

# Chapter 6: Chemical Reactivity and Mechanisms

**Today! Chapter 6:**

**Kinetics and Thermodynamics (6.1-6.6)**

**Friday Chapter 6: Mechanisms (6.7 - 6.10, 6.12)**  
**(We'll come back to 6.11 later.)**

Calculate the enantiomeric excess for a sample in which the Ratio of diastereomers determined is 3.5:1.

$$\text{enantiomeric excess (e.e.)} = \frac{\text{excess of a single enantiomer}}{\text{entire mixture}}$$

$$= \frac{3.5-1}{3.5+1} \times 100\%$$

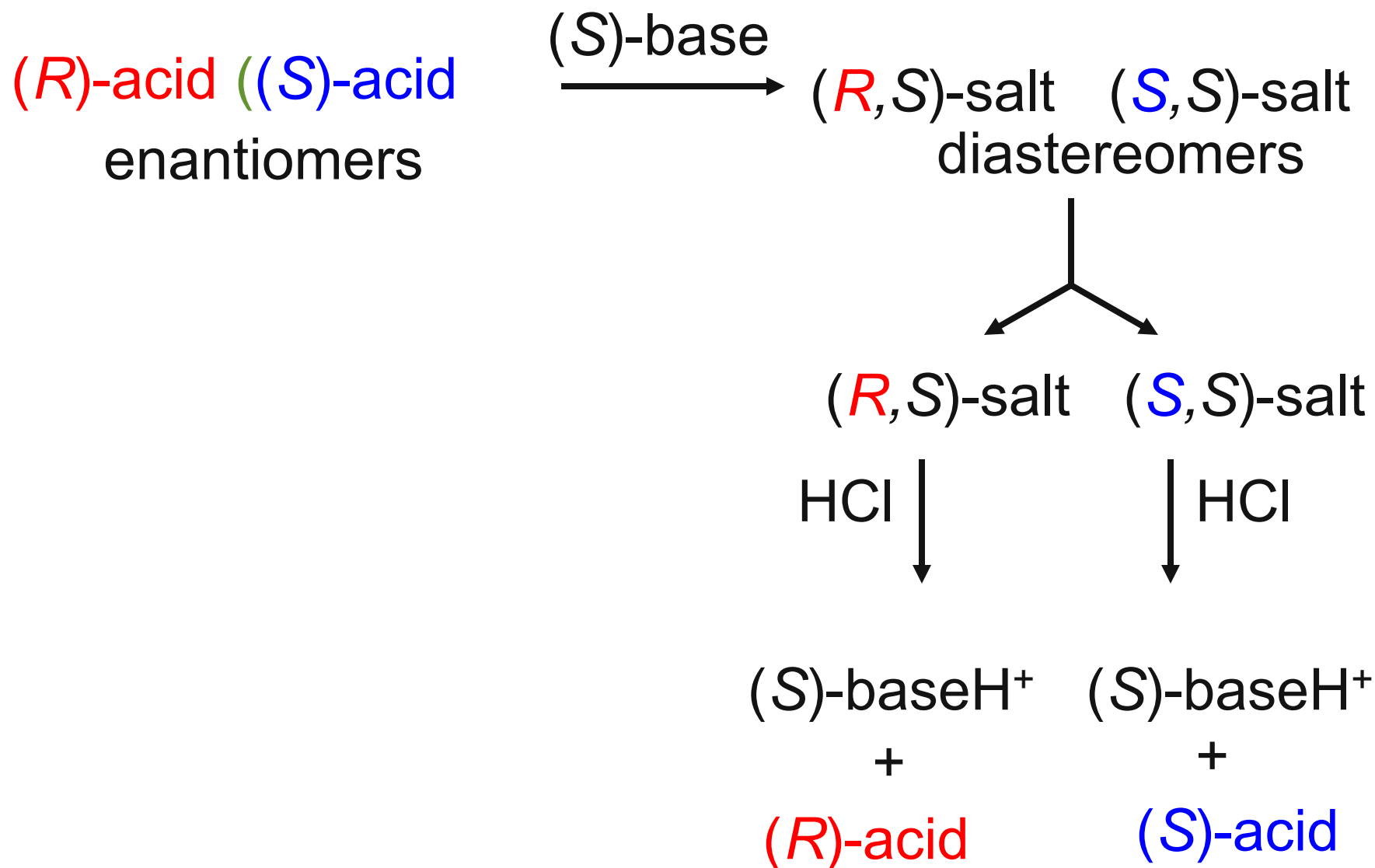
$$\text{e.e.} = 55\%$$

Or if you think about it – If I have 7/9ths and 2/9ths in a mixture (total of 9/9ths) – the e.e. is going to be (7-2)/9ths = 5/9ths

# Resolution of Enantiomers

- To separate compounds from one another, most methods take advantage of the differences in physical properties of the compounds to be separated:
  - Distillation separates compounds with different boiling points.
  - Recrystallization separates compounds with different solubilities.
  - Can you think of more methods of separation or purification?

# Resolution of a Racemic Mixture



Thermodynamics is the branch of chemistry that deals with the energy changes accompanying chemical and physical changes.



$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}_2\text{O}][\text{HA}]}$$

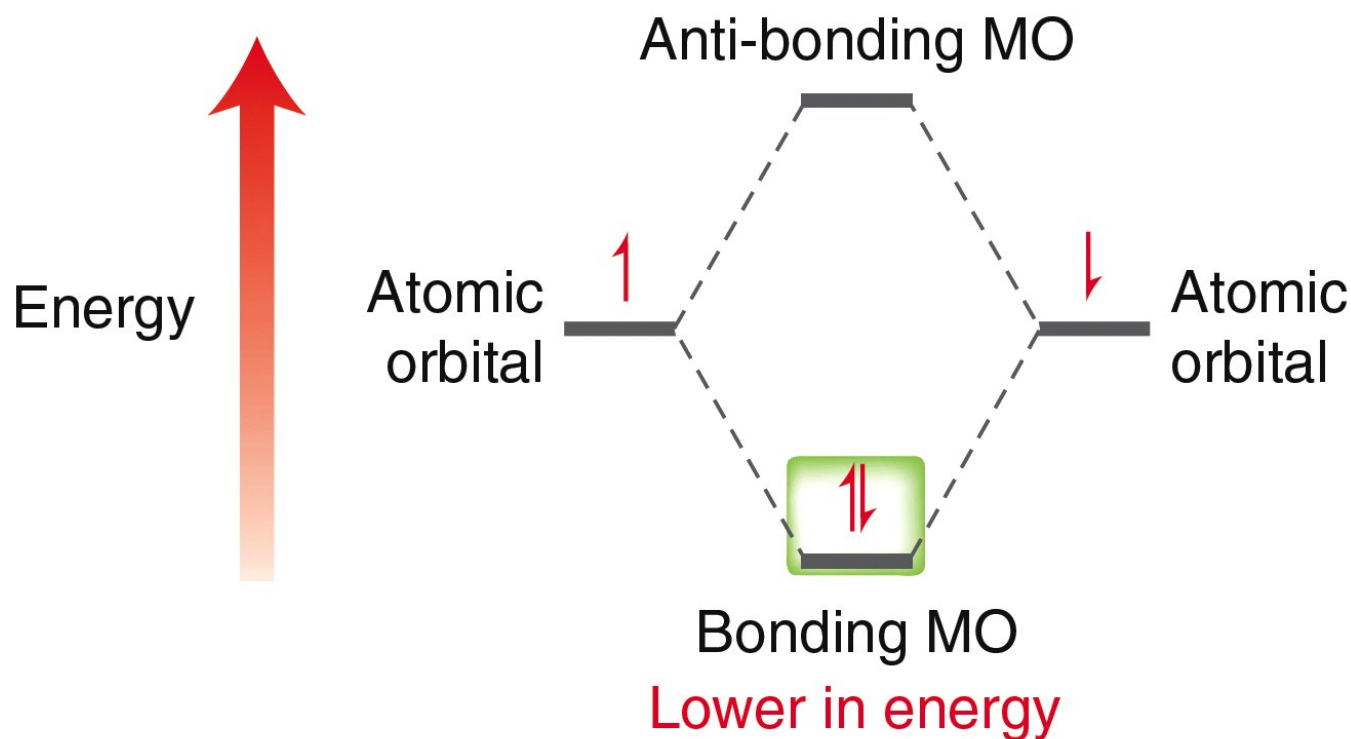


$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[\text{C}]^s [\text{D}]^t}{[\text{A}]^m [\text{B}]^n}$$

■ Reactions can go either forward or backward to reach equilibrium

# Enthalpy

- Enthalpy ( $\Delta H$  or  $q$ ) is the heat energy exchange between the reaction and its surroundings at constant pressure.

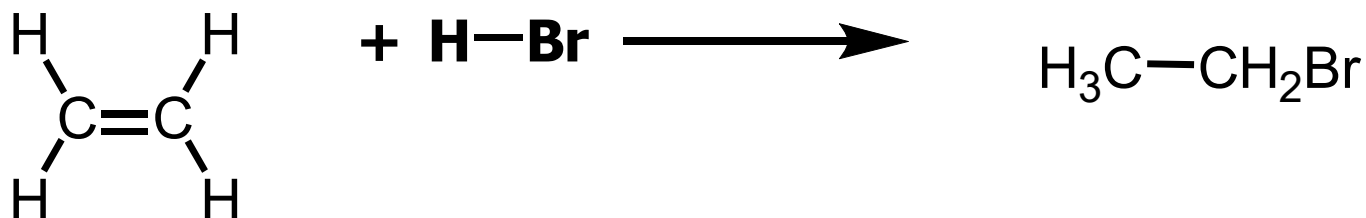


# Enthalpy – Bond Dissociation Energies

	KJ/MOL	KCAL/MOL		KJ/MOL	KCAL/MOL
Bonds to H			C–C bonds		
H–H	435	104	CH <sub>3</sub> –CH <sub>3</sub>	368	88
H–CH <sub>3</sub>	435	104	CH <sub>3</sub> CH <sub>2</sub> –CH <sub>3</sub>	356	85
H–CH <sub>2</sub> CH <sub>3</sub>	410	98	(CH <sub>3</sub> ) <sub>2</sub> CH–CH <sub>3</sub>	351	84
H–F	569	136	CH <sub>3</sub> –Br	293	70
H–Cl	431	103	CH <sub>3</sub> –I	234	56
H–Br	368	88	CH <sub>3</sub> –OH	381	91
H–I	297	71	X–X		
H–OH	498	119	F–F	159	38
			Cl–Cl	242	58

Similar table on **p.238** in your book.

$\Delta H^\circ$  can be calculated from bond dissociation energies



$$\pi \text{ bond of ethene} \quad \overline{\Delta H^\circ} = 63 \text{ kcal/mol}$$

$$\text{C}-\text{H} \quad \overline{\Delta H^\circ} = 101 \text{ kcal/mol}$$

$$\text{H}-\text{Br} \quad \overline{\Delta H^\circ} = 87 \text{ kcal/mol}$$

$$\text{C}-\text{Br} \quad \overline{\Delta H^\circ} = 69 \text{ kcal/mol}$$

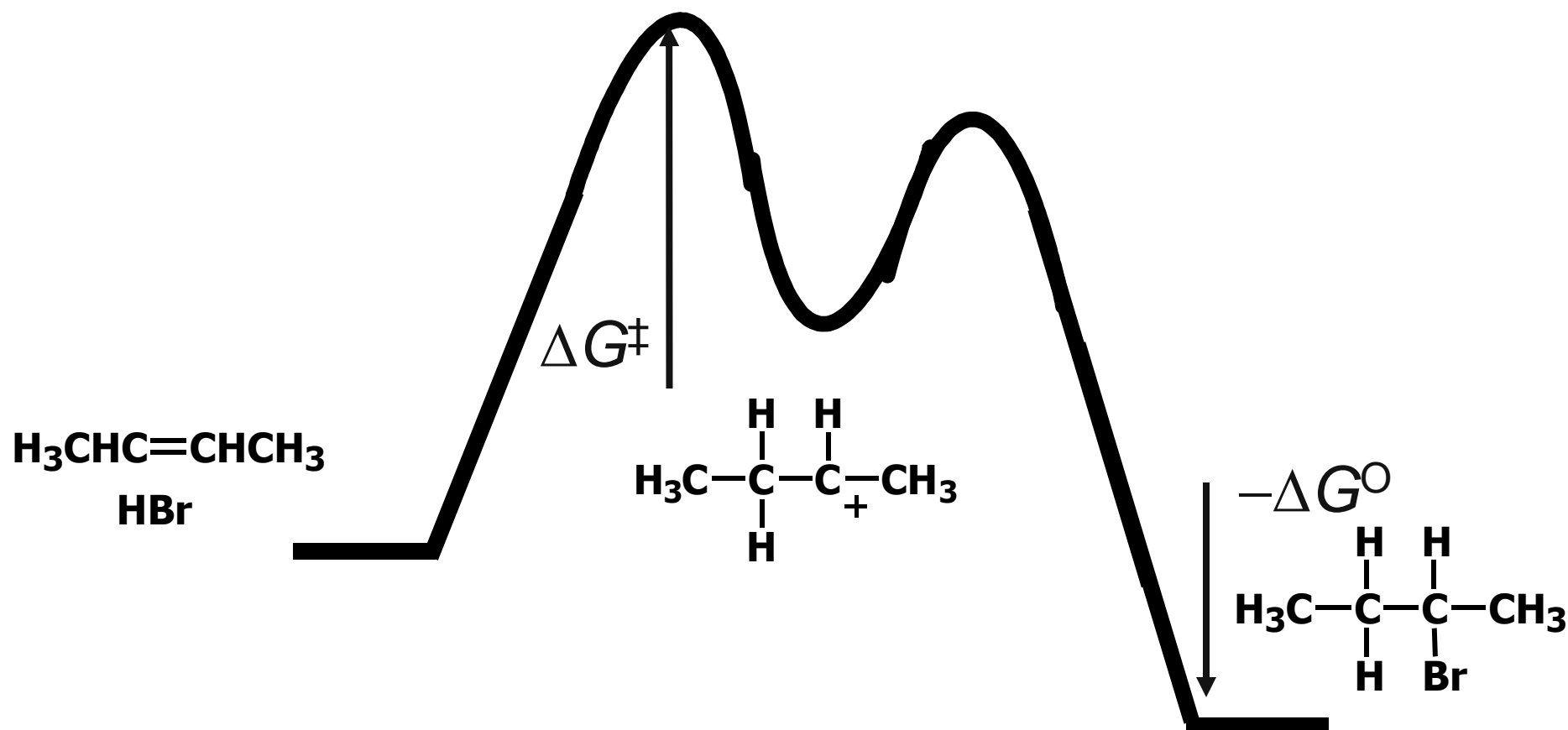
$$H^\circ_{\text{total}} = 150 \text{ kcal/mol}$$

$$H^\circ_{\text{total}} = 170 \text{ kcal/mol}$$

$$\begin{aligned} \Delta H^\circ \text{ for the reaction} &= \Delta H^\circ \text{ for bonds being broken} - \Delta H^\circ \text{ for bonds being formed} \\ &= 150 \text{ kcal/mol} - 170 \text{ kcal/mol} \\ &= -20 \text{ kcal/mol} \end{aligned}$$

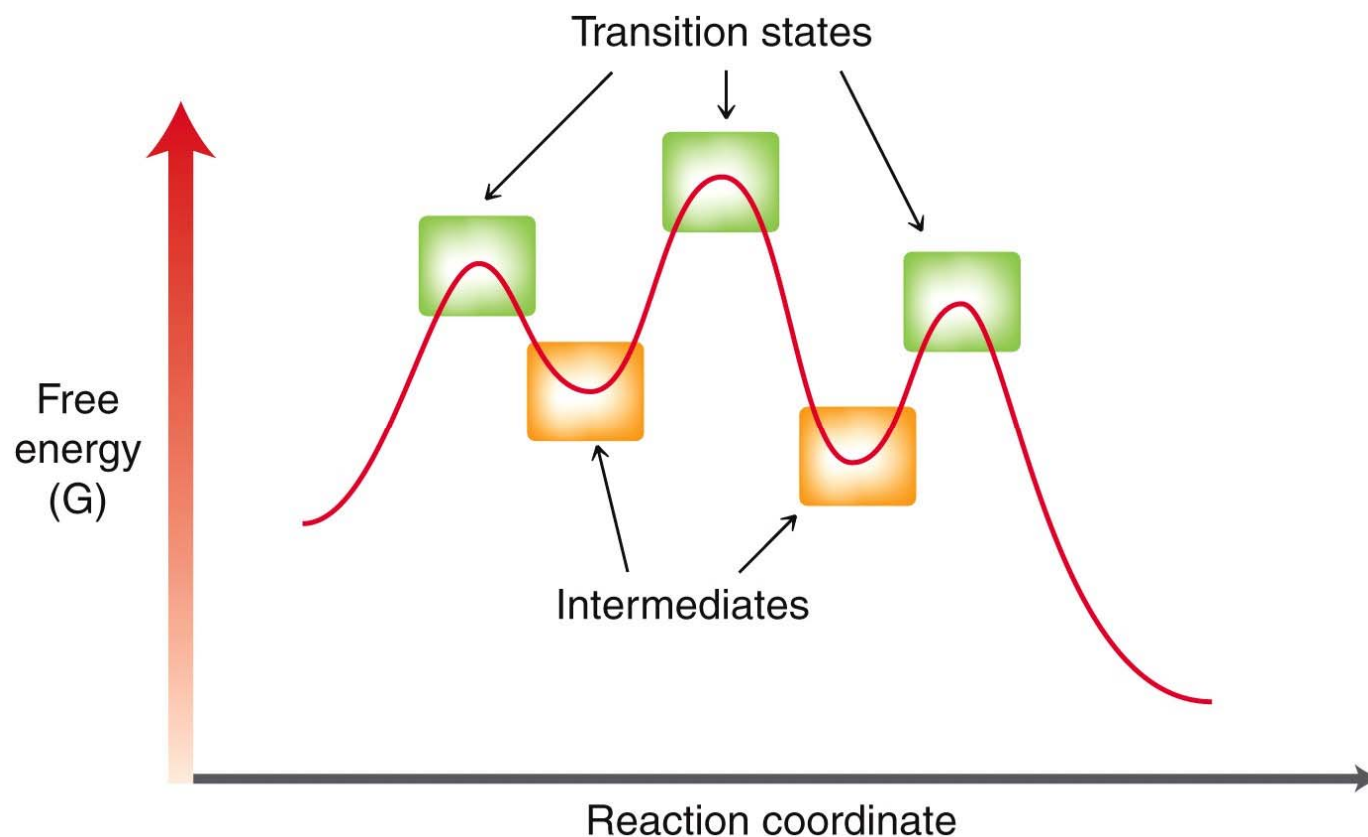


# Electrophilic Addition of HBr to 2-Butene



The rate-limiting step controls the overall rate of the reaction

# Energy Diagrams – Transition States vs. Intermediates

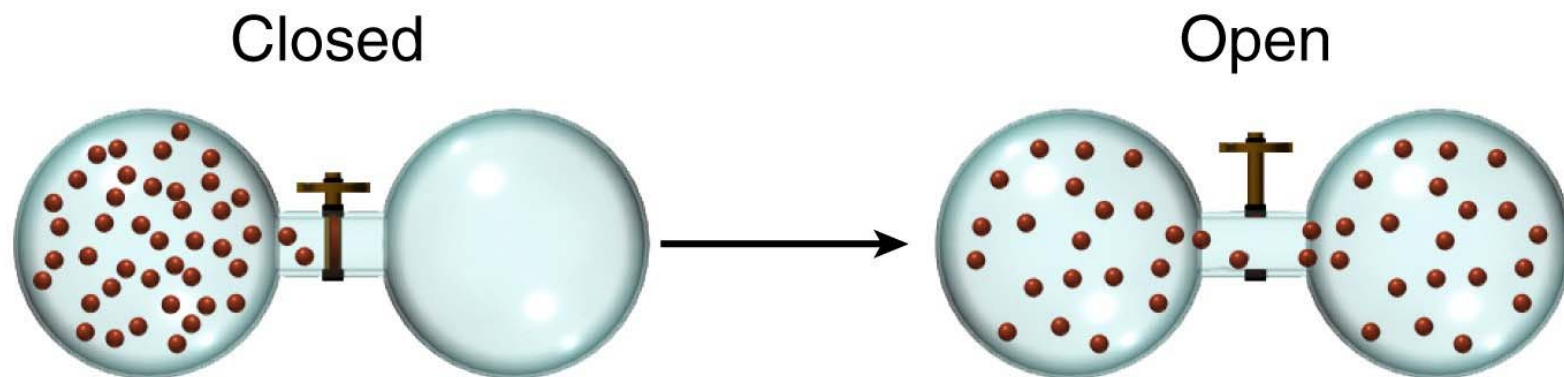


Transition states have partial bonds

Intermediates or intermediate products have fully formed bonds

# Entropy $\Delta S$

- Consider the ENTROPY and ENTHALPY change for the following process:



- The number of possible translational distributions for the molecules increases with increasing volume. HOW?

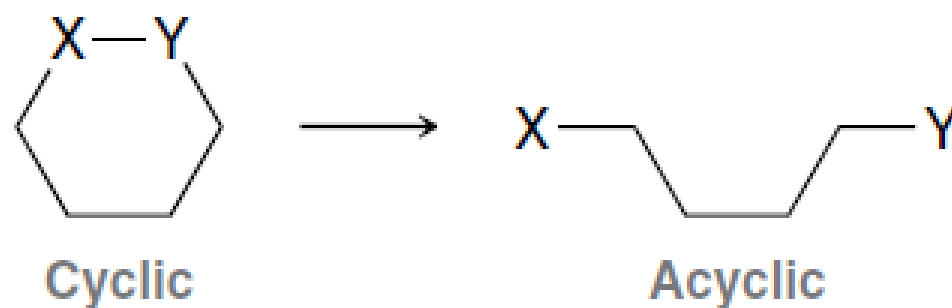
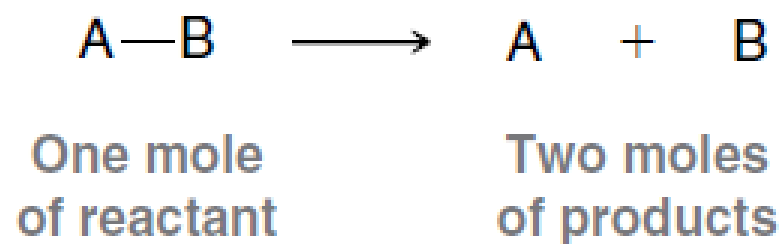
Entropy is freedom of motion - often described as randomness

$+\Delta S$  means the products have more freedom than the reactants

# Entropy $\Delta S$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

- For each of the reactions below, predict the sign for  $\Delta S_{\text{sys}}$ .



# Gibbs Free Energy

From  $K_{eq}$ , we can calculate the Free Energy

- The ratio of products to reactants is controlled by their relative **Gibbs free energy**
- This energy is released on the favored side of an equilibrium reaction
- The change in Gibbs free energy between products and reactants is written as “ $\Delta G$ ”

Gibbs standard free energy change ( $\Delta G^\circ$ )

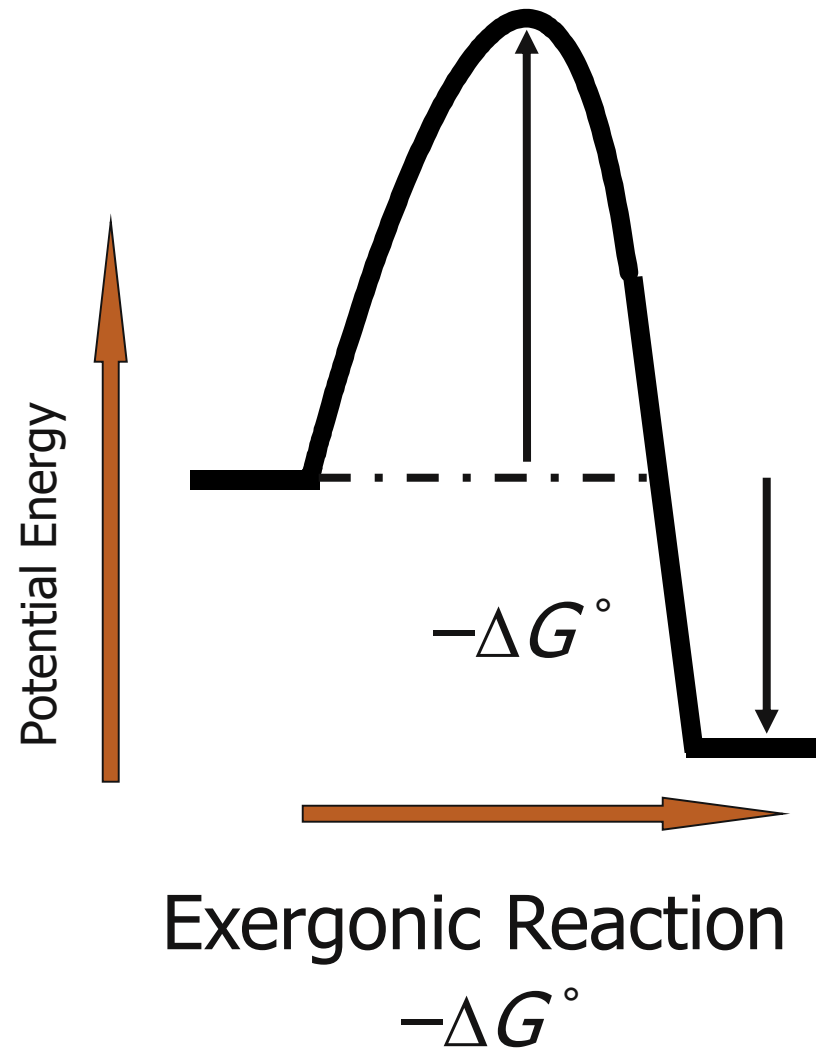
$$\Delta G^\circ = -RT \ln K_{eq} = -2.303RT(\log K_{eq})$$

$$\Delta G^\circ = \text{free energy products} - \text{free energy reactants}$$

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

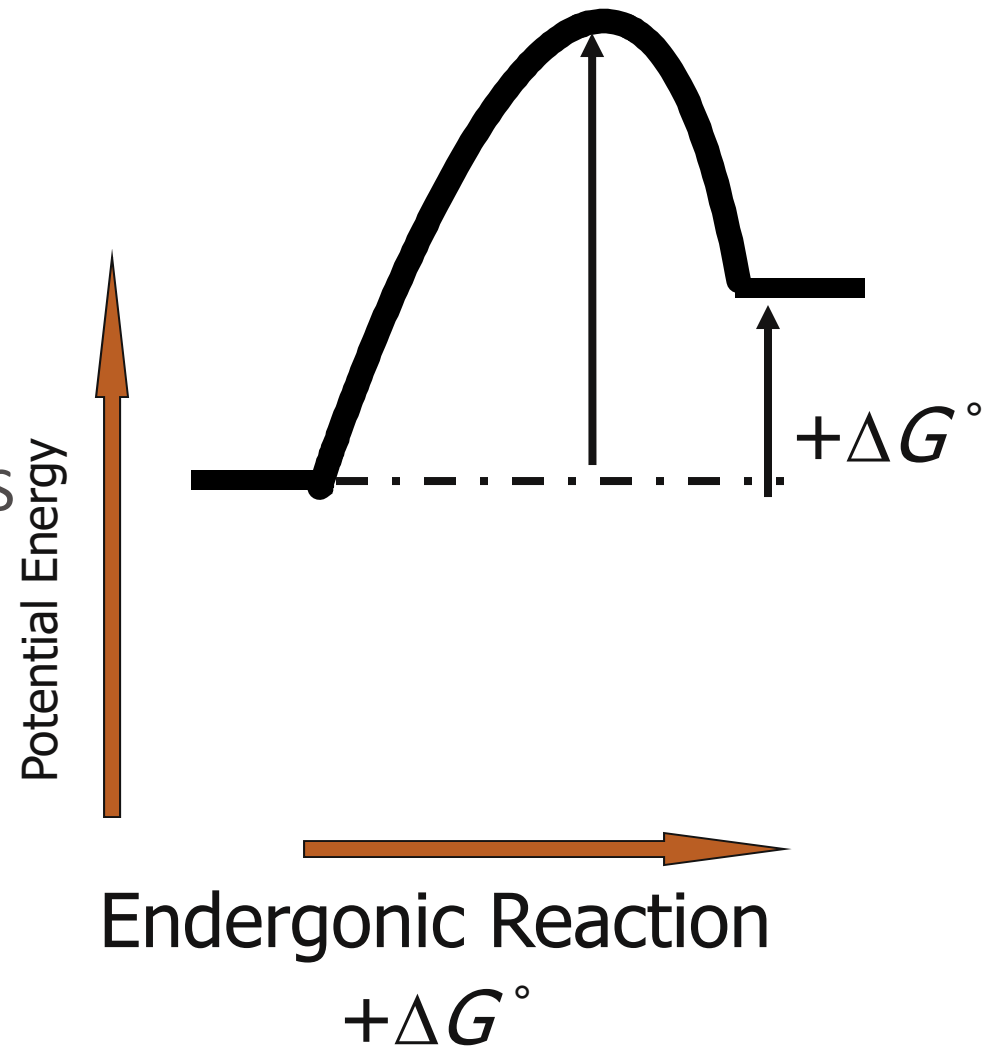
# Gibbs Free Energy $\Delta G$

- If a process at a given temperature is calculated to have a (-)  $\Delta G$ , the process is EXERGONIC.
  - It will be SPONTANEOUS and favor the products.
  - Note that  $G$  is plotted rather than  $H$ .
- Energy is released to the surroundings



# Gibbs Free Energy $\Delta G$

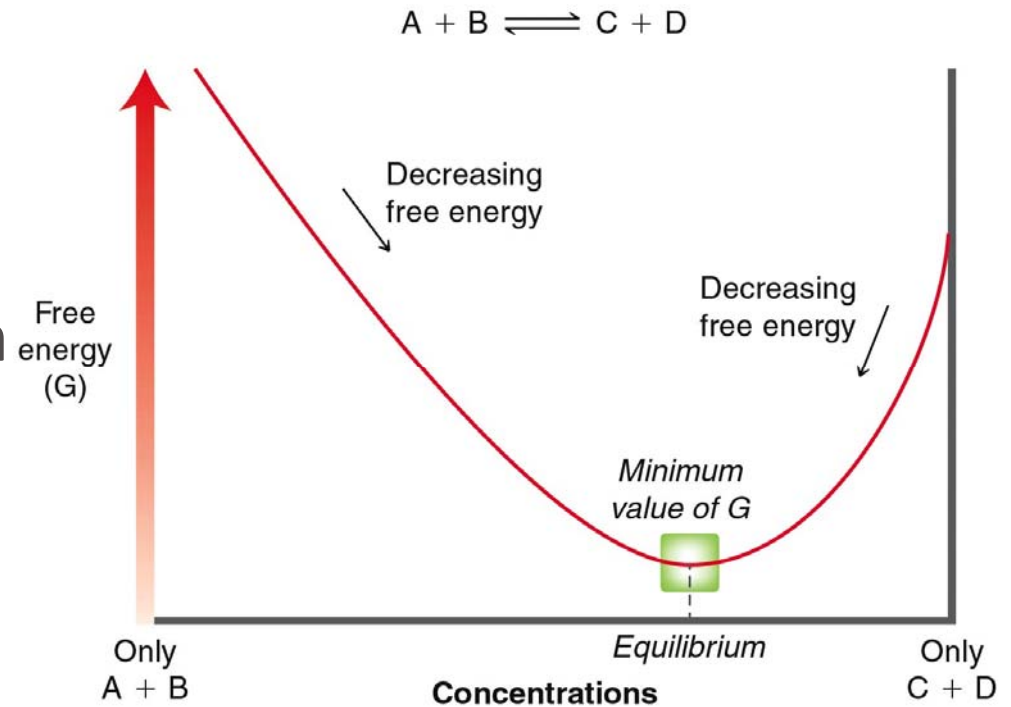
- If a process at a given temperature is calculated to have a (+)  $\Delta G$ , the process is ENDERGONIC.
  - It will be NONSPONTANEOUS and favor the reactants.
  - What does it mean exactly to FAVOR the reactants?
- Energy is absorbed from the surroundings



# Equilibria



- Equilibrium is also the state with the lowest free energy overall.
- Why does the equilibrium mixture have the lowest  $G$ ?
- How would  $S_{\text{tot}}$  compare for a mixture of A, B, C, and D versus only C and D?



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Kinetics is the study of reaction rates – how fast reactants form and products are consumed.

Rate of a reaction =

$$\left( \begin{array}{c} \text{number of collisions} \\ \text{per unit time} \end{array} \right) \times \left( \begin{array}{c} \text{fraction with} \\ \text{sufficient energy} \end{array} \right) \times \left( \begin{array}{c} \text{fraction with} \\ \text{proper orientation} \end{array} \right)$$



Rate  $\sim$  [A]



Rate =  $k[\text{A}][\text{B}]$

Second order rate constant



Rate =  $k[\text{A}]$

First order rate constant



Rate =  $k[\text{A}]^2$

Second order rate constant

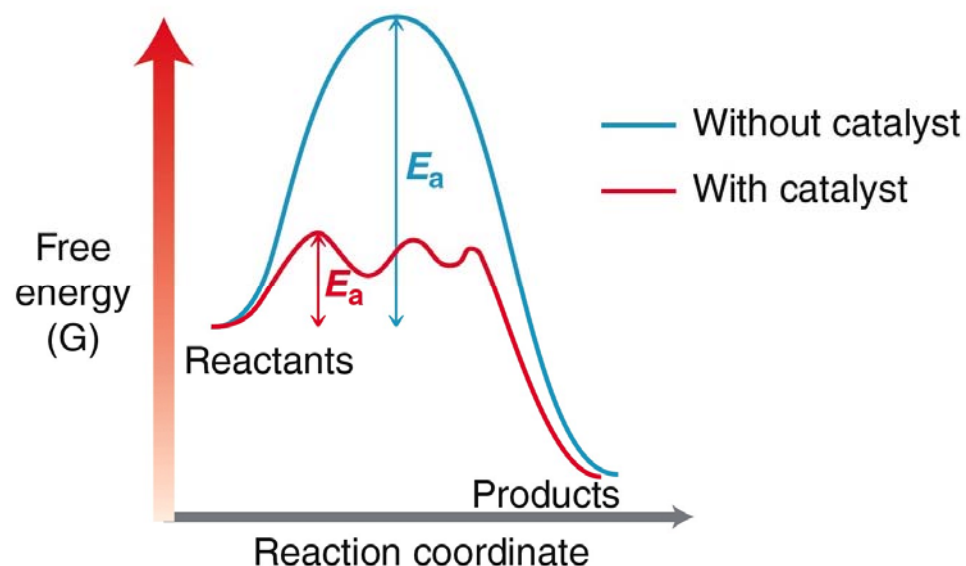
*The rate-limiting step is the step that controls the overall rate of the reaction.*

# Kinetics

- The reaction rate (the number of collisions that will result in product production in a given period of time) is affected by multiple factors.
  1. The concentrations of the reactants
  2. The activation energy
  3. The temperature
  4. Geometry and sterics
  5. The presence of a catalyst

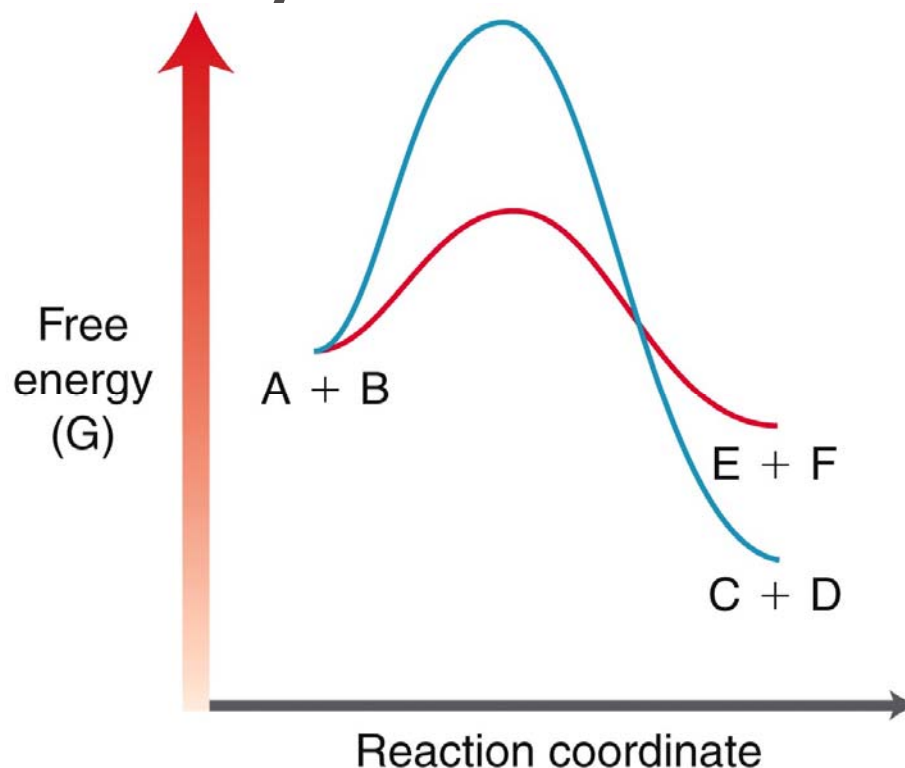
# Kinetics – Factors that Affect Rates

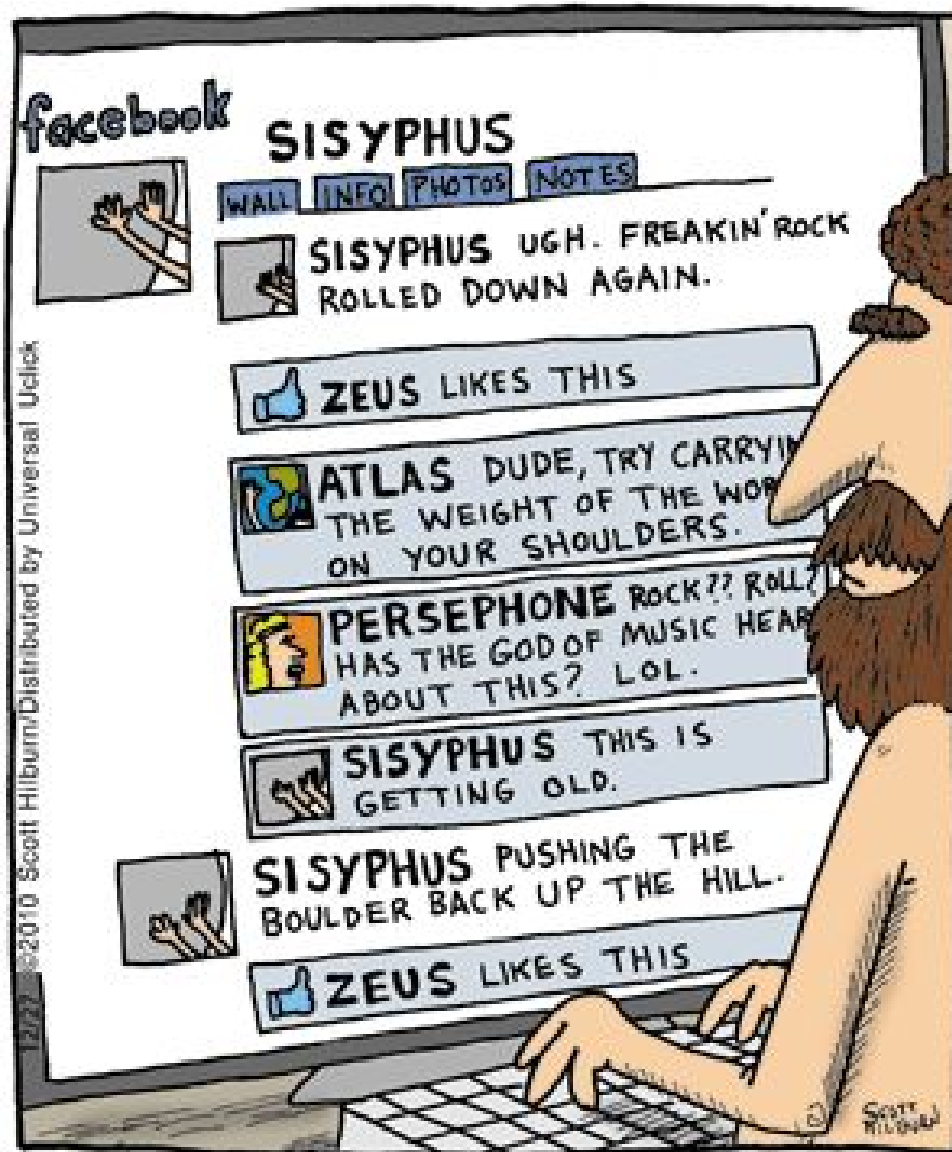
- How might geometry and sterics affect the reaction rate?
- How might the presence of a catalyst affect the reaction rate?



# Energy Diagrams – Kinetics vs. Thermodynamics

- For this energy diagram, which pathway is kinetically favored?
- Which pathway is thermodynamically favored?
- How can temperature be used to control which set of products predominate?





**Friday Chapter 6: Mechanisms (6.7 - 6.10, 6.12)**  
**(We'll come back to 6.11 later.)**

*Suggested Homework Problems Chapter 5*  
#4, 9, 19, 23, 31, 36, 38 (a-c), 39 (a-e), 45, 55

*Suggested Homework Problems Chapter 6*  
#4, 7, 11, 17, 24, 26, 28, 34-36