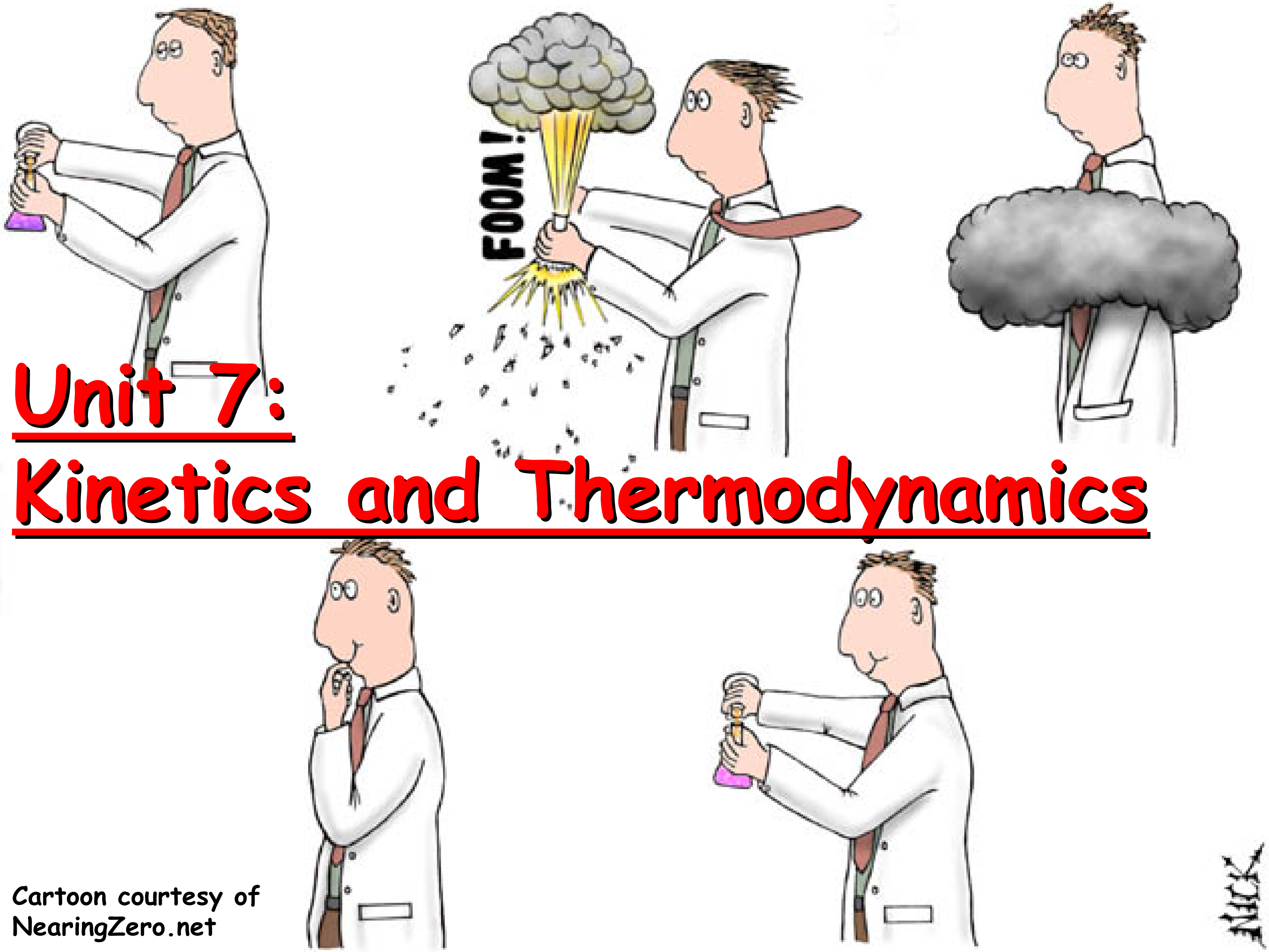
Unit 7: Kinetics and Thermodynamics



Cartoon courtesy of NearingZero.net

Heat (Enthalpy) Change

The amount of heat energy released or absorbed during a process.

Endothermic:

Processes in which energy is absorbed as it proceeds, and surroundings become colder

Exothermic:

Processes in which energy is released as it proceeds, and surroundings become warmer

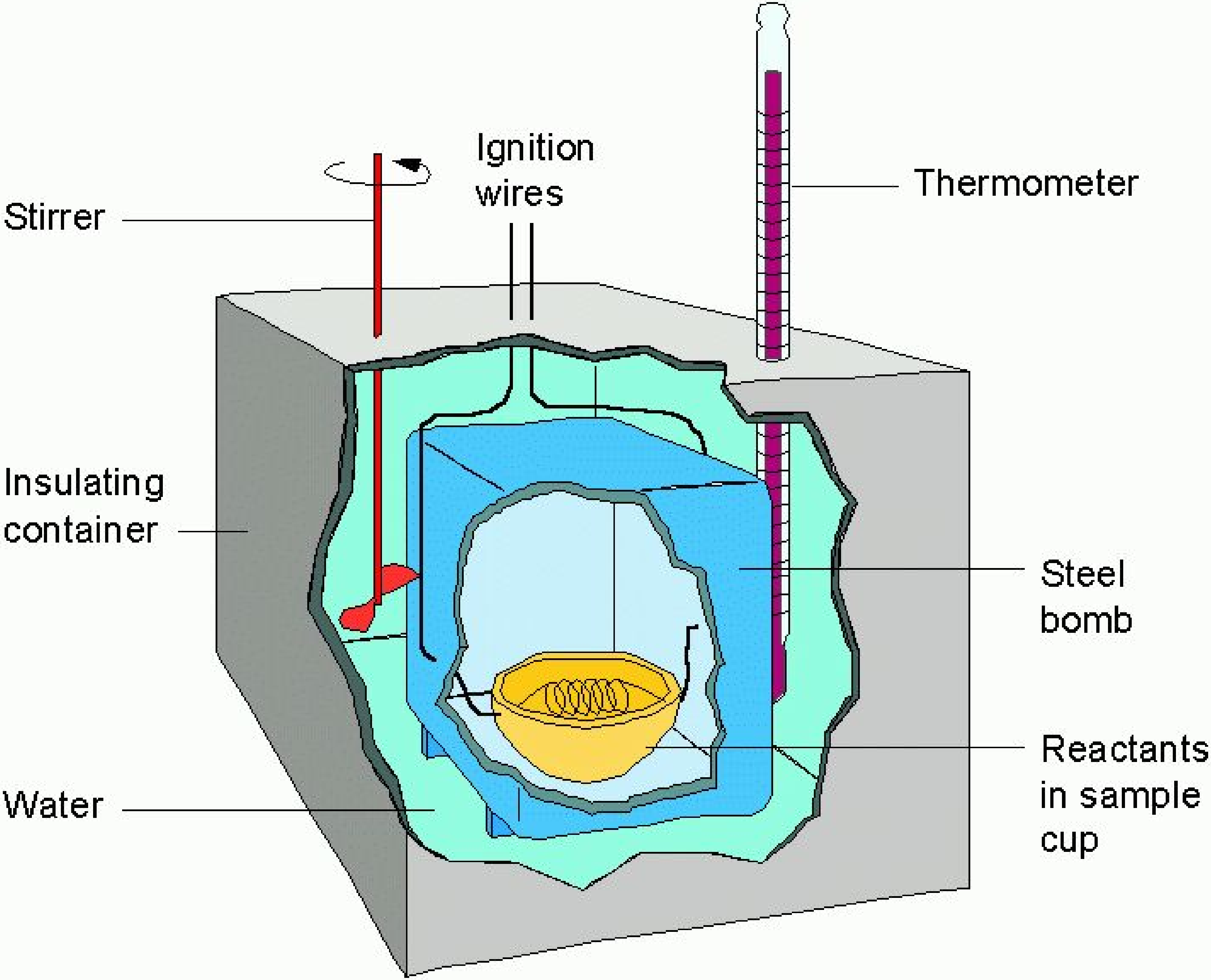
Units for Measuring Heat

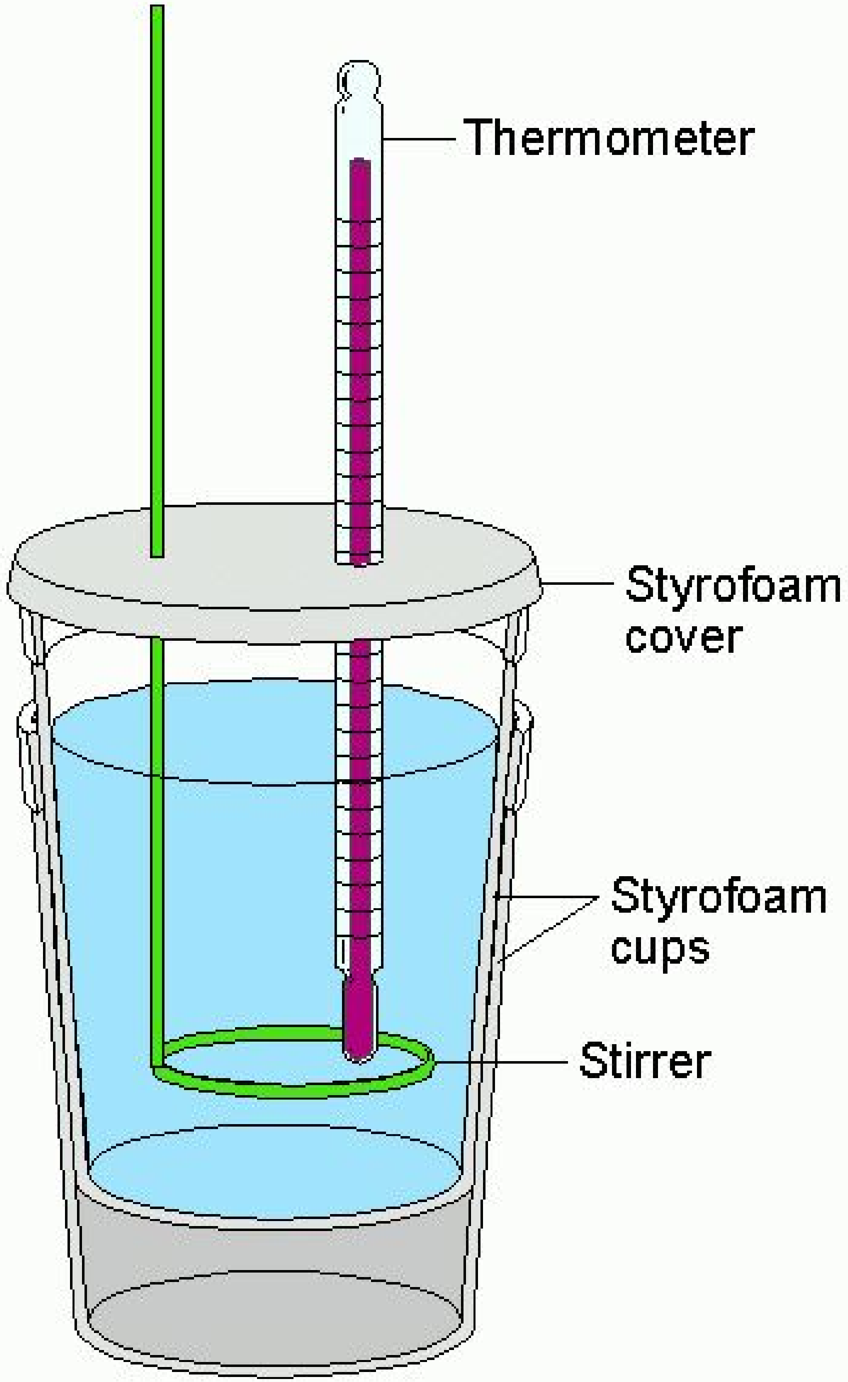
The **Joule** is the SI system unit for measuring heat:

$$1 \quad J = N \cdot m = \frac{kg \cdot m^2}{s^2}$$

The **calorie** is the heat required to raise the temperature of 1 gram of water by 1 Celsius degree

$$1 calorie = 4.18 \, Joules$$

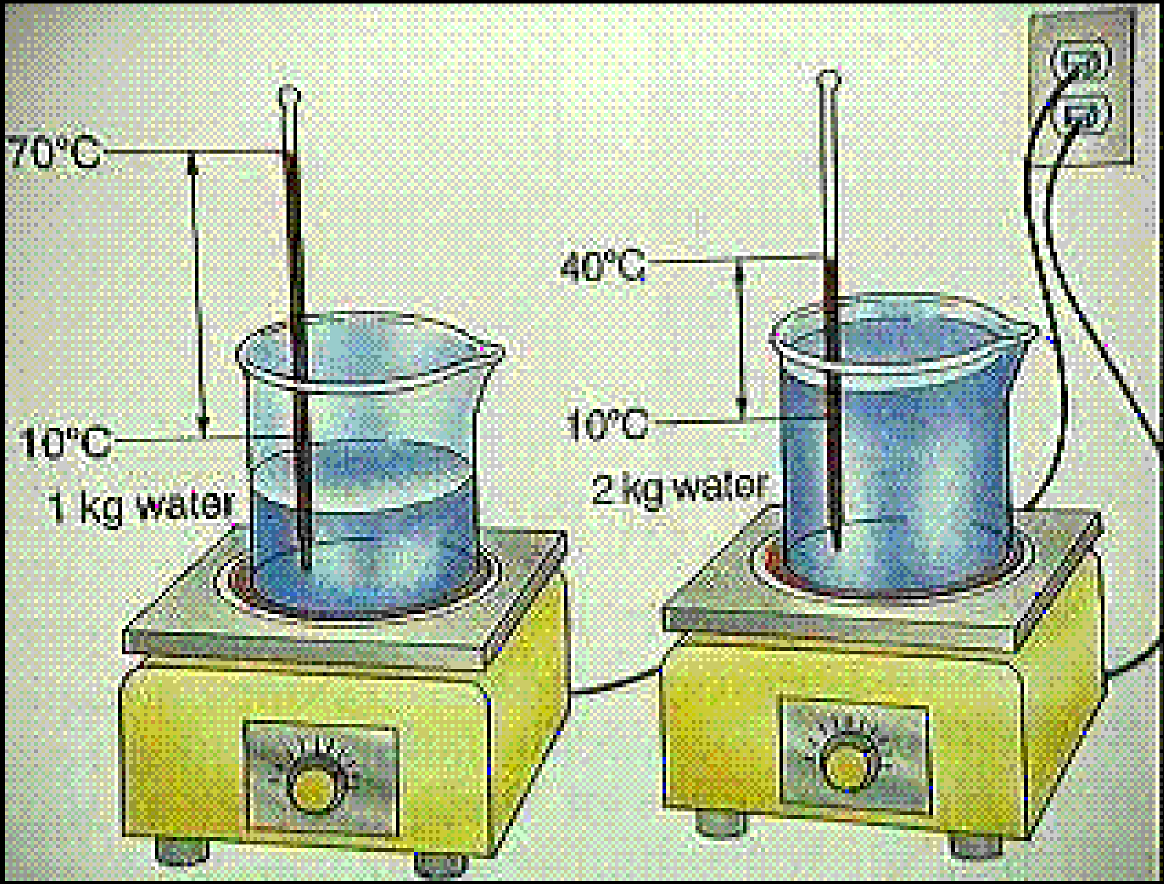

Ignition wires
Stirrer
Thermometer
Insulating container
Steel bomb
Reactants in sample cup
Water



A Cheaper Calorimeter

Specific Heat

The amount of heat required to raise the temperature of one gram of substance by one degree Celsius.



Calculations Involving Specific Heat

$$c_p = \frac{q}{m \cdot \Delta T}$$ OR $$q = c_p \cdot m \cdot \Delta T$$

c_p = Specific Heat

q = Heat lost or gained

ΔT = Temperature change

m = Mass

Table of Specific Heats

Substance	Specific heat J/(g·K)
Water (*l*)	4.18
Water (*s*)	2.06
Water (*g*)	1.87
Ammonia (*g*)	2.09
Benzene (*l*)	1.74
Ethanol (*l*)	2.44
Ethanol (*g*)	1.42
Aluminum (*s*)	0.897
Calcium (*s*)	0.647
Carbon, graphite (*s*)	0.709
Copper (*s*)	0.385
Gold (*s*)	0.129
Iron (*s*)	0.449
Mercury (*l*)	0.140
Lead (*s*)	0.129

Latent Heat of Phase Change

Molar Heat of Fusion

The energy that must be absorbed in order to convert one mole of solid to liquid at its melting point.

Molar Heat of Solidification

The energy that must be removed in order to convert one mole of liquid to solid at its freezing point.

Latent Heat of Phase Change #2

Molar Heat of Vaporization

The energy that must be absorbed in order to convert one mole of liquid to gas at its boiling point.

Molar Heat of Condensation

The energy that must be removed in order to convert one mole of gas to liquid at its condensation point.

Latent Heat - Sample Problem

Problem: The molar heat of fusion of water is 6.009 kJ/mol. How much energy is needed to convert 60 grams of ice at 0°C to liquid water at0°C?

$$\frac{60\ g\ H_2O}{} \left| \frac{1\ mol\ H_2O}{18.02\ g\ H_2O} \right| \frac{6.009\ kJ}{1\ mol} = 20.00\ kiloJoules$$

Mass of ice

Molar Mass of water

Heat of fusion

Heat of Solution

The **Heat of Solution** is the amount of heat energy absorbed (endothermic) or released (exothermic) when a specific amount of solute dissolves in a solvent.

Substance	Heat of Solution (kJ/mol)
NaOH	-44.51
NH_4NO_3	+25.69
KNO_3	+34.89
HCl	-74.84

Chemical Kinetics

The area of chemistry that concerns reaction rates.

Key Idea: Molecules must collide to react.

However, only a small fraction of collisions produces a reaction. Why?

Collision Model

Collisions must have enough energy to produce the reaction (must equal or exceed the activation energy).

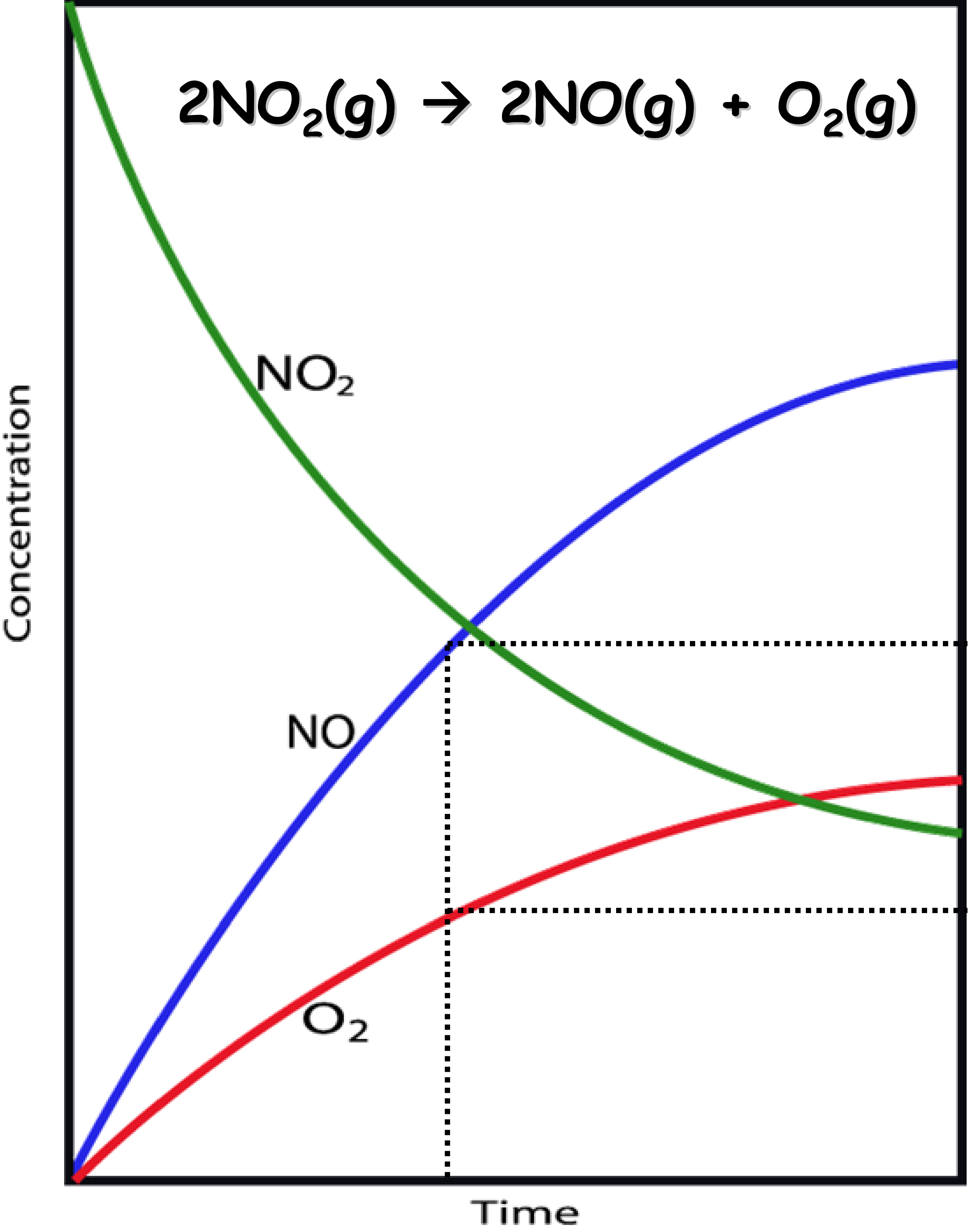
Orientation of reactants must allow formation of new bonds.

Reaction Rate

The change in concentration of a reactant or product per unit of time

$$Rate = \frac{[A]\, at\, time\, t_2 - [A]\, at\, time\, t_1}{t_2 - t_1}$$

$$Rate = \frac{\Delta[A]}{\Delta t}$$



Reaction Rates:

1. Can measure disappearance of reactants
2. Can measure appearance of products
3. Are proportional stoichiometrically

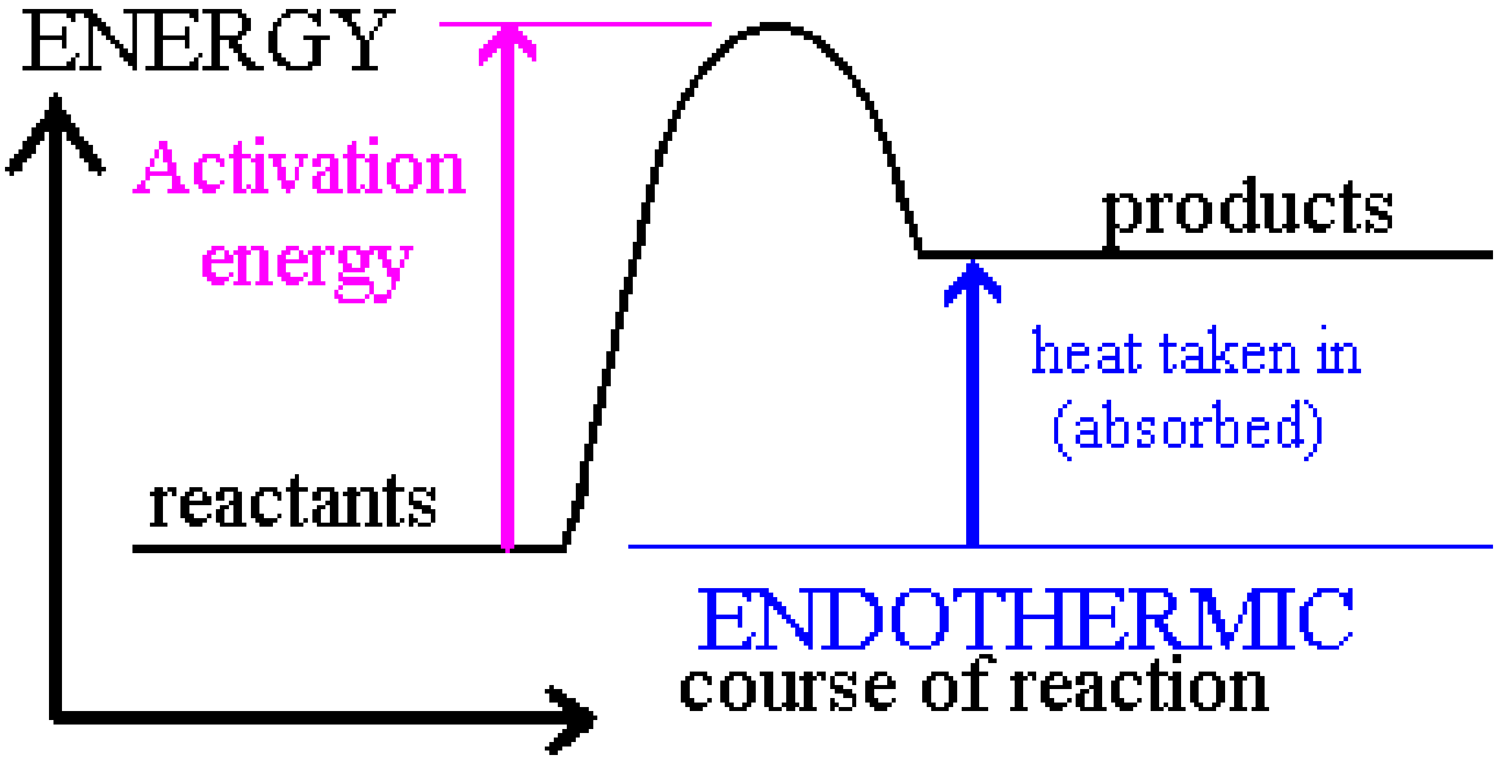
Activation Energy

The minimum energy required to transform reactants into the activated complex

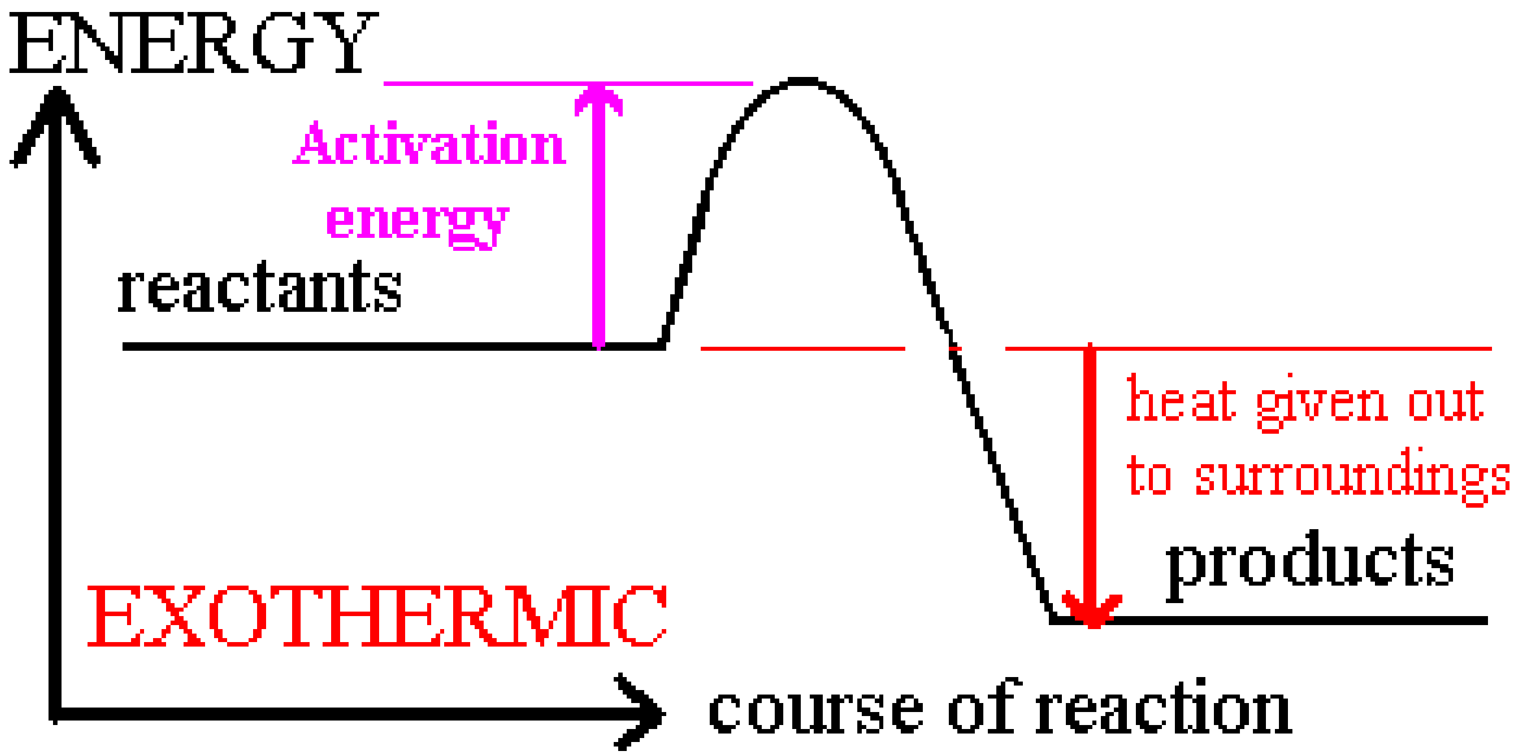
(The minimum energy required to produce an effective collision)

Flame, spark, high temperature, radiation are all sources of activation energy

Endothermic Reactions



Exothermic Reactions



Factors Affecting Rate

- Temperature
  Increasing temperature always increases the rate of a reaction.
- Surface Area
  Increasing surface area increases the rate of a reaction
- Concentration
  Increasing concentration USUALLY increases the rate of a reaction
- Presence of Catalysts

Catalysis

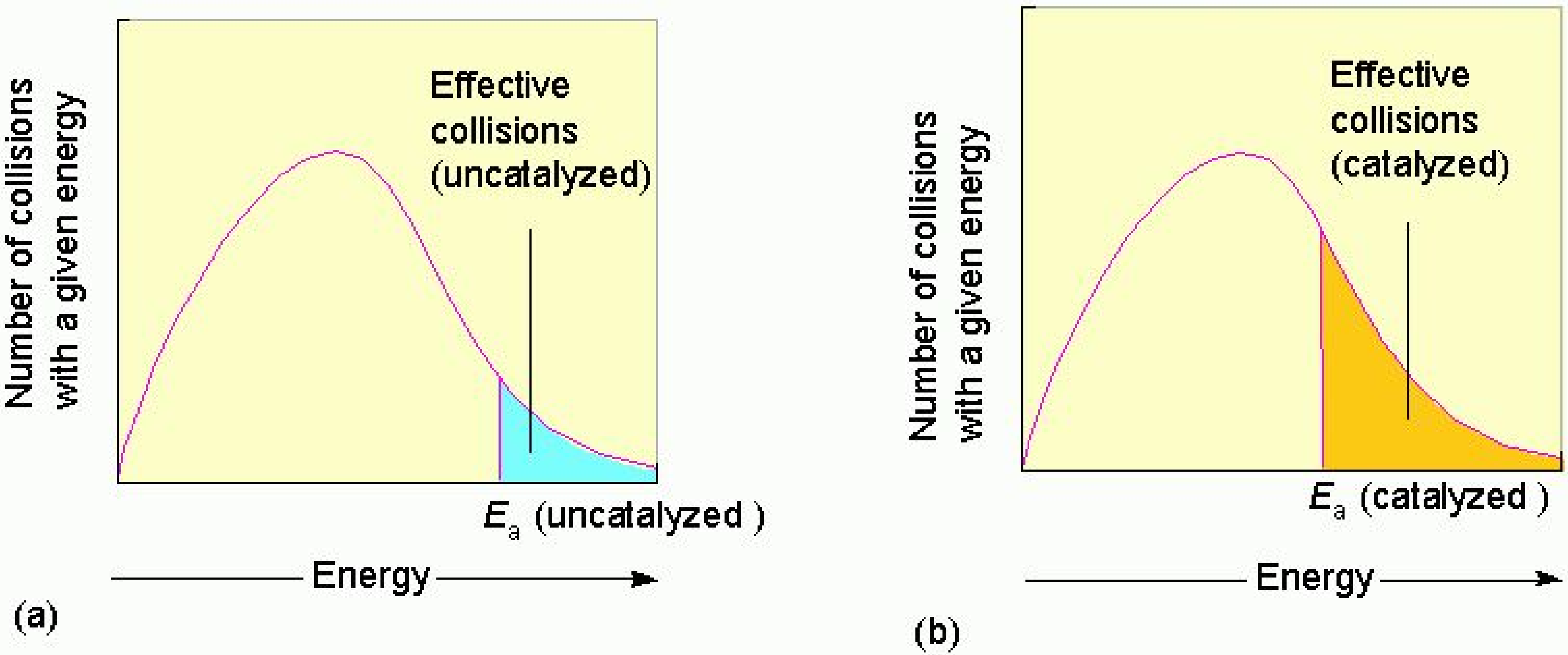
- **Catalyst**: A substance that speeds up a reaction without being consumed

- **Enzyme**: A large molecule (usually a protein) that catalyzes biological reactions.

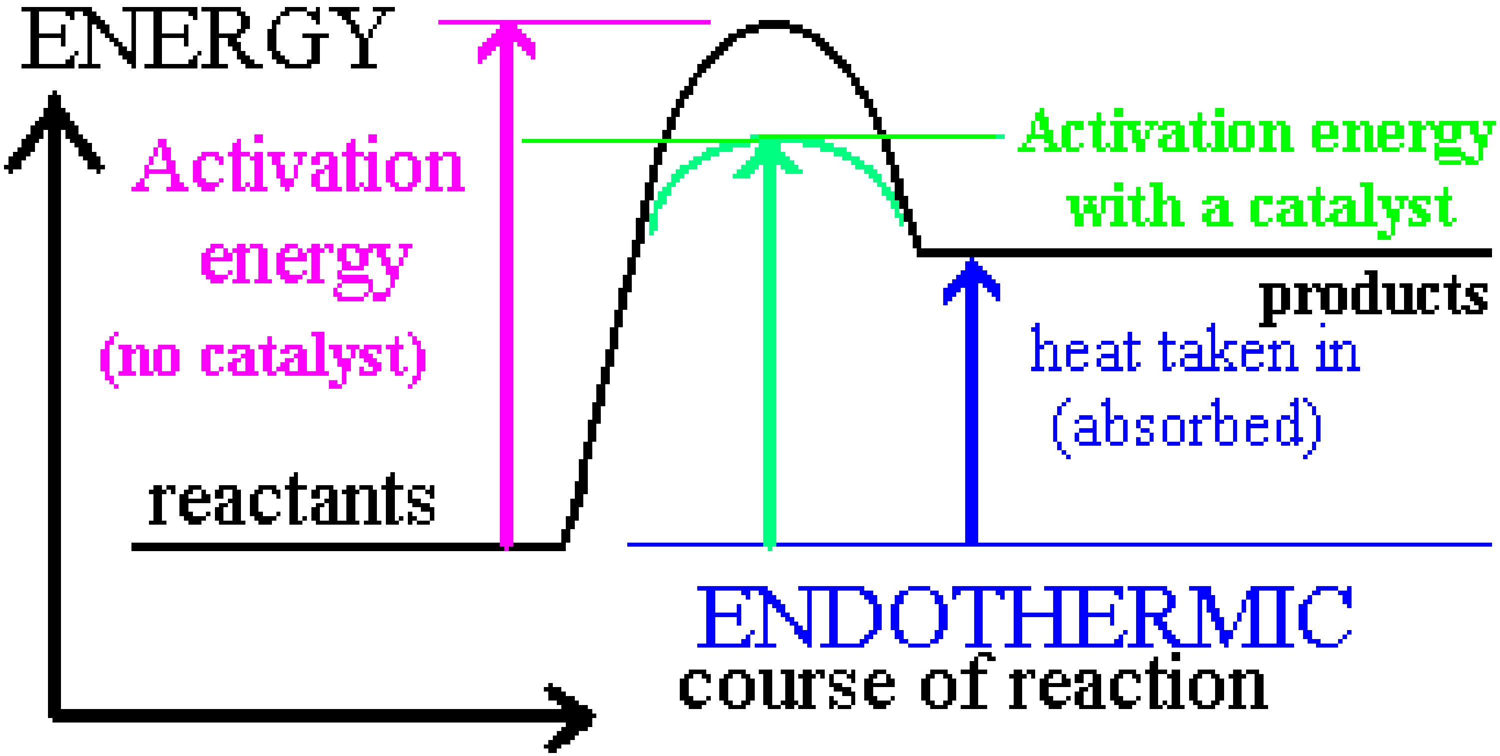
- **Homogeneous catalyst**: Present in the same phase as the reacting molecules.

- **Heterogeneous catalyst**: Present in a different phase than the reacting molecules.

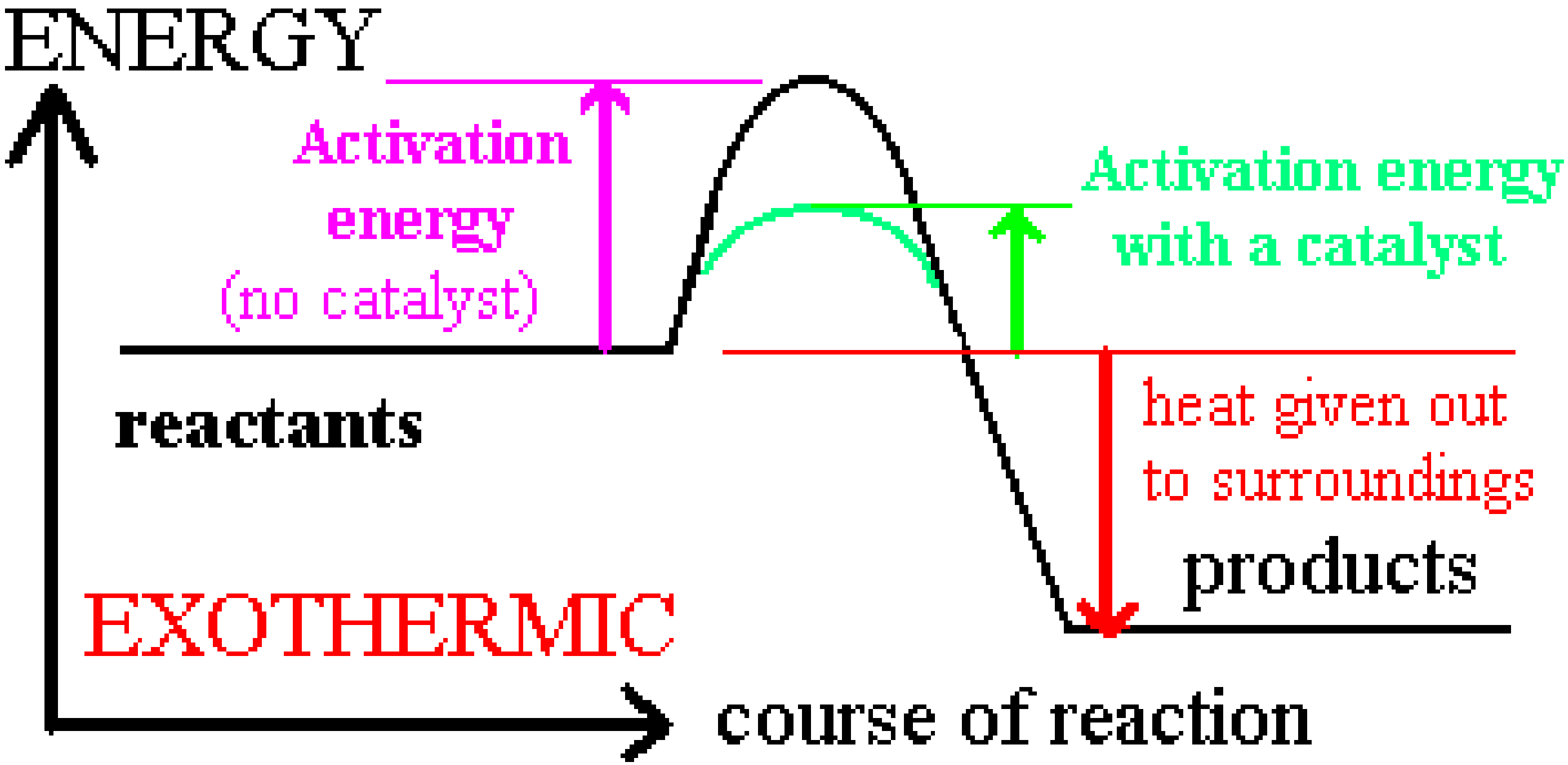
Catalysts Increase the Number of Effective Collisions



Endothermic Reaction with a Catalyst



Exothermic Reaction with a Catalyst



Chemical Equilibrium

Reversible Reactions:

A chemical reaction in which the products can react to re-form the reactants

Chemical Equilibrium:

When the rate of the forward reaction equals the rate of the reverse reaction and the concentration of products and reactants remains unchanged

$$2HgO(s) \leftrightarrows 2Hg(l) + O2(g)$$

Arrows going both directions ($\leftrightarrows$) indicates equilibrium in a chemical equation

LeChatelier's Principle

When a system at equilibrium is placed under stress, the system will undergo a change in such a way as to relieve that stress.

Le Chatelier Translated:

When you take something away from a system at equilibrium, the system **shifts** in such a way as to **replace what you've taken away**.

When you add something to a system at equilibrium, the system **shifts** in such a way as to **use up what you've added**.

LeChatelier Example #1

A closed container of ice and water at equilibrium. The **temperature** is raised.

Ice + Energy $\leftrightarrows$ Water

The equilibrium of the system shifts to the __right__ to use up the added energy.

LeChatelier Example #2

A closed container of N_2O_4 and NO_2 at equilibrium. NO_2 is added to the container.

$$N_2O_4\,(g) \;+\; \text{Energy} \;\leftrightarrows\; 2\,NO_2\,(g)$$

The equilibrium of the system shifts to the ___left___ to use up the added NO_2.

LeChatelier Example #3

A closed container of water and its vapor at equilibrium. Vapor is removed from the system.

water + Energy $\leftrightarrows$ vapor

The equilibrium of the system shifts to the __right__ to replace the vapor.

LeChatelier Example #4

A closed container of N_2O_4 and NO_2 at equilibrium. The **pressure** is **increased**.

$$N_2O_4\,(g) \;+\; \text{Energy} \;\leftrightarrows\; 2\,NO_2\,(g)$$

The equilibrium of the system shifts to the __left__ to lower the pressure, because there are fewer moles of gas on that side of the equation.

Enthalpy and Entropy

Reactions tend to proceed in the direction that lowers the energy of the system (H, enthalpy).

Reactions tend to proceed in the direction that increases the disorder of the system (S, entropy).

Spontaneity of Reactions

Reactions proceed spontaneously in the direction that lowers their free energy, G.

$$\Delta G = \Delta H - T\Delta S$$

If ΔG is negative, the reaction is spontaneous.

If ΔG is positive, the reaction is NOT spontaneous.

ΔH, ΔS, ΔG and Spontaneity

$$\Delta G = \Delta H - T\Delta S$$

H is enthalpy, T is Kelvin temperature

Value of ΔH	*Value of $T\Delta S$*	*Value of ΔG*	*Spontaneity*
Negative	Positive	Negative	Spontaneous
Positive	Negative	Positive	Nonspontaneous
Negative	Negative	???	Spontaneous if the absolute value of ΔH is greater than the absolute value of $T\Delta S$ (low temperature)
Positive	Positive	???	Spontaneous if the absolute value of $T\Delta S$ is greater than the absolute value of ΔH (high temperature)

Reaction Mechanism

- The series of steps by which a chemical reaction occurs.
- A chemical equation does not tell us how reactants become products
- It is a summary of the overall process.

Example:

$$6CO_2 + 6H_2O \xrightarrow{\text{light}} C_6H_{12}O_6 + 6O_2$$

has many steps in the reaction mechanism

Rate-Determining Step

In a multi-step reaction, the slowest step is the rate-determining step. It therefore determines the rate of reaction.