

Thermodynamics

5.1 The Nature of Energy

Thermodynamic is the study of energy and its transformation.

Thermochemistry is the study of the relationship between chemical reactions and energy changes involving heat.

Kinetic Energy and Potential Energy

Kinetic energy (E_k) is the energy of motion.

Potential energy is the stored energy. It is the energy an object possesses by virtue of its position or composition. Example: electrostatic energy.

Potential energy can be converted into kinetic energy.

Units of Energy

SI unit is the joule, J

From $E_k = 1/2 m v^2$, $1J = 1 \text{ kg} \times \text{m}^2/\text{s}^2$

Traditionally, we use the **calories** as a unit of energy

$1 \text{ cal} = 4.184 \text{ J}$ (exactly)

The nutritional Calorie, Cal = 1,000 cal.

System and Surroundings

A **system** is the part of the universe we are interested in studying.

Surroundings are the rest of the universe.

Example: if we are interaction between hydrogen and oxygen in a cylinder, then the hydrogen and oxygen in the cylinder form a system

Transferring Energy; work and Heat

From physics;

Force is a push or pull on an object

Work is the energy used to move an object against a force

$$w = F \times d$$

Heat is the energy transferred from a hotter object of a colder one.

Energy is the capacity to do work or to transfer heat.

5.2 The First Law of Thermodynamics

The first law of thermodynamics states that energy cannot be created or destroyed. It is the law of conservation of energy.

The energy of (system + surroundings) is constant.

Thus any energy transferred from a system must be transferred to the surrounding (and vice versa).

Internal Energy

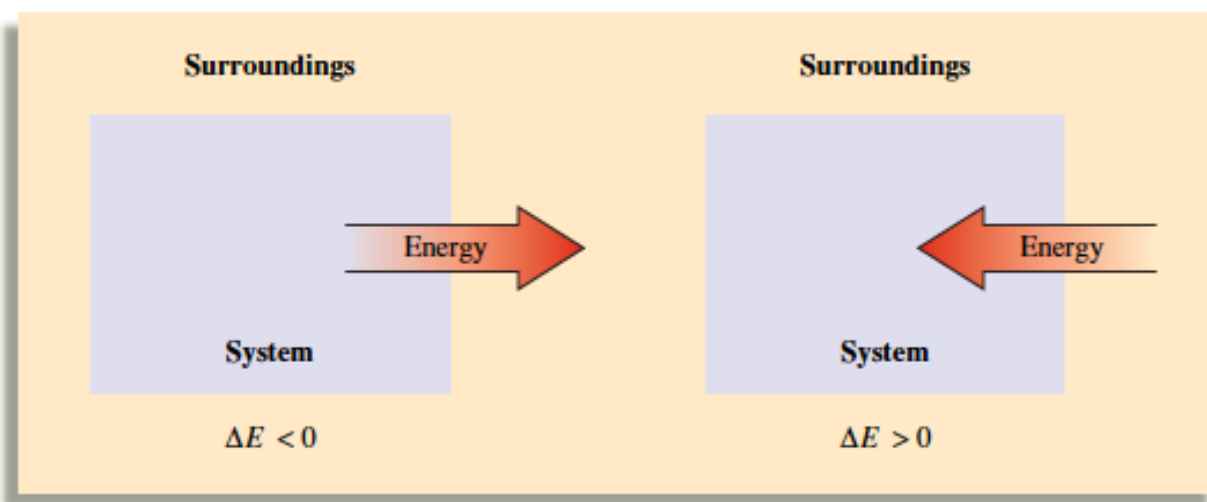
The total energy of a system is called the **internal energy**. It is the sum of all the kinetic and potential energies of all components of the system.

Absolute internal energy cannot be measured, only changes in internal energy. Changes in internal energy:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Negative change in internal energy indicates that the system has lost energy to the surrounding $\Delta E < 0$. (**exothermic**)

Positive change in internal energy indicates that the system has gained energy from the surrounding $\Delta E > 0$. (**endothermic**)



Relating E to Heat and Work

From the first law of thermodynamics:

When a system undergoes a physical or chemical change, the change in internal energy is given by the heat added to or liberated from the system plus the work done on or by the system:

$$\Delta E = q + w$$

Heat flowing from the surroundings to the system is positive, $q > 0$.

Work done by the surroundings on the system is positive, $w > 0$.

Endothermic and Exothermic Processes.

An **endothermic** process is one that absorbs heat from the surroundings. ($\Delta E > 0$). An endothermic reaction feels cold.

An **exothermic** process is one that transfers heat to the surroundings. ($\Delta E < 0$). An exothermic reaction feels hot.

State Functions

A **state function** depends only on the initial and final states of a system. It does not depend on how the internal energy is used.

Example ;

The altitude difference between Denver and Chicago does not depend on whether you fly or drive, only on the elevation of the two cities above the sea level.

Similarly, the internal energy of 50 g of H_2O (l) at 25 °C does not depend on whether we cool 50 g of H_2O liquid from 100 °C to 25 °C or heat 50 g of H_2O (l) at 0°C to 25 °C.

A state function does not depend on how the internal energy is used.

Example:

The same internal energy of a battery is used to produce heat and light in a flashlight, or heat and work in a toy car.

5.3 Enthalpy (H),

Enthalpy (H) is the **heat transferred** between the system and the surroundings during a chemical reaction carried out under **constant pressure**. Again, we can only measure the change in enthalpy ΔH .

The enthalpy of a substance is a measure of the energy that is released or absorbed by the substance when bonds are broken and formed during a reaction.

Mathematically,

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = E + P \Delta V$$

$$w = -P \Delta V$$

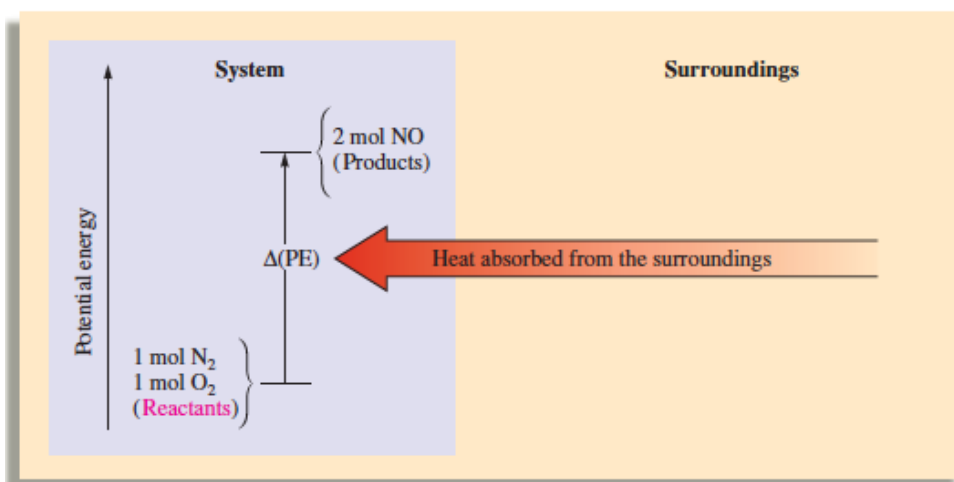
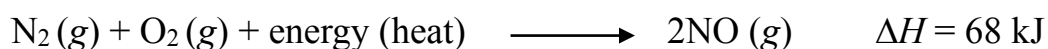
$$\Delta E = q + w$$

$$\Delta H = \Delta E + P \Delta V = q_p + w - w = q_p.$$

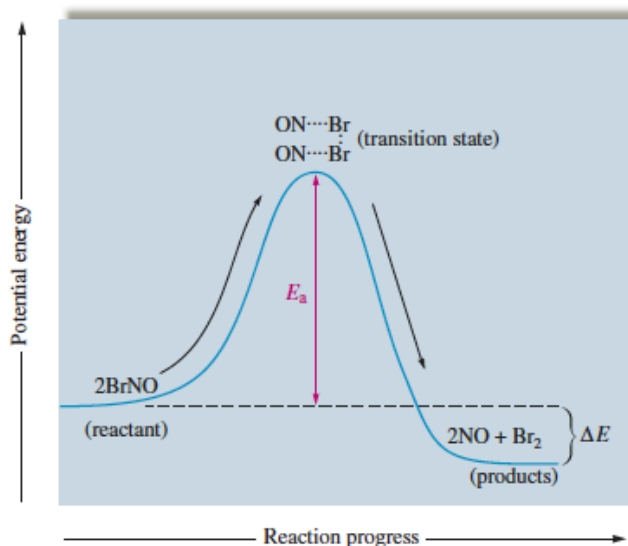
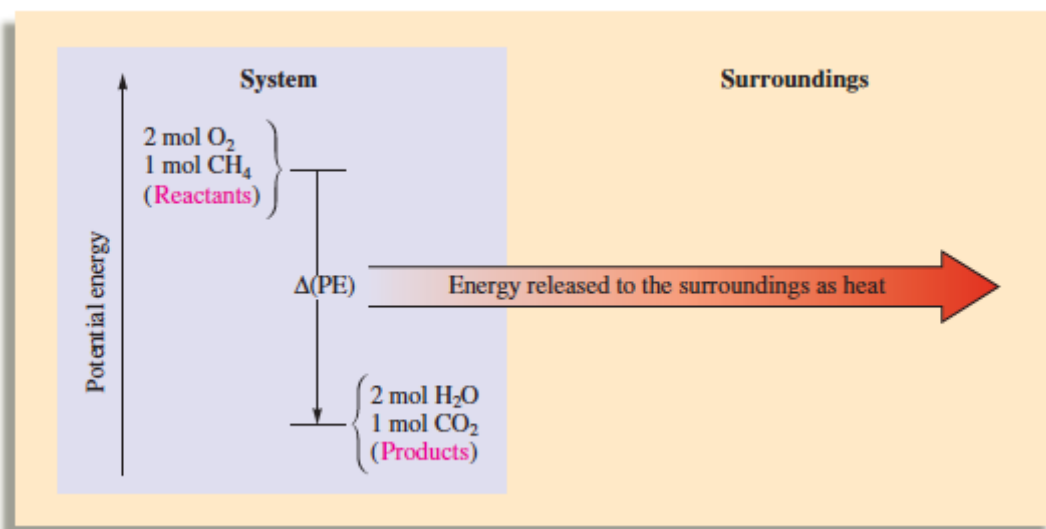
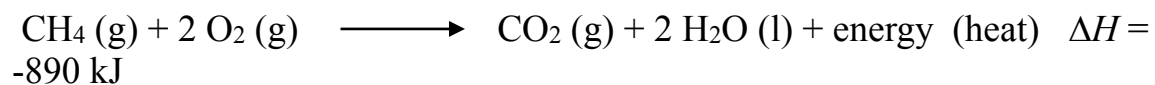
For most reaction $P \Delta V$ is small, thus

$$\Delta H = \Delta E = q_p \quad \underline{\underline{(1)}}$$

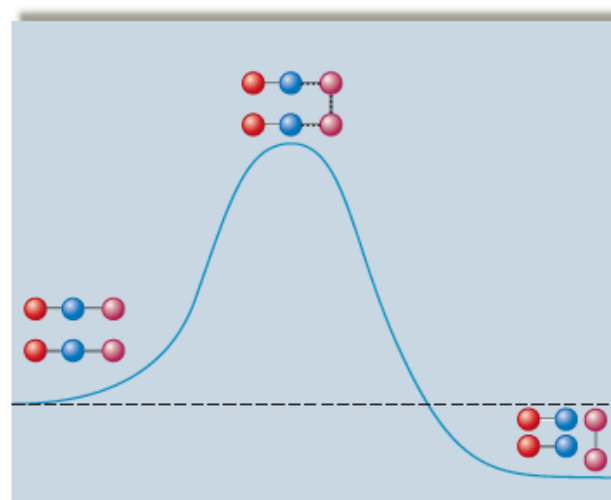
Heat transferred from surroundings to the system has a positive enthalpy (i.e., $\Delta H > 0$ for an endothermic reaction). The products are at higher energy level.



Heat transferred from system to the surroundings has a negative enthalpy (i.e, $\Delta H < 0$ for an exothermic reaction). The products are at lower energy levels.



(a)



(b)

E_a : the activation energy

5.4. Enthalpies of Reactions (ΔH_{rxn})

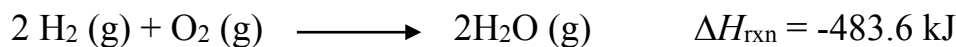
Enthalpy is a state function. It depends only on the initial and final states of a system. It does not depend on how the internal energy is used

For a reaction,

$$\Delta H_{\text{rxn}} = H (\text{products}) - H (\text{reactants}) \quad \underline{(2)}$$

The enthalpy change that accompanies a reaction is called the enthalpy of reaction or heat of reaction (ΔH_{rxn}).

Consider the *thermochemical equation* for the production of water:



The equation tells us that 483.6 kJ of energy are released to the surroundings when water is formed. This reaction is exothermic.

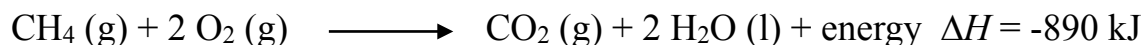
Enthalpy is an extensive property

1) The *magnitude* of enthalpy is directly proportional to the amount of reactant consumed.

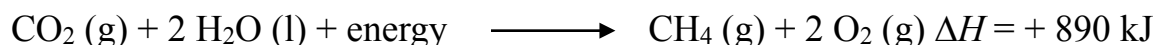
Example: If one mole of CH_4 is burned in oxygen to produce CO_2 and water, 890 kJ of heat is released to the surroundings. If two moles of CH_4 are burned then $2 \times 890 = 1780$ kJ of heat is released.

2) The sign of ΔH depends on the direction of the reaction. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.

Example:



So:



3) Enthalpy change depends on state:



5.5 Calorimetry

Calorimetry is a measurement of heat flow.

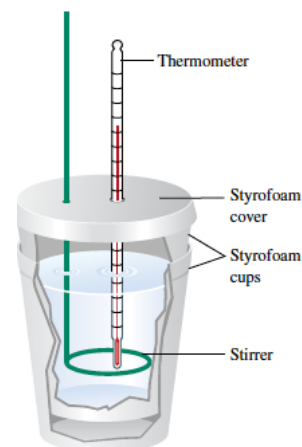
Calorimeter is an apparatus that measures heat flow.

Heat Capacity and Specific Heat

Heat capacity is the amount of energy required to raise the temperature of an object by 1°C.

Molar heat capacity is the heat capacity of 1 mole of substance.

Specific heat, or specific heat capacity is the heat capacity of 1 g of a substance.



$$\text{Heat, } q = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T$$

Be careful of the sign of q .

Constant Pressure Calorimetry

Most common technique; use atmospheric pressure as the constant pressure.

Easiest method: use a coffee cup calorimeter:

$$q_{\text{soln}} = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T = -q_{\text{rxn}}$$

For dilute aqueous solution, the specific heat of the solution will be close to that of pure water.

$$\text{Heat lost by the substance} = \text{Heat gained by water}$$

Recall: $\Delta H = q_p$

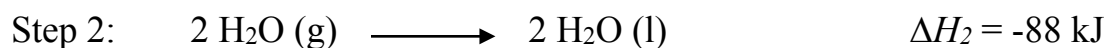
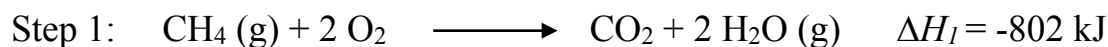
$$\Delta H = q_p = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T$$

$$\Delta H = q_p = m C_p \times \Delta T \quad (3)$$

5.6, Hess's Law (4)

Hess's Law: if a reaction is carried out in a series of steps, ΔH for the reaction is the sum of ΔH for each of the steps.

The ΔH is independent of the number of steps and the nature of the path.



ΔH is sensitive to the states of the reactants and products.

Hess's law allows us to calculate enthalpy data for reactions which are difficult to carry out directly.

5.7 Enthalpy of Formation

If a compound is formed from its constituent elements, then the enthalpy change for the reaction is called enthalpy of formation, ΔH_f .

Standard enthalpy of formation of a compound, ΔH_f° , is the enthalpy change for the formation of 1 mole of compound with all substances in their standard states.

The standard enthalpy of formation of the most stable form of an element is zero.

Standard state (standard conditions) refers to the substance at 1 atm and 25°C (e.g standard enthalpy, ΔH°)

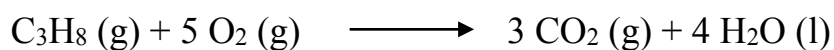
Using Enthalpy of Formation to Calculate Enthalpies of Reaction

$$\Delta H^{\circ}_{\text{rxn}} = \sum n \Delta H^{\circ}_{\text{f}}(\text{products}) - \sum m \Delta H^{\circ}_{\text{f}}(\text{reactants}). \quad (5)$$

Where n and m are the stoichiometric coefficients.

Example:

Calculate the $\Delta H^{\circ}_{\text{rxn}}$ for:



$$\Delta H^{\circ}_{\text{rxn}} = 3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ}) - 1(-103.85 \text{ kJ}) - 5(0) = -2220 \text{ kJ}.$$

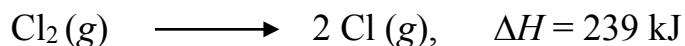
TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	$\Delta H^{\circ}_{\text{f}}$ (kJ/mol)
$\text{NH}_3(\text{g})$	-46
$\text{NO}_2(\text{g})$	34
$\text{H}_2\text{O}(\text{l})$	-286
$\text{Al}_2\text{O}_3(\text{s})$	-1676
$\text{Fe}_2\text{O}_3(\text{s})$	-826
$\text{CO}_2(\text{g})$	-394
$\text{CH}_3\text{OH}(\text{l})$	-239
$\text{C}_8\text{H}_{18}(\text{l})$	-269

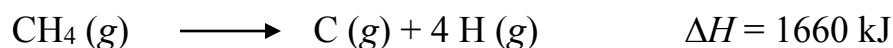
8.8 Strengths of Covalent Bonds.

The energy required to break a covalent bond is called the bond **enthalpy**, D .

That is for the Cl_2 molecule, $D(\text{Cl-Cl})$ is given by ΔH for the reaction:



When more than one bond is broken:



The bond enthalpy is a fraction of ΔH for the atomization reaction:

$$D(\text{C-H}) = 1/4 \Delta H = 1/4 (1660 \text{ kJ}) = 415 \text{ kJ}.$$

The bond enthalpy is always a positive quantity.

Bond Enthalpies and the Enthalpies of Reactions

We can use bond enthalpies to calculate the enthalpy for a chemical reaction.

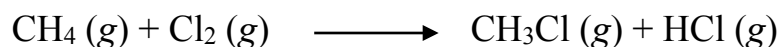
We recognize that in any chemical reaction bonds need to be broken and then new bonds form.

The enthalpy of the reaction is given by:

The sum of the bond enthalpies for bonds broken less the sum of bond enthalpies for bonds formed. Where ΔH_{rxn} is the enthalpy for a reaction.

$$\Delta H_{\text{rxn}} = \sum n D(\text{bonds broken}) - \sum m D(\text{bonds formed}) \quad (5)$$

We illustrate the concept with the reaction between methane, CH_4 and chlorine:



In this reaction one C-H bond and one Cl-Cl bond are broken while one C-Cl bond and one H-Cl bond are formed.

So

$$\Delta H_{\text{rxn}} = [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})] = -104 \text{ kJ.}$$

The overall reaction is exothermic which means that the bonds formed are stronger than the bonds broken.

The above result is consistent with Hess's law.

Bond Enthalpy and Bond Length

The distance between the nuclei of the atoms involved in a bond is called **bond length**.

Multiple bonds are shorter than single bonds.

We can show that multiple bonds are stronger than single bonds.

As the number of bonds between atoms increases, the atoms are held closer and more tightly together.

TABLE 8.5 Bond Lengths for Selected Bonds			
Bond	Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	Single	154	347
C=C	Double	134	614
C≡C	Triple	120	839
C—O	Single	143	358
C=O	Double	123	745
C—N	Single	143	305
C=N	Double	138	615
C≡N	Triple	116	891

Enthalpy (H):

flow of energy (heat exchange) at constant pressure when two systems are in contact:

1) Enthalpy of reaction (ΔH_{rxn}) amount of heat released (negative values) or absorbed (positive values) by a chemical reaction at constant pressure in $\text{kJ/mol}_{\text{rxn}}$.

2) Enthalpy of combustion (ΔH_{comb}) heat absorbed or released by burning (usually with O_2) in $\text{kJ/mol}_{\text{rxn}}$; note that combustion reactions yield oxides of that which is combusted.

3) Enthalpy of formation (ΔH_f): heat absorbed or released when ONE mole of compound is formed from elements in their standard states in $\text{kJ/mol}_{\text{rxn}}$.

4) Enthalpy of fusion (ΔH_{fus}): heat absorbed to melt (overcome IMFs) 1 mole of solid to liquid @ MP expressed in $\text{kJ/mol}_{\text{rxn}}$.

5) Enthalpy of vaporization (ΔH_{vap}): heat absorbed to vaporize or boil (overcome IMFs) 1 mole liquid to vapor @BP in $\text{kJ/mol}_{\text{rxn}}$.

Enthalpy (H):

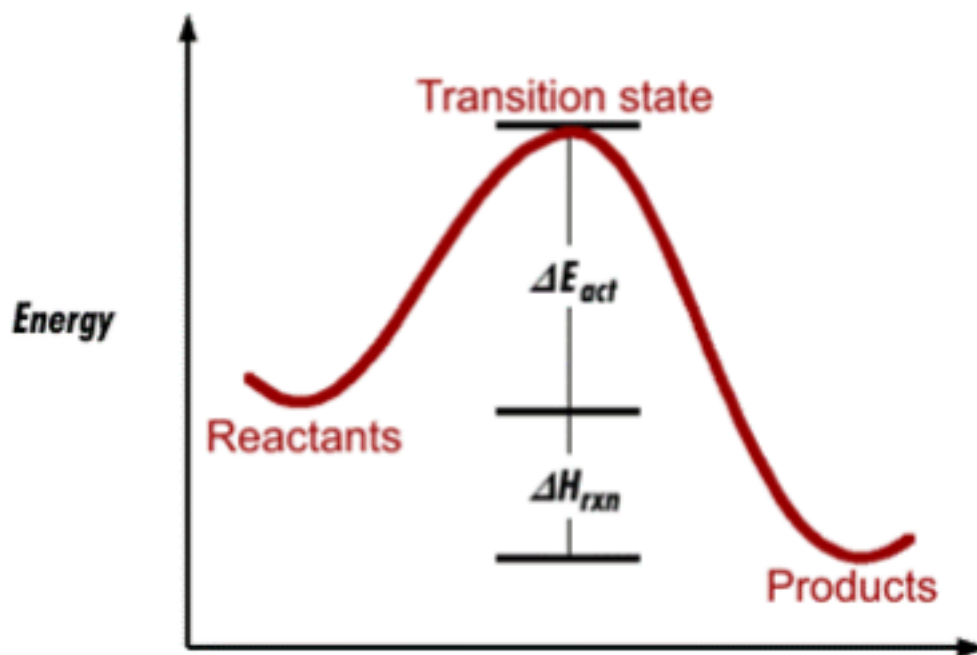
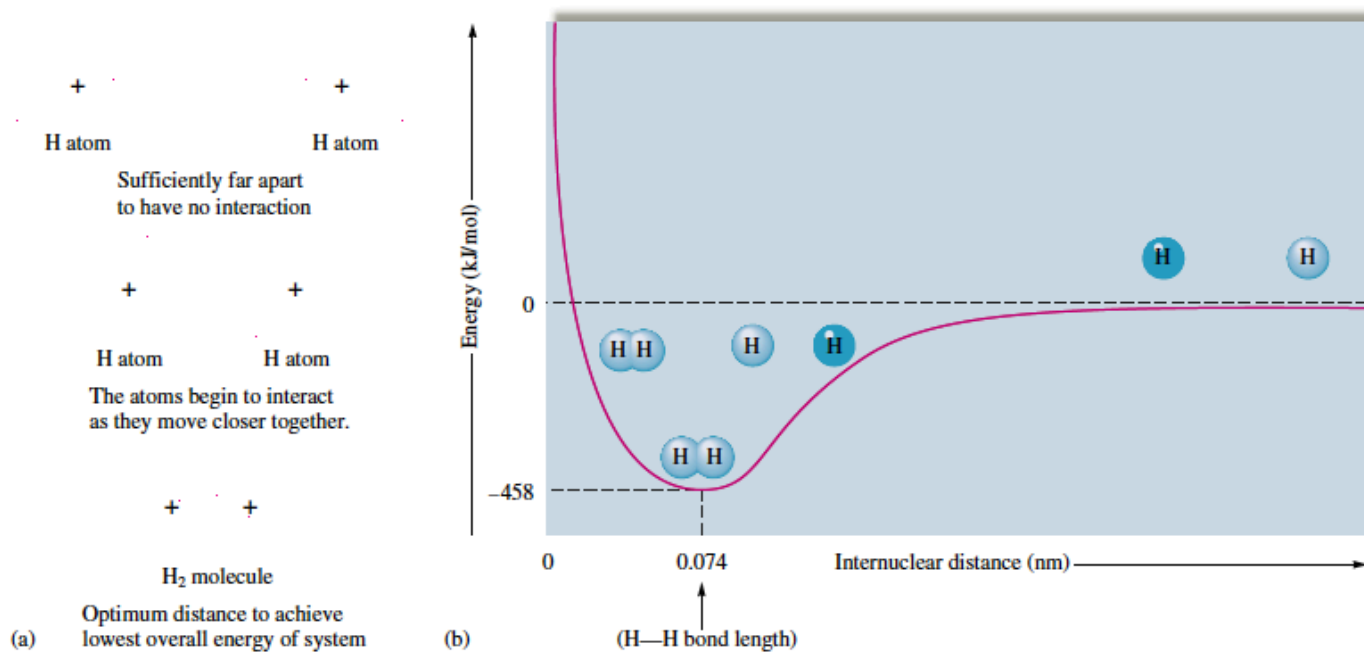
Measure only the change in enthalpy ΔH (the difference between the potential energies of the products and the reactants)

ΔH is a state function

$\Delta H_r = q_p$ at constant pressure (i.e. atmospheric pressure).

Enthalpy can be calculated from several sources including

- 1) Stoichiometry
- 2) Calorimetry
- 3) From tables of standards values
- 4) Hess's Law
- 5) Bond energies



Catalyst:

A catalyst speeds up the reaction without being consumed.

It works by providing a lower-energy pathway for the reaction (lower the activation energy).

It has no effect on the energy of the energy of the reactants, the energy of the products, or ΔH_{rxn} for the reaction.

