**Energy/Reaction Coordinate Diagrams**

*Thermodynamics, Kinetics*

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**Thermodynamic Quantities**

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]

\[ \Delta G, \Delta H, \Delta S, \Delta E \text{ are state functions} \]

Gibbs standard free energy change (\( \Delta G^o \))

Enthalpy (\( \Delta H^o \)): the heat given off or absorbed during a reaction

Entropy (\( \Delta S^o \)): a measure of freedom of motion

If \( \Delta S^o \) is small, compared to \( \Delta H^o \), then \( \Delta G^o \approx \Delta H^o \)

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**Example: Photosynthesis**

Energy Capture (Endergonic Reaction)

\[ n \text{ CO}_2(g) + n \text{ H}_2\text{O}(g) + \text{energy} \rightarrow \]

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]

\[ \Delta H^o = ? \]

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**Entropy (\( \Delta S \))**

* Most reactions are **EXOTHERMIC** and \( \Delta G^o = \Delta H^o = (-) \)
* But, there are many **ENDOTHERMIC** reactions such as photosynthesis that occur.
* In this case, entropy is significant and must be considered in order for the reaction to be spontaneous and \( \Delta G^o = (-) \)
* **ENTROPY (\( \Delta S \))** is molecular disorder and related to an increase in molecular degrees of freedom, in this case rotational and vibrational energy states.

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**Photosynthesis**

Energy Capture (Endergonic Reaction)

\[ n \text{ CO}_2(g) + n \text{ H}_2\text{O}(g) + \text{energy} \rightarrow \]

\[ n \text{ CO}_2(g) + n \text{ H}_2\text{O}(g) \]
**Photosynthesis**  
Energy Capture (Endergonic Reaction)  
\[ n \text{ CO}_2(g) + n \text{ H}_2\text{O}(g) + \text{energy} \rightarrow (\text{CH}_2\text{O})_n(aq) + n \text{ O}_2(g) \]  
Energy  
\[ \Delta E_{\text{Reaction}} = E_{\text{Product}} - E_{\text{Reactants}} \]  
\[ \Delta E_{\text{Reaction}} = (+) \]  
An Endergonic (Endergonic Reaction)  
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  
\[ \Delta G^\circ = ? \Delta S^\circ = ? \]

**Burning Gasoline (Octane)**  
Exothermic Reactions: Energy Release  
\[ 2 \text{C}_8\text{H}_{18} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O} \]  
Energy  
\[ \Delta E_{\text{Reaction}} = E_{\text{Product}} - E_{\text{Reactants}} \]  
\[ \Delta E_{\text{Reaction}} = (-) \]  
Products  
\[ 16 \text{CO}_2 + 18 \text{H}_2\text{O} \]  
\[ \Delta H^\circ = \Delta H^\circ = (-) \]  
Are isomers the same thermodynamically?
**Thermodynamics & Kinetics**

- \( \Delta G, \Delta H, \Delta S, \Delta E \) are state functions; independent of reaction pathway. They do not predict the rate of reaction, which depends on pathway.
- The reaction rate (the number of effective collisions in a period of time) relates to many factors.
  1. The concentrations of the reactants
  2. The phase of the reactants (s,l,g)
  3. The activation energy (temperature)
  4. The pressure for gas phase reactions
  5. Geometry/steric effects of reactants and intermediates
  6. Catalysts

**Kinetics – Rate Laws**

The rate is mathematically represented by a rate constant \( k \) and the concentration of reactants:

\[
\text{Rate} = k \cdot [\text{reactants}] 
\]

The ORDER is represented by \( x \) and \( y \) in the rate law equation:

\[
\text{Rate} = k [A]^x [B]^y 
\]

The overall order = \( x + y \)

**Energy of Activation (Ea)**

- Notice the activation energy \( (E_a) \); it is the critical energetic barrier that must be overcome in order for a reaction to occur.
- There are different \( E_a \) barriers for different reactions, and \( E_a \) may vary for the same reaction depending on its mechanism.

**Factors that Affect Rates**

- Temperature is a measure of a system’s AVERAGE kinetic energy.
- How does temperature affect the number of collisions and relate to the Energy of activation?
Which reaction would likely require a higher boiling organic solvent for the reaction to occur above room temperature in a reasonable amount of time?

**Question**

**Answer**

- B. Higher temperature = higher energy = more collisions

Factors that Affect Rates

- Geometry and steric effects impact the reaction rate.
- A catalyst can have a profound influence, lowering the Energy of activation and altering the mechanism.

Energy Diagrams

**Kinetics vs. Thermodynamics**

- KINETICS relates to pathway, mechanism and Ea
- THERMODYNAMICS relates to a state function: $\Delta G, \Delta H, \Delta S, \Delta E$

Energy Diagrams

**Kinetics vs. Thermodynamics**

- Which products are thermodynamically favored (i.e. more stable)? C + D (lower free energy)
- Which products are kinetically favored (i.e. form faster)? C+ D (lower Ea)

**Question**

A reaction solvent with a relatively low b.p. favors products E + F.

- **A = True; B = False**
Question

For this energy diagram, which pathway is kinetically favored?

Red = A; Blue = B

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Question

For this energy diagram, which pathway is thermodynamically favored?

Red = A; Blue = B

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Question

The reaction on the right does not occur at room temperature.

- A lower boiling solvent will favor the formation of C + D.

A = True; B = False

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Energy Diagrams
Transition States

- A transition state occurs at an energy maxima.
  The one on the left shows a Br-bond breaking and a Cl-bond forming.
- Transition states cannot be isolated or directly observed.
- What might explain why transition states are so unstable?

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Energy Diagrams
Intermediates

- An intermediate occurs at an energy minimum.
  - Intermediates often exist long enough to be observed.
  - Bonds are NOT in the process of breaking or forming.
For each of the diagrams below, will the transition state structure be more similar to the reactants or the products?

**The Hammond Postulate**

T.S. in exothermic reactions resemble reactants; endothermic resemble products

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**Question**

Does the T.S. below resemble the bromide or chloride?

A) Bromide; B) Chloride

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**Nucleophiles and Electrophiles React**

**General Organic Reactions**

- Draw all possible resonance structures for the following molecule.
- Consider all formal charges and partial $\delta^+$ and $\delta^-$ charges. Label each of those atoms nucleophilic (nu) or electrophilic (el) in each resonance structure.

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**Nucleophiles and Electrophiles**

**General Organic Reactions**

- Using $\text{OH}^-$ as a nucleophile and $\text{H}^+$ as an electrophile, draw all possible products for their respective reactions with your resonance structures showing arrows to show electron movements.