- The heat has not increased the motion of the water particles, so the temperature will remain the same.

B. Liquid to Gas

- As water is heated, the particles gain energy & move faster & faster.
- The temperature rises until the liquid reaches the boiling point.
- The temperature does not continue to rise after the boiling point.
- Instead the heat is used to help the particles move more freely & escape from the surface of the liquid.
- Particles that are set free are now in the gas state.

Sublimation (Solid ⇔ Gas):

Sublimation is the process by which a heated solid directly changes into its gaseous state i.e. vapour state. These vapours on cooling directly give solid. Such substances are called sublimates. Examples are ammonium chloride, ammonia, ~~naphthalene balls, camphor~~, etc.

Freezing (Liquid → Solid):

When liquids are cooled the thermal energy of particles decreases. Thus the cohesive forces between the particles strengthen to such extent that the particles can not have relative motion with each other and they occupy the fixed positions. Thus liquid gets converted into solid (freezes).

Evaporation or Vaporization (Liquid → Gas):

The process of conversion of a substance from the liquid state to its vapour state at any temperature below boiling point is called evaporation or vaporization.

Some particles from liquid surface possess kinetic energy sufficient to overcome the attractive forces from remaining particles of the liquid and become completely free and escape out as a gas particle in the surroundings. This phenomenon is called evaporation or vaporization.

Heat Cycle – Melting Ice

Heat cycle – Vapourization

Enthalpy for State Changes...

- The heat flow at constant pressure is equal to the difference in enthalpy (heat content) between products and reactants
- The symbol for enthalpy is H
- We measure changes in enthalpy using a calorimeter and a reaction run at constant pressure:
  - $\Delta H = H_{products} - H_{reactants}$
- The sign of the enthalpy change is the same as for heat flow:
  - $\Delta H > 0$ for endothermic reactions
  - $\Delta H < 0$ for exothermic reactions
  - ***Enthalpy is a state variable***

Enthalpy of Reactions

(a) Exothermic

(b) Endothermic
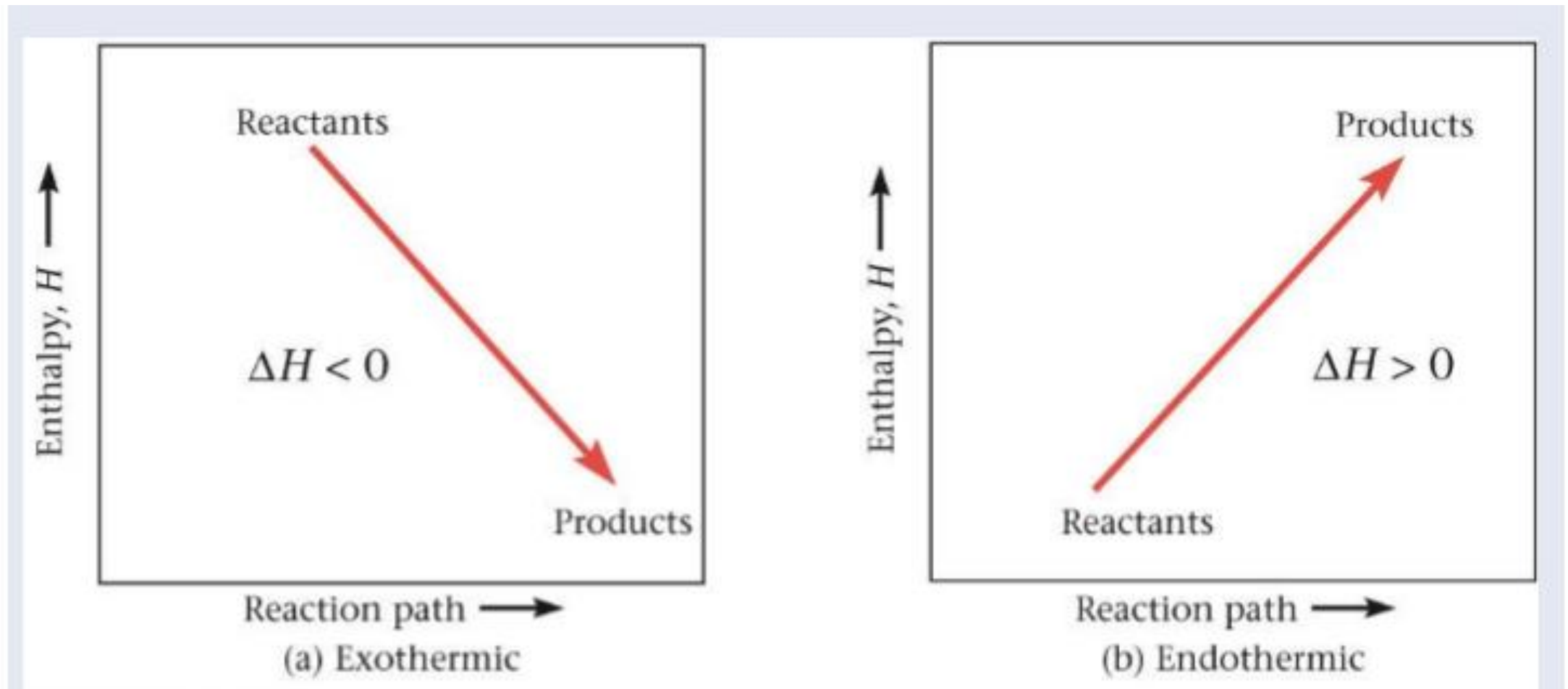
Bond Enthalpy

- Chemical bonds store *energy*
- The *bond enthalpy is defined as* ΔH *when one mole of chemical bonds is broken in the gaseous state*

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = +436 \text{ kJ}$$

$$Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H = +243 \text{ kJ}$$
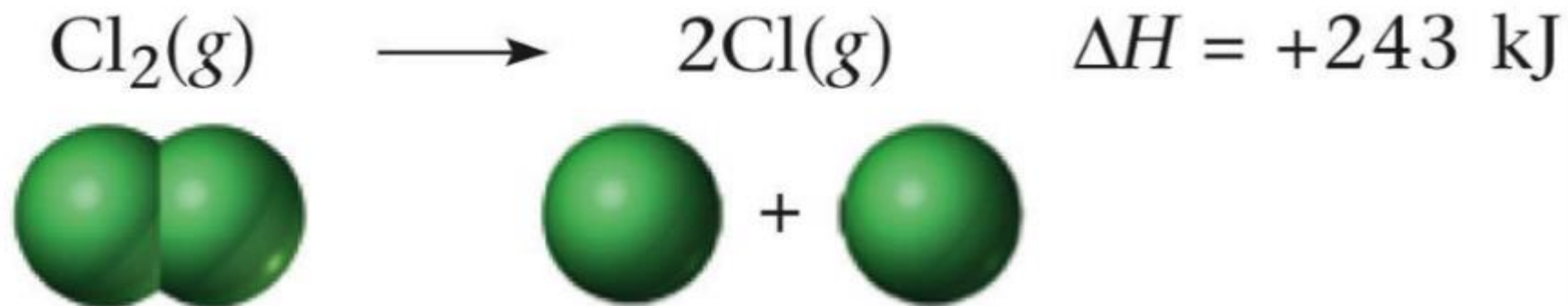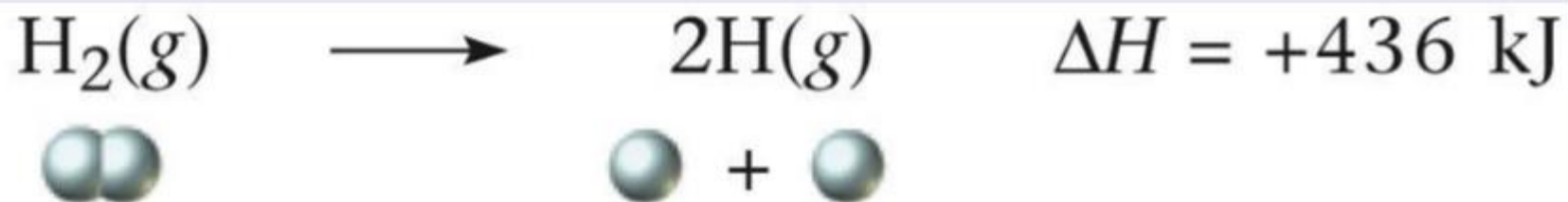
Thermochemical Equations

- A thermochemical equation is a chemical equation with the ΔH for the reaction included
- Example
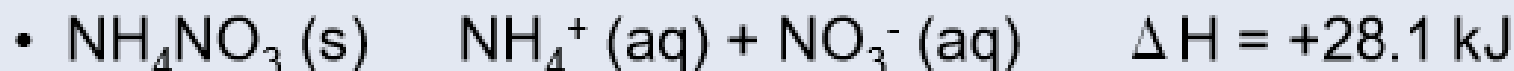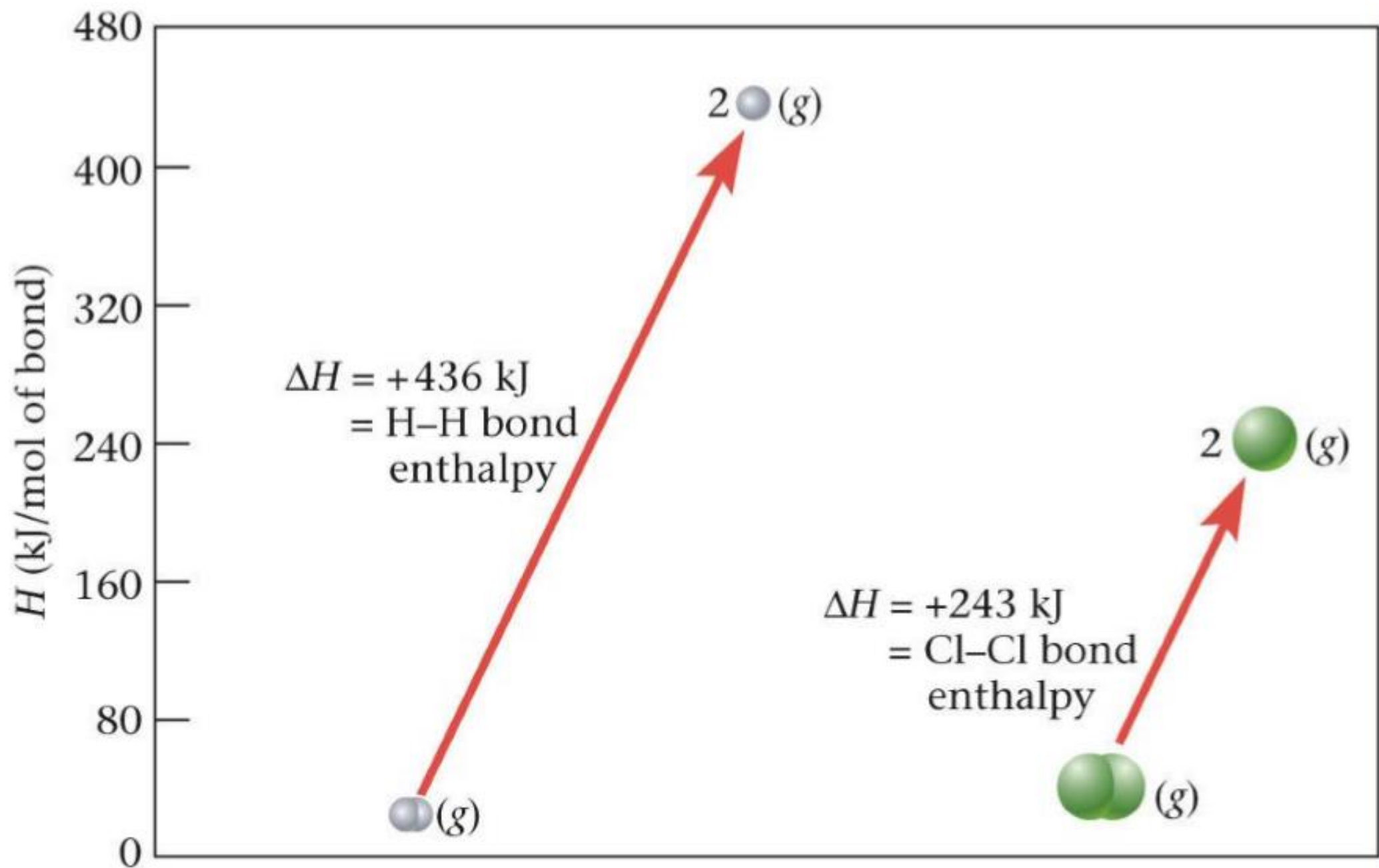 - NH_4NO_3 (s) NH_4^+ (aq) + NO_3^- (aq)
    - Experiment gives qreaction = 351 J for one gram of ammonium nitrate
    - For one mole, this is

$$\frac{351J}{1.00g} \times \frac{80.05g}{1mol} = 2.81X10^4 J = 28.1kJ$$

  - The thermochemical equation is
    - NH_4NO_3 (s) NH_4^+ (aq) + NO_3^- (aq) $\Delta H = +28.1$ kJ

- ***The bond enthalpy is always a positive quantity***
  - Energy is required to break a chemical bond
- When a chemical bond forms, the sign of the enthalpy change is negative
- For **endothermic** reactions
  - The **bonds are stronger in the reactants than in the products,** and/or
  - There are **more bonds in the reactants than in the products**

Inter Molecular Analysis

- Structure of Water molecule and Shape: