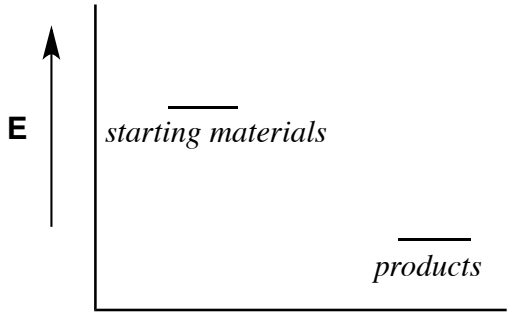
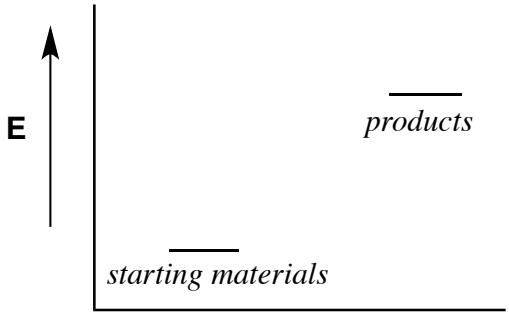
Chapter 6: Chemical Reactivity and Mechanisms

[Sections: 6.5-6.6]

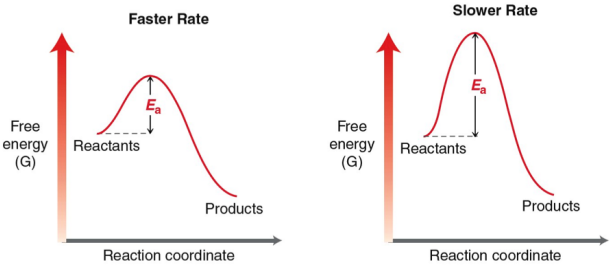
Reaction Coordinates and Activation Energies





- *the ΔE between starting materials and products determines the final equilibrium distribution*
- *the activation barrier, or activation energy (E_a), is the energy required to initiate a reaction*
- *the activation barrier determines the rate of a reaction*
- *the "rate" of a reaction is a measure of how quickly products are formed (or, conversely, how quickly starting materials are lost)*
- *high E_a = slow reaction; small E_a = fast reaction*
- *generally, large –ΔE = small E_a (but not always)*
- *the highest point of energy = transition state (TS)*
- *endothermic reactions also have activation barriers and TS*

comparing the rates of two reactions



for a reaction to occur:

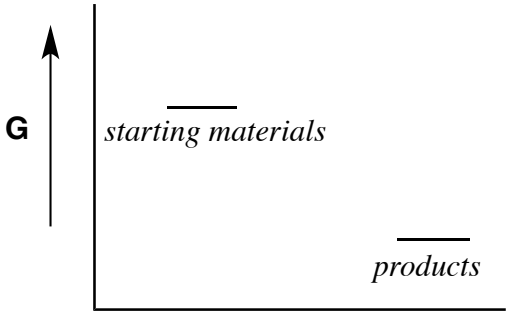
- *molecules must collide*
- *molecules must have proper orientation*
- *molecules must have sufficient energy*

$HCl + NaOH \longrightarrow$

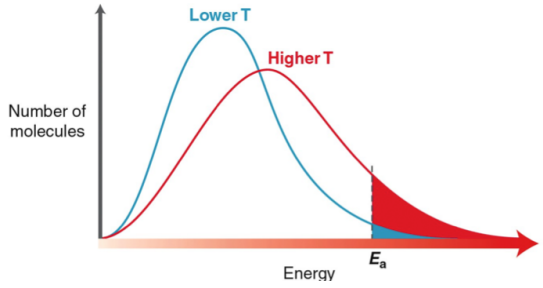
$Cl—H \quad \overset{\ominus}{O}H$

if a reaction doesn't occur:

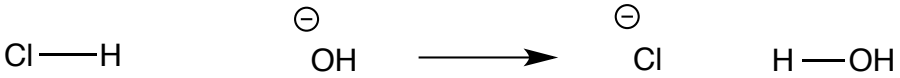
- *increase temperature*
- *change solvent*
- *include a catalyst*



the effect of temperature on rate



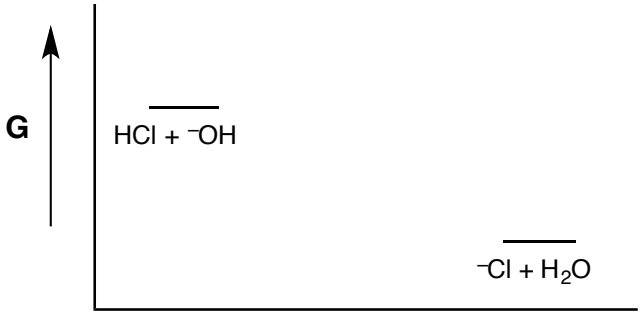
Transition States



curved arrow notation

- *from areas of electron density*
- *towards areas of low electron density (positive charge)*
- *shows movement of electrons, NOT atoms!*

Predict the transition state:

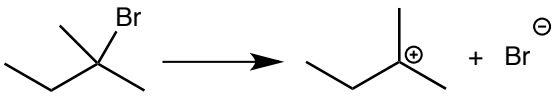


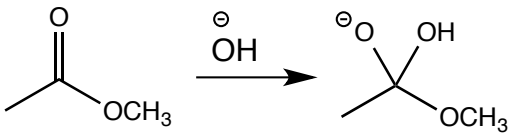
- *a transition state structure is characterized by partially made and/or broken bonds*
- *it occurs at the energy maximum between starting materials and products since it always has partial bonds*
- *it has a fleeting lifetime*
- *we can predict the structure from knowledge of the reaction*

Examples: Provide curved arrows to describe the transformation and predict the transition states for each of the reactions below:

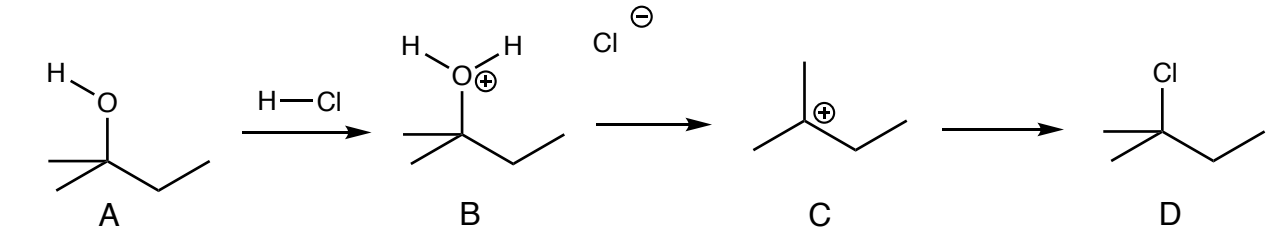
Plan of attack:

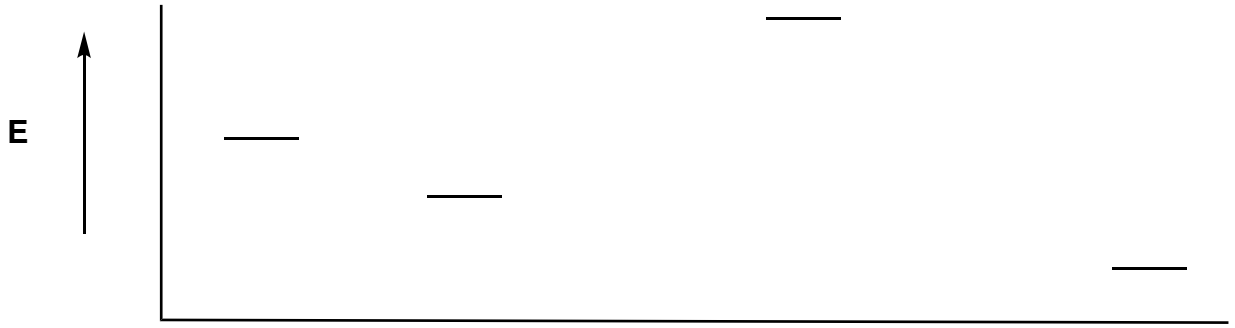
i. identify the constituent parts on either side of the equation
2. identify which bonds have been made and/or broken
3. draw good curved arrows that form and or break the necessary bonds
4. any bonds formed or broken are *partial* (i.e. ---) in the TS
5. any charges formed or lost are *partial* (i.e. δ) in the TS





Multiple-Step Reactions





A → B
B → C
C → D

exo/endo? uni/bi?

overall rxn exo/endo?
intermediates?
TS?
RDS?

- *the overall reaction may be exothermic or endothermic*
- *each individual step is characterized as being exo or endothermic*
- *each step has an activation barrier associated with it (E_a)*
- *each step is characterized as unimolecular (one molecule required to get to the transition state) or bimolecular (two molecules required to get to the transition state)*
- *starting materials vs. products vs. intermediates vs. transition states*
- *the step with the highest Ea will be the slowest step in the reaction*
- *the slow step in the reaction = rate determining step (RDS)*
- ***differences in rates of reactions can be attributed to differences in what takes place during the RDS***

Chapter 6 *Essential Concepts*

1. Be able to define and identify starting materials, products, intermediates and transition states on a reaction coordinate.
2. Understand how to estimate activation energies from a reaction coordinate and how activation energy impacts reaction rates
3. Know the three factors that are critical for reactions to take place
4. Know how and why temperature affects the rate of a reaction and how solvent and catalysts can affect reactivity
5. Be able to use curved arrows to either describe how a reaction step has taken place or, if given reaction arrows, how to predict the product outcome
6. Be able to draw a transition state for a reaction and identify which bonds are being made and/or broken and the partial charges on involved atoms.
7. Understand what a rate determining reaction is and how to locate which step is rate determining given a reaction coordinate