

Entropy - disorder - the tendency for both matter ( $\Delta S$ ) and energy to become homogenized.

- to order a system effectively costs energy, and a system that creates disorder effectively experiences a release in energy.

Free energy - the raw difference in energy of a set of reactants and products adjusted for the effects of entropy.

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

↳ potential energy - amount of energy actually available for a chemical reaction.

$\Delta S > 0$  increasing entropy  
 $\Delta S < 0$  decreasing entropy

heat of reaction  $\longrightarrow$  enthalpy  
equilibrium  $\longrightarrow$  free energy

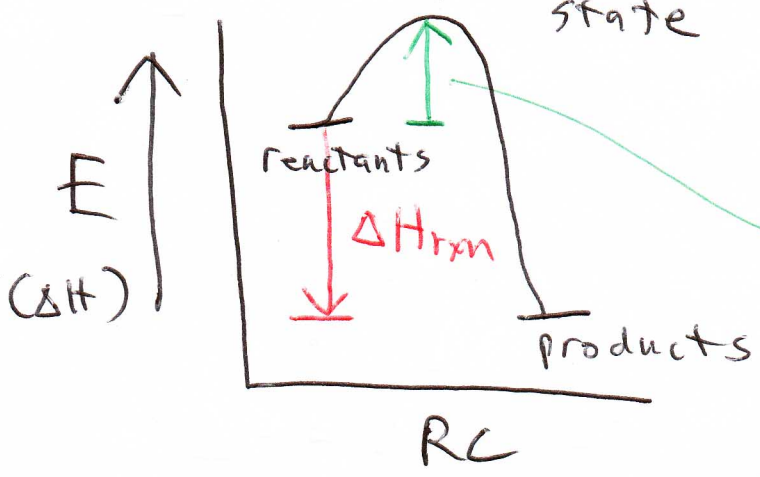
Hess's Law - the change in energy ( $\Delta H$ ) for a chemical reaction depends only on the identity of the reactants and products, and NOT at all on how the reaction occurs.

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 individual reactions.

# Reaction coordinate diagram (RCD)

- Shows the energy of one instance of a chemical rxn as reactants are fully converted into products,



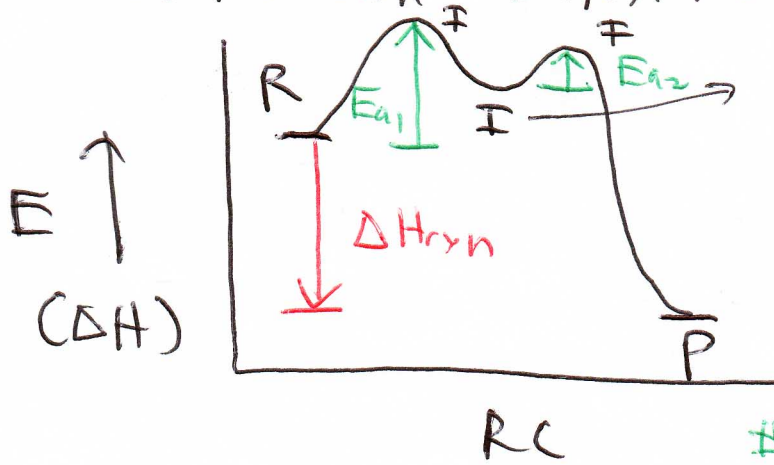
reaction coordinate - the most likely (most energetically favorable) pathway for a reaction.

Activation energy ( $E_a$ ) - the energy needed to reach the transition state for a rxn to be possible.

$\Delta H_{rxn}$  = difference in energy of products + reactants =  $E_{products} - E_{reactants}$

## Kinetics

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



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

# of transition states = # of reaction steps

Rate-limiting Step (RLS) - In a multistep chemical reaction, the rate of reaction is normally controlled by one particular step, the most "difficult" step in the sequence → generally, it is the step with highest activation energy.



Rate  $R = \frac{\Delta[\text{reactant}]}{\Delta T}$   
 ↑  
 average rate

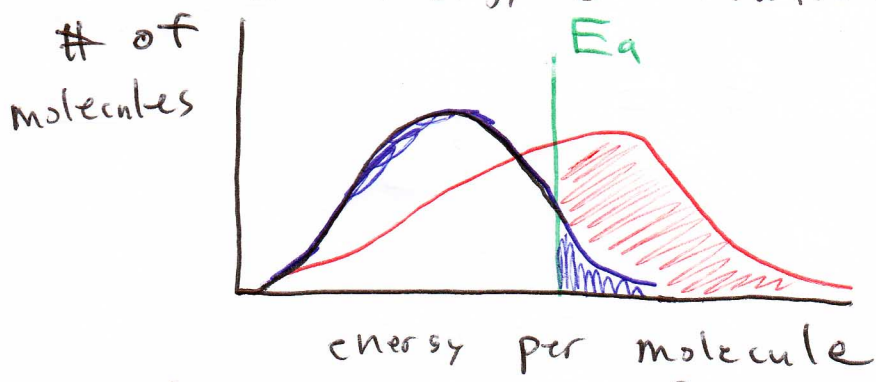
or  $R = \frac{\delta[\text{reactant}]}{\delta T}$   
 ↑  
 instantaneous rate

$R = k [A]^a [B]^b \dots$   
 ↑ rate constant      \* Only the reactants in the RLS are included in the rate law.

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

↑  
 steric factor - how difficult is it for the molecules to orient themselves properly in order to react

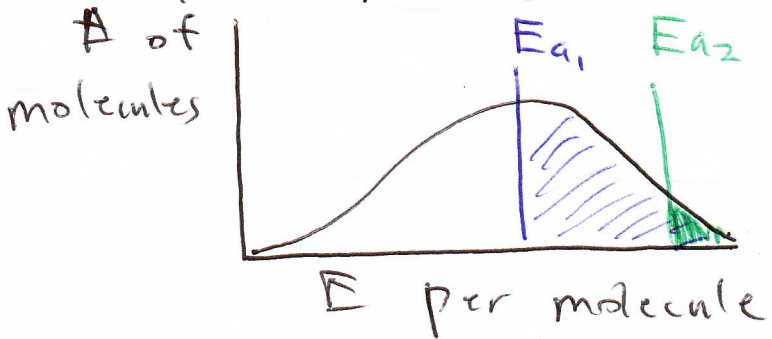
Molecular energy distribution



- At any temperature, there is a distribution of different 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,

→ The RLS is the step with the largest  $E_a$

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

Reaction order - # of molecules participating in #4  
an individual reaction step.

1st order - unimolecular - only one molecule

2nd order - bimolecular - 2 molecules

3rd order - termolecular - 3 molecules