

Entropy - disorder - tendency for both matter and (ΔS) energy to become homogenized.

- to order a system ($\Delta S < 0$) effectively costs energy, and a system that becomes disordered ($\Delta S > 0$) experiences an effective release of energy

Free energy (ΔG) - the energy difference between a set of reactants and products, adjusted for the effects of entropy

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

↑ potential energy - the amount of energy actually available to/from a chemical rxn
heat of rxn \longrightarrow enthalpy
equilibrium \longrightarrow free energy

Hess's law - the change in energy (ΔH) for a chemical reaction depends only on the identity of the reactants and products, and not at all on how the reaction occurs.

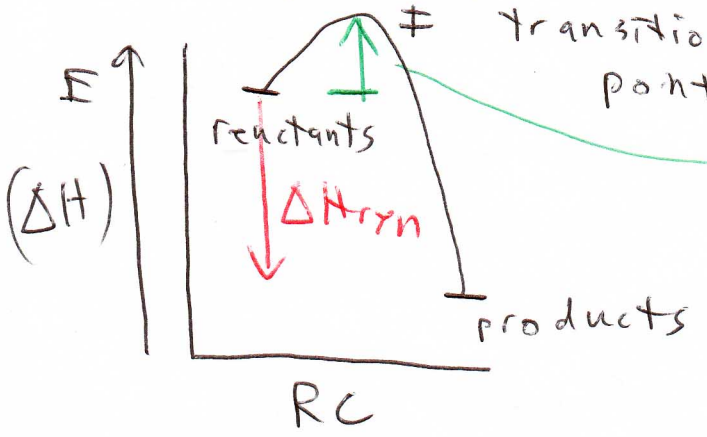
enthalpy is a state function

- If a larger rxn can be expressed as a sequence of smaller reactions, the energy change for the overall reaction is the sum of all of the individual reactions

Reaction coordinate diagram (RCD)

- Shows the energy of one instance of a reaction as reactants are fully converted into products

reaction coordinate - the most likely (most energetically favorable) pathway for a reaction,



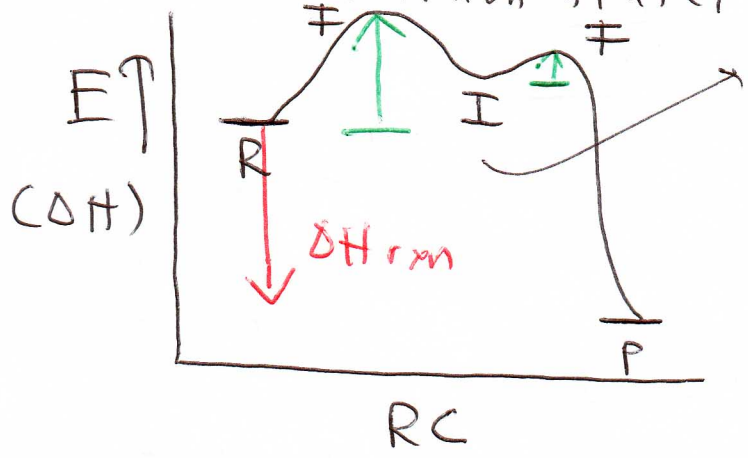
‡ transition state - highest energy point in a single elementary step.

Activation energy - the energy needed to reach a transition so that a rxn can occur

$$\Delta H_{rxn} = E_{products} - E_{reactants}$$

Kinetics

- A chemical reaction may be composed of one or more elementary steps, each of which has its own transition state.



intermediate - a chemical species that forms during a reaction but might not be isolatable.

Rate-limiting step (RLS) - In a multistep chemical rxn, the rate of reaction is normally controlled by one particular step → Generally, it is the step with the highest activation energy

$$\text{Rate: } R = \frac{\Delta[\text{reactants}]}{\Delta T}$$

$$= k [A]^a [B]^b \dots$$

↑
rate constant

* Only the reactants in the RLS are included in the rate law.

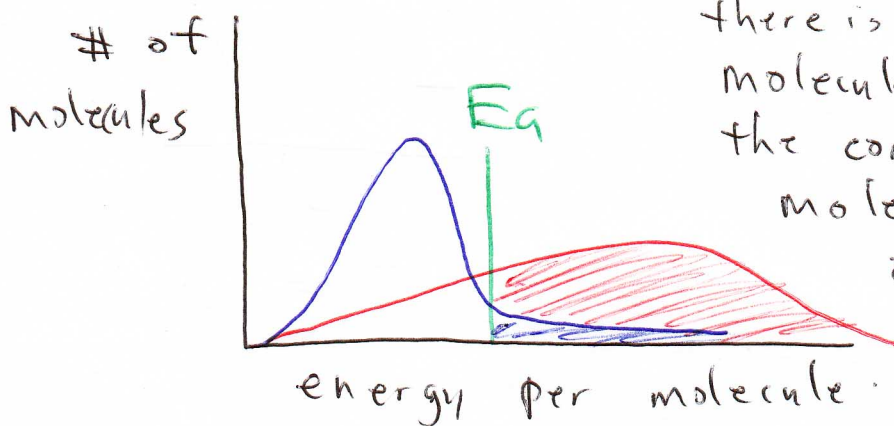
$$k = A e^{-E_a/RT}$$

Arrhenius expression

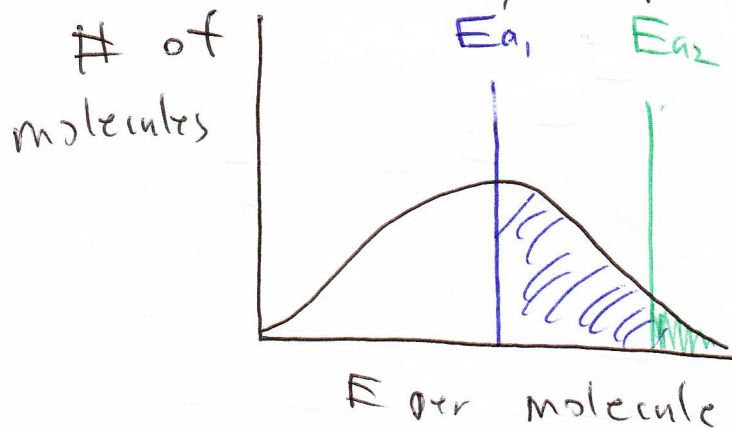
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↑
Steric factor - how difficult it is for molecules in a rxn to orient themselves properly

Molecular energy distribution - At any temperature, there is a distribution of molecular energies caused by the constant collision of molecules with each other.



- At higher T, a larger fraction of molecules would have the energy to pass over a transition state,



- At the same T, a higher E_a will result in fewer molecules able to reach the transition state

[] of the reactants in the RLS affects the rate of rxn because the greater the concentration, the greater chance of successful molecular collisions,

Reaction order - # of molecules participating in an individual step

1st order - unimolecular - only one molecule

2nd order - bimolecular - two molecules

3rd order - termolecular - 3 molecules