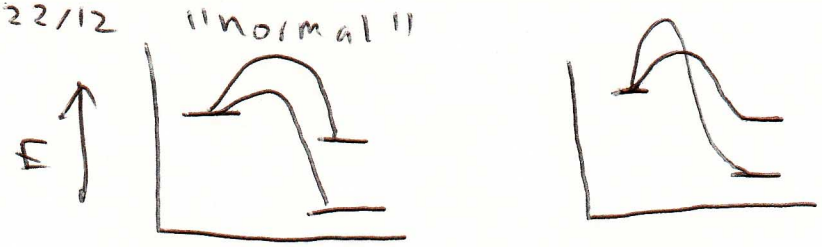
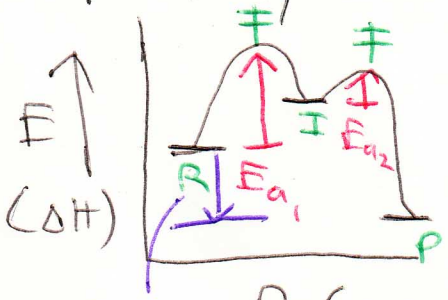
"normal"



reaction coordinate diagram – shows the change in energy of a rxn along the most-likely reaction pathway (2D simplification of a multi-dimensional graph)



R-reactants I-intermediates P-products

‡-transition state

• # of transition states = # of individual steps

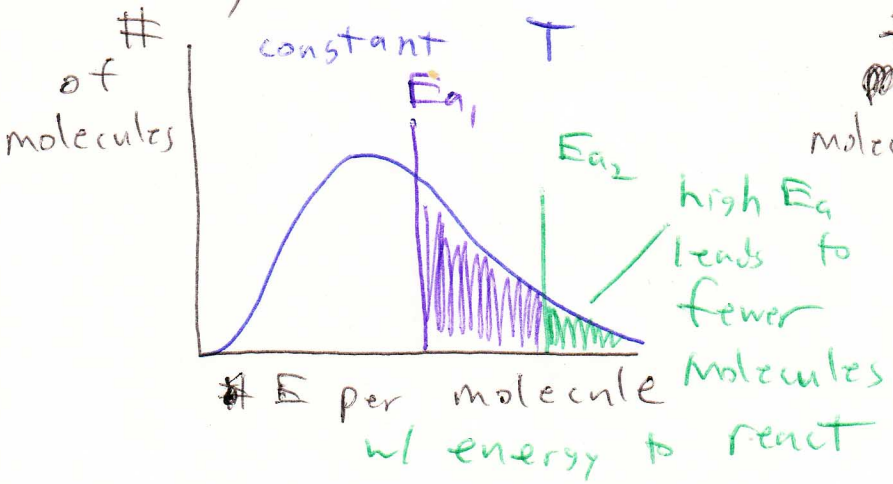
ΔH_{rxn} Ea activation energy

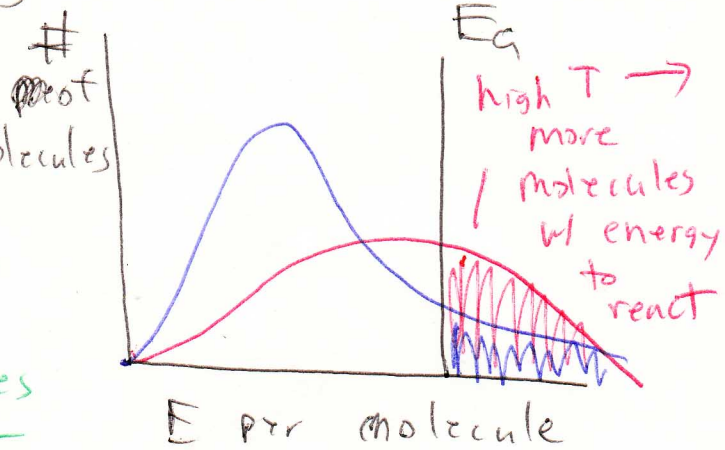
• Only those reagents involved in the rate-limiting step (RLS) are found in the rate law.

• There is not relationship between the overall stoichiometric equation, the rate law, and # of steps.

Arrhenius expression: $k = A e^{-E_a/RT}$ (A: steric factor (fraction of productive collisions); E_a: Activation energy; T: temperature)

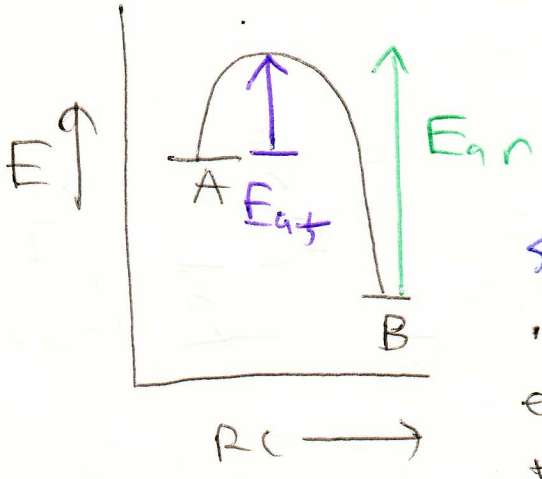
Energy distribution diagrams





Idealized rxn: $A \rightleftharpoons B$

- Assume both forward + reverse rxns are single-step unimolecular reactions
- Assume $A_f = A_r$



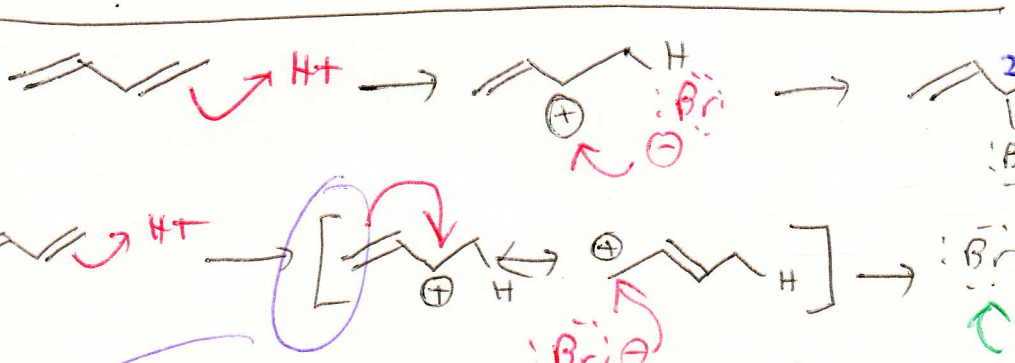
@ Equilibrium $R_f = R_r$

$R_f = k_f[A]$; $R_r = k_r[B]$

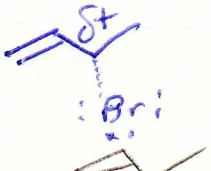
$k_f[A] = k_r[B]$

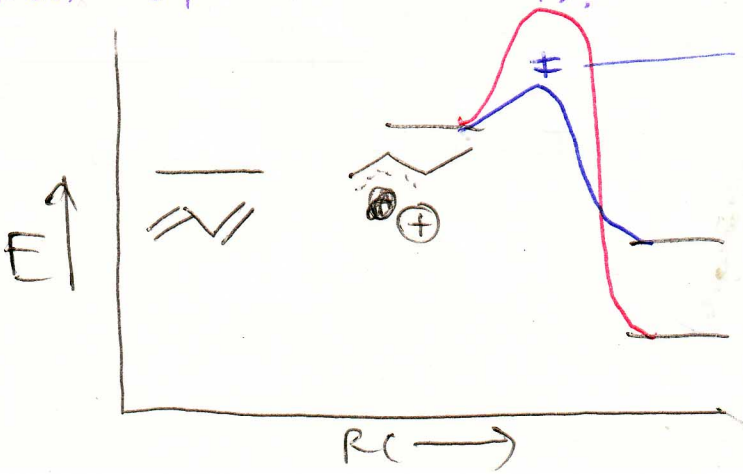
Since $E_{af} < E_{ar}$, $k_f > k_r$

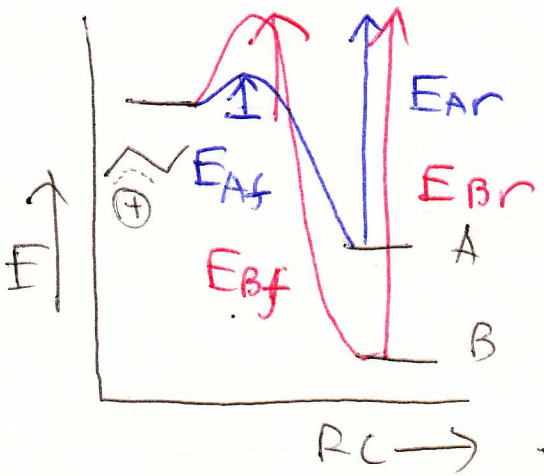
- Although rates are equal at equilibrium, rate constants do not have to be; which will affect the [reactants] vs [products]



The intermediate is a delocalized carbocation; there are not two distinct carbocations. Any difference of energy that may result occurs once bond formation w/ Br^- starts.







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

- At low enough temp, a rxn can become effectively irreversible, since both reverse E_a's are larger than the forward. In this situation, the forward rxn w/ the lowest E_a will occur, even if it causes a less thermodynamically favorable product to form → kinetic control
- At high T, all reaction rates increase (and the rxn is reversible). Although the kinetic product may still initially form, it has the chance to reverse and potentially form B. Since B is the lowest-energy product, it is less likely to reverse and will therefore accumulate over time → thermodynamic control

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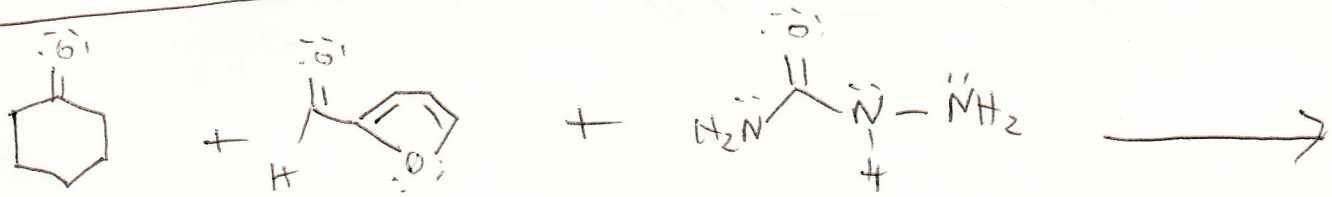
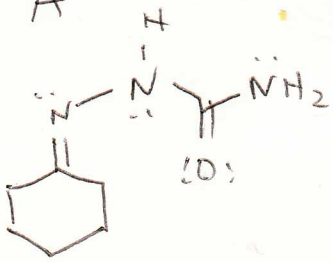
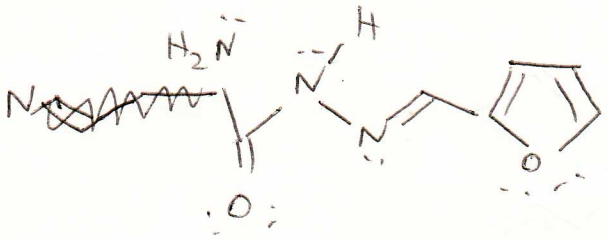


A + B + semicarbazone →



A'



B'

semicarbazone