

Thermochemistry

Significant digits:

- Add / Subtract keeps same number of decimals as number with fewest has.
- Multiply / divide keeps same number of significant digits as number with fewest SF.

Moles

$$- 6.022 \cdot 10^{23} \quad n = \frac{m}{M}$$

Energy

Kinetic energy (E_k): Energy of an object in motion.

Potential energy (E_p): Energy due to position or composition

- Energy always being transformed from one form to another
- Potential energy can be stored in

Conservation of Energy

- Energy cannot be destroyed or created. Only converted.
- Energy is "wasted" in changing forms due to entropy.

The amount of energy released or absorbed in a chemical rxn is equal to the difference between the potential energy of the bonds in reactants and products.

A chemical system is composed of the reactants and products being studied.

The surroundings are all matter that is not part of the system.

In an open system, both energy and matter can be exchanged with its surroundings.

In a closed system, energy can be exchanged but not matter.

An isolated system allows neither energy or matter to move into or out of the system.

Heat (q) is the transfer of energy from a substance to another.

↳ Magnitude: How much energy

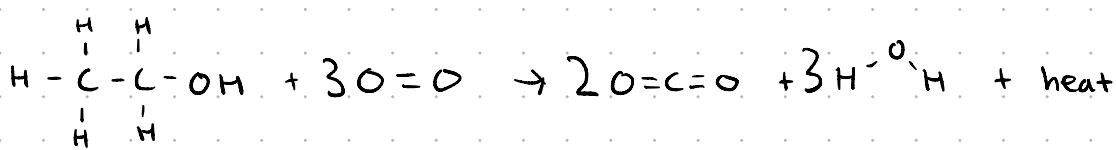
↳ Sign: Direction of energy transfer

✓ +: absorbing energy
↳ endothermic

↓ -: releasing energy
↳ exothermic

Energy in Reactions

Combustion of ethanol:



Reactants

$$(-\text{H} \cdot 5) \rightarrow 413(\text{g})$$

$$(-\text{C} \cdot 1) \rightarrow 348(\text{l})$$

$$(-\text{O} \cdot 1) \rightarrow 358(\text{l})$$

$$\text{O}-\text{H} \cdot 1 \rightarrow 463(\text{l})$$

$$\text{O}=\text{O} \cdot 3 \rightarrow 495(3)$$

$$= 4719 \text{ kJ} \cdot \text{mol}^{-1}$$

Products

$$(\text{C}=\text{O} \cdot 4) \rightarrow 799(\text{g})$$

$$\text{O}-\text{H} \cdot 6 \rightarrow 463(6)$$

$$= 5974 \text{ kJ} \cdot \text{mol}^{-1}$$

↳ Amount of energy released when forming product bonds
Forming bonds releases energy - Exothermic.

↳ Amount of energy required to break reactant bonds.
Breaking bonds requires energy - endothermic.

$$4719 - 5974 = -1255 \text{ kJ} \cdot \text{mol}^{-1}$$

Exothermic reaction

- A chemical system is composed of the reactants and products being studied. The surroundings are all the matter that is not part of the system.
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$\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$

$$q = mc\Delta T - \text{Change in temperature } ^\circ\text{C or K}$$

↳ Mass/g

Thermal energy (q) / J or kJ

↳ Positive: endothermic

↳ Negative: exothermic

Temperature (T) is a measure of the average kinetic energy of particles in a sample of matter.

$$- 1^\circ\text{C} = 273.16 \text{ K}$$

$$- \text{Room temp } (22^\circ\text{C}) = 295.15 \text{ K}$$

Enthalpy (H) is the heat content of a substance referring to how much energy is stored.

- Measured in Joules (J)

- Calories (cal) - quantity of heat required to raise the temperature of 1g of water liquid by 1°C .

$$\hookrightarrow 1\text{ cal} = 4.18 \text{ J}$$

$$\hookrightarrow 1\text{ Cal} = 1000\text{ cal} = 1\text{ kcal} = 4.18 \text{ kJ}$$

ΔH (Enthalpy change) is how much energy is released when a chemical reaction occurs ("heat of reaction").

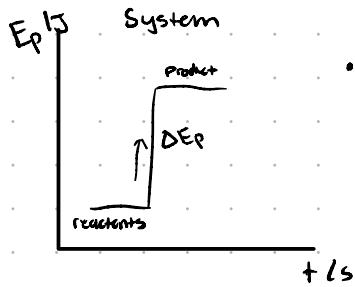
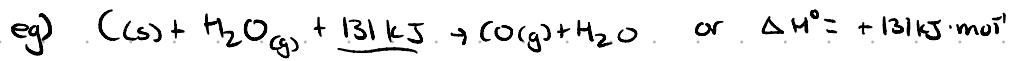
- ΔH equal to flow of q , in and out of system - assuming pressure const.

$$-\Delta H_{\text{System}} = \text{flow}_{\text{System}}$$

Types of Reactions

Endothermic

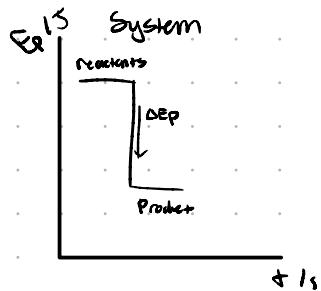
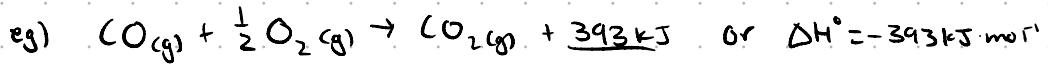
- Energy is added to the system
- $H_{\text{products}} > H_{\text{reactants}}$



- E_p increase as energy is absorbed from surroundings.

Exothermic

- Energy is removed from the system
- $H_{\text{reactants}} > H_{\text{products}}$

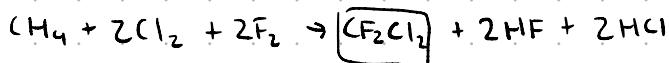


- E_p decrease as E is removed from the system.

Bond Dissociation Energies

$\Delta H = \text{sum of energies required to break old bonds (positive)} + \text{sum of energies released in the formation of new bonds (negative)}$

ex)



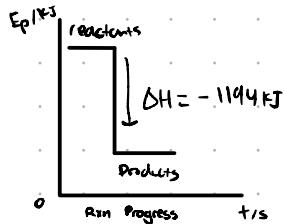
$$\begin{array}{l} (-\text{H} : 413.4) \\ (\text{Cl}-\text{Cl} : 239.2) \\ (\text{F}-\text{F} : 154.2) \end{array} = 2438$$

$$\begin{array}{l} (\text{C}-\text{C} : 339.2) \\ (\text{F}-\text{C} : 485.2) \\ (\text{H}-\text{F} : 565.2) \\ (\text{H}-\text{Cl} : 427.2) \end{array} = 3632$$

$$\begin{aligned} \Delta H &= 2438 - 3632 \\ &= -1194 \text{ kJ} \end{aligned}$$

exothermic

Enthalpy Diagram.

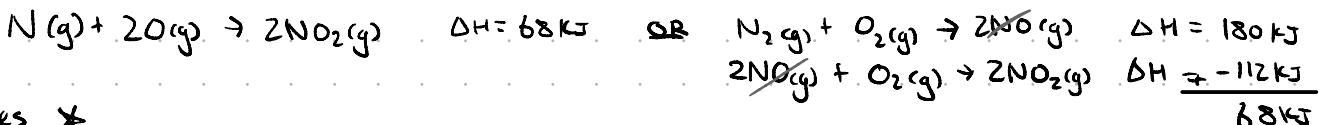


- Bond breaking is endothermic.
- Bond forming is exothermic.
- ΔH can be calculated with bond dissociation energies.

Hess' Law

- There is more than one possible route to get from reactants to products and ΔH will be the same.
- Enthalpy in a chemical process is independent of the path taken. This means that you can look at a set of reactions and products and no matter the set of reactions between, the same ΔH exists.

ex)

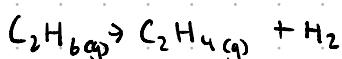


Rules *

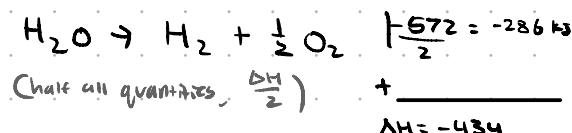
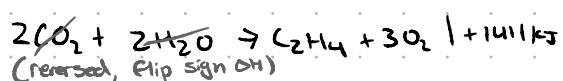
- Reversing rxn. must also reverse sign of ΔH and exothermic \leftrightarrow endothermic.
- Magnitude of ΔH is directly proportional to n of reactants and products.
- If coefficients are multiplied then ΔH also is.

- wrong side
- what not want
- what wrong quantity
if stuck ↵

ex) Find enthalpy:

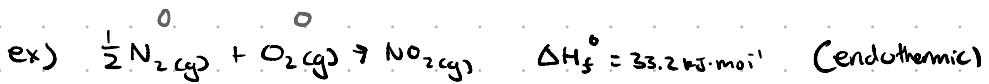


- i) $\text{C}_2\text{H}_6\text{(g)} + 3.5\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 3\text{H}_2\text{O(l)} \quad \Delta H = -1659 \text{ kJ}$
- ii) $\text{C}_2\text{H}_4\text{(g)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)} \quad \Delta H = -1411 \text{ kJ}$
- iii) $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)} \quad \Delta H = -572 \text{ kJ}$



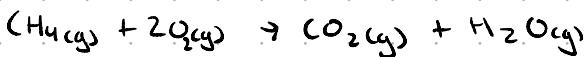
Standard Enthalpies of Formation

- The standard enthalpy of formation (ΔH_f°) of a compound is the change in enthalpy that occurs when 1 mol of compound is formed from its elements, with all substances in their standard state.
- ↳ A substance is in its standard state when its most stable form at standard temperature and pressure (STP → 25°C, 100 kPa)
- ↳ Most elements are solid in their standard state except noble gases, diatomic elements Br and Hg.
(liquid)
- ΔH_f° of element in its standard state is 0.

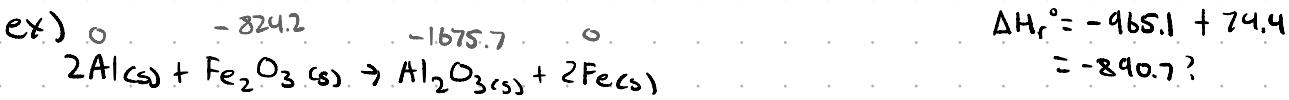
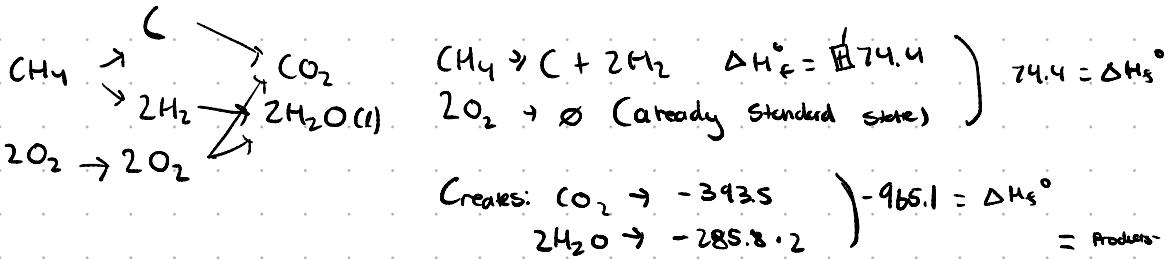


- Only 1 mol of product is created because this is how ΔF_f° equations are written.

Calculate ΔH with ΔH_f°



reverse sign because it's from CH₄



$$\Delta H_r^\circ = -1675.7 - (-824.2)$$

$$= -851.5 \text{ kJ/mol}$$

Rates of Chemical Reactions

Determine amounts of products

- Color change
- Mass of solid reacted / gas produced
- Conductivity
- pH

Average reaction rate is calculated by:

$$\text{rate}_1 = \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1}$$
$$= \frac{\Delta[A]}{\Delta t}$$

Relative rates of reaction:



↳ For every 1 mol of NO_2 consumed, 1 mol of NO is produced

↳ 0.5 mol O_2

↳ O_2 produced, 2 mol NO_2 consumed.

Factors affecting Reaction Rates

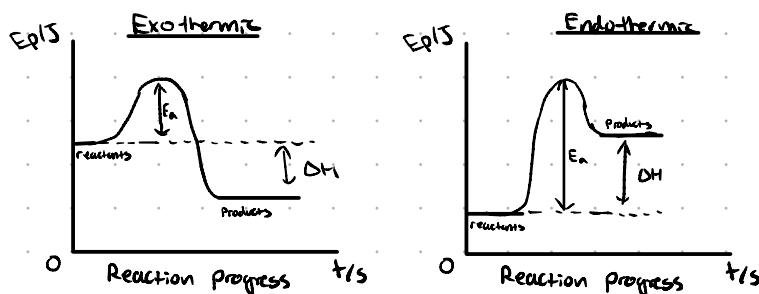
- Chemical nature of reactants
 - ↳ Sugar vs vitamin C (solubility)
 - ↳ Na oxidizes quickly in O_2 but Fe takes longer.
- Concentration of reactants
 - ↳ Rate of rxn will ↑ with higher concentrations of reactants.
 - ↳ Mg dissolve in higher $[\text{HCl}]$ than lower $[\text{HCl}]$ (3m vs 1m)
- Surface area (SA)
 - ↳ By ↑ SA, more opportunities for reactant to be exposed to other reactant.
 - ↳ Sugar cube vs granulated.
- Temperature of reaction system
 - ↳ Rxns happen quicker if carried out in ↑ temperature.
↳ i.e. baking a cake.
- Presence of a catalyst
 - ↳ Catalysts are substances that change the rate of rxn but not used up or changed by rxn.
 - ↳ i.e. enzymes are "biological catalysts".
 - ↳ Heterogeneous catalyst exists in different state of matter from reactants.
 - ↳ Homogenous catalysts exist in same state of matter as reactants.

Collision Theory

- Collision theory helps to explain why these factors affect the rate of chemical rxns.
- It states that rxns only occur if reactant molecules, atoms or ions **collide** in the **correct orientation** and with enough **E_k** that the bonds will break and new ones will form (making the products).
- The rate of a reactions depends on the **frequency of collisions** that convert reactants into products. An increase in the frequency of **effective collisions** leads to a higher reaction rate.

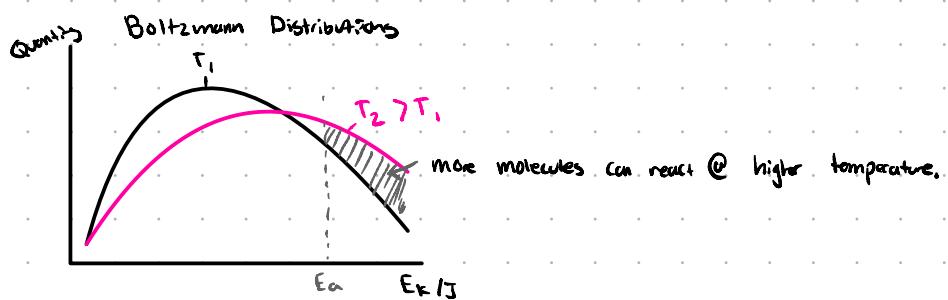
Activation Energy (E_a)

- Molecules need the right amount of kinetic energy to react. The minimum amount of energy a reactant must have for a collision to be effective is called activation energy (E_a).
- E_a has two purposes: Break existing bonds and form new bonds.
- E_p is stored in bonds within reactants and E_k in their movement. Without enough E_k, bonds won't break and rxn will not progress.
- Transition states are at the top of activation hill. They are unstable and exist briefly.



Temperature

- Temperature is closely related to the amount of E_k in a substance.
- In a sample, a **range of temperatures** exist and only some have enough E_k to react (E_a).
- With ↑ temperature, average E_k will ↑ and more reactant particles will have the energy to react.

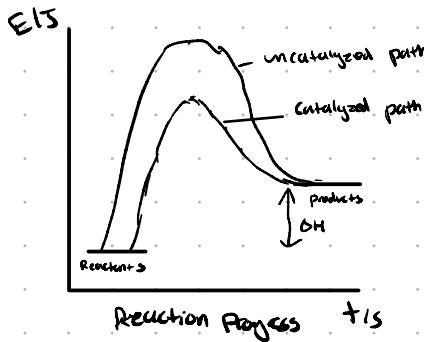


Concentration + Surface Area

- Molecules with more complicated shapes react slower because it's harder to have effective collisions.
- Molecules with single bonds will react faster than those with double bonds because less energy is required to break them.
- Reactions involving ions will react faster than covalent bonds because actual bonds need to be broken and reformed.
- With a higher concentration of a reactant, the probabilities of collisions ↑. With more collisions, more effective collisions are possible.
- SA increases reaction rate because more react particles are available to react with other reactants.

Catalyst Theory

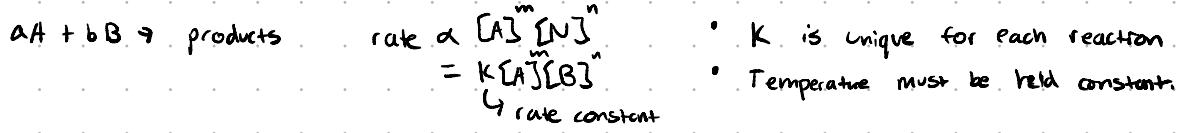
- For any reaction to occur, the E_k of colliding reactants must be greater than or equal to the activation energy.
- Catalysts do not increase collisions or kinetic energy of reactants, they lower E_a.
- Catalysts provide an alternative path for a reaction which has a lower E_a requirement.
 - Results in more effective collisions.



- Less energy is required to react thus improving the rate of reaction.

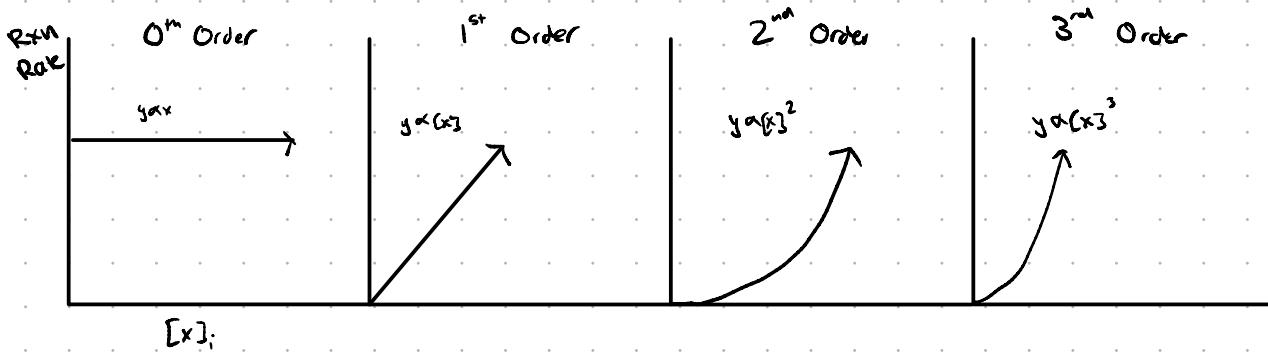
Rate Laws

- A rate law is an equation that connects the rate of a reaction with the concentration of its reactants at a given temperature and pressure.
- Only the reactants matter.
- Since temperatures and concentrations change as reaction proceeds, we look at initial concentrations.



K is unique for each reaction
Temperature must be held constant.

- The exponents can only be determined experimentally.
 - ↳ Exponents called order of reaction; if reaction is 1st order with respect to A.
- Total order of reaction is sum of each individual order. Used to predict reaction rates.
- Rate law tells us what will happen to the rate if we multiply the concentration of reactant [R] by x:
 - ↳ If [A] is 2, rate will multiply by 2 ($2^1 = 2$), for [A]



Units of K

TOTAL OVERALL ORDER	UNITS OF K
0	$\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
1	s^{-1}
2	$\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
3	$\text{L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$

Reaction Mechanisms

- A reaction mechanism is a series of elementary steps by which a chemical reaction occurs.
- An elementary step is a step that involves a 1, 2, or 3 entity collision that cannot be explained by simpler reactions.
- A reaction intermediate is an entity that is formed and consumed within the reaction sequence.
 - Neither a reactant or product, technically.
- The rate determining step is the slowest step in a reaction mechanism. It helps determine overall rate + rate law.
- 3 different entities in elementary steps are rare due to the low probability that three entities will collide in the right orientation with the right kinetic energy at the same time.

Slowest
elementary
step

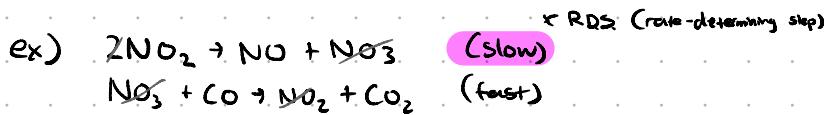
Rate Law
equation



↳ This tells us the rate law if we know the
rate-determining step

Plausible Reaction Mechanism

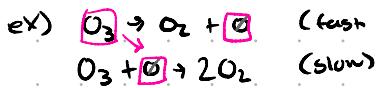
- Sum of the elementary steps will give you the overall balanced equation.
- Reaction mechanism does not contradict experimentally determined rate law.



* RDS (rate-determining step)

- Rate law equation: $\text{rate} = k[\text{NO}_2]^2$
- Overall balanced: $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$
- Intermediate: NO_3

- If slowest step reactant is an intermediate (formed + consumed), use process for how it was created.



$$\text{Rate} = k[\text{O}_3]^2 \text{ because } \text{O}_3 + \text{O}_3 \rightarrow [\text{O}_3]^2$$