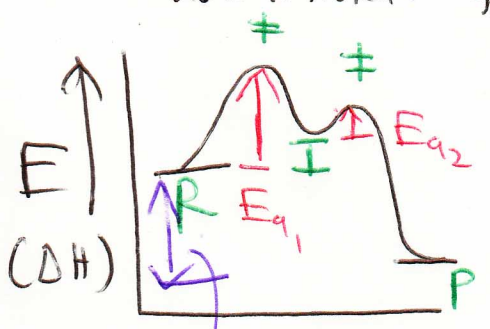


reaction coordinate - energetically most-likely pathway through a rxn; a 2D simplification of a multi-dimensional graph



R - reactants
 I - intermediates
 P - products
 ‡ - transition states

• # of transition states = # of individual steps

• Only those reagents in the rate-limiting step (RLS) are found in the rate law.

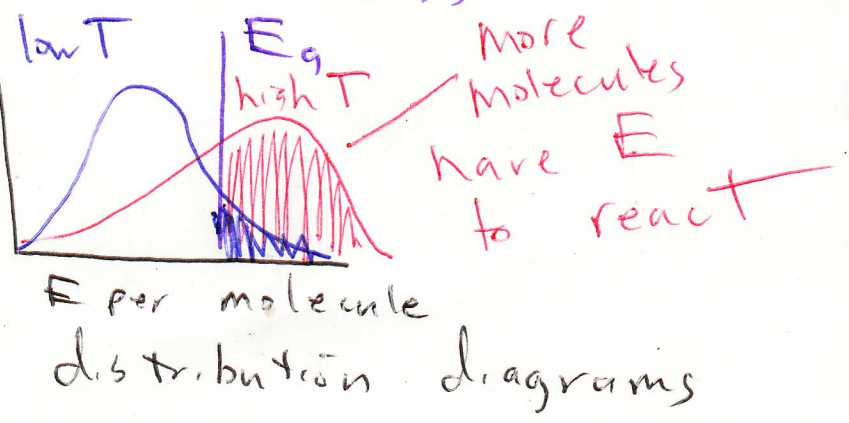
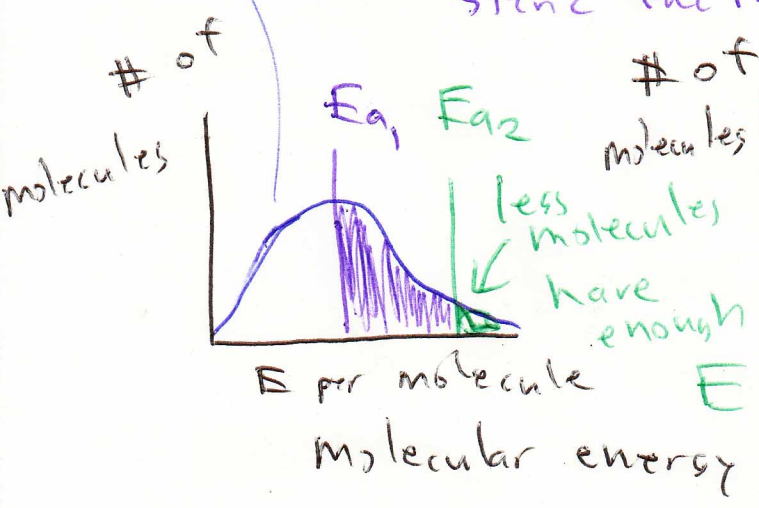
• There is no relationship between the # of reagents in the overall stoichiometric equation and the rate law.

Arrhenius expression

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

one T

E_a - activation energy
 A - steric factor (fraction of productive collisions)

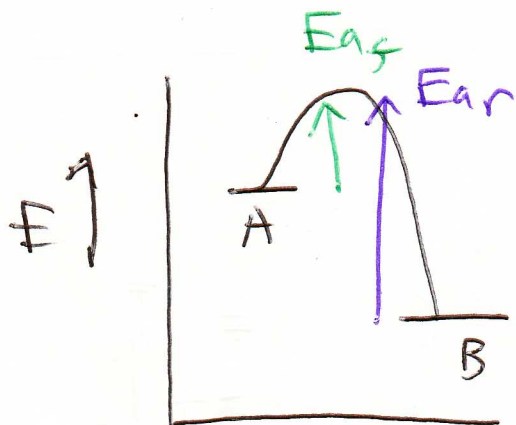


distribution diagrams

Idealized rxn: $A \rightleftharpoons B$

3

- Both forward + reverse rxns are one-step, 1st order w/ same A (stoic factor)



@ Equilibrium $R_f = R_r$

$$R_f = k_f [A]$$

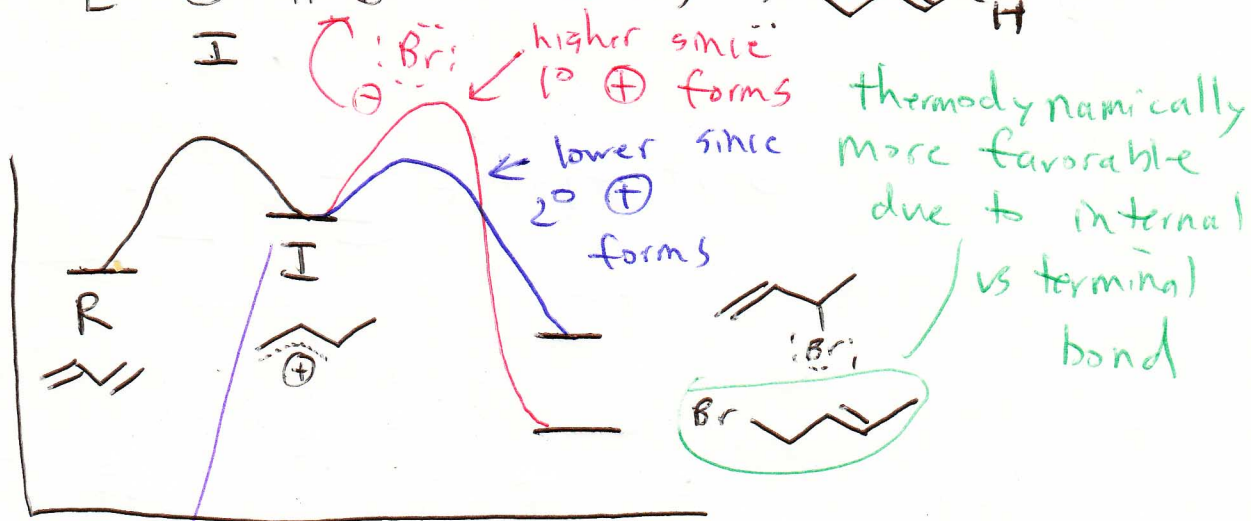
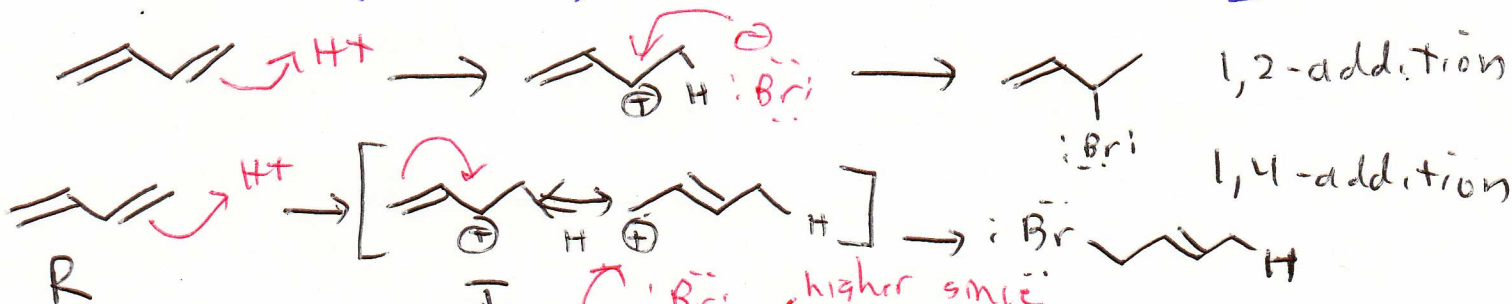
$$R_r = k_r [B]$$

$$k_f [A] = k_r [B]$$

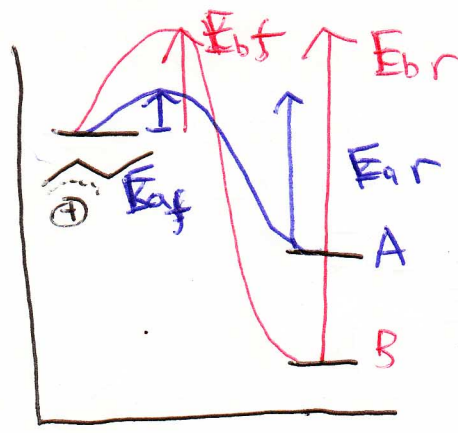
@ Equilibrium, rates may be equal, but rate constants are

not, which will influence [reactants] vs [products]

• Since $E_{ag} < E_{ar}$, $k_f > k_r \rightarrow [A] < [B]$



The intermediate is a delocalized carbocation; there are not two distinct carbocations. Any energy difference that occurs takes place once the bond w/ bromide starts to form.



$$E_{br} > E_{ar} > E_{bf} > E_{af}$$

• At low enough temp, a rxn can become effectively irreversible (reverse barriers larger than the forward barriers). In this situation,

the forward rxn with the lowest barrier is going to determine the product that forms; Since $E_{bf} > E_{af}$, A will predominate, even though thermodynamically it is not the most favored product → kinetic control

• At high T, all rxn rates increase and the rxn can become reversible. This means, the kinetic product may form initially, but has a chance to reverse and potentially form B. Since B is the lowest energy product, the rate of its reverse rxn is the lowest, so B will accumulate over time

→ thermodynamic control

