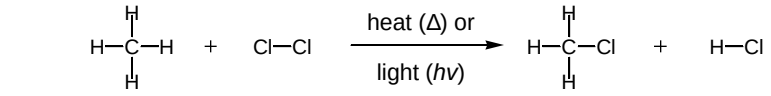
Chemistry 5.12 Spring 2003, Week 3 / Day 2
Handout #7: Lecture 11

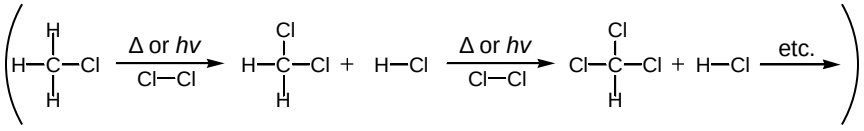
Outline

IX. Free Radical Reactions **(Read Chapter 4)**
- A. Chlorination of Methane **(4-2)**
  - 1. Mechanism **(4-3)**
- B. Review of Thermodynamics **(4-4,5)**
- C. Review of Kinetics **(4-8,9)**
- D. Reaction-Energy Diagrams **(4-10)**
  - 1. Thermodynamic Control
  - 2. Kinetic Control
  - 3. Hammond Postulate **(4-14)**
  - 4. Multi-Step Reactions **(4-11)**
  - 5. Chlorination of Methane **(4-7)**

Suggested Problems: 4-35–37,40,43

IX. A. Radical Chlorination of Methane





- Why is light or heat necessary?
- How fast does it go?
- Does it give off or consume heat?
- How fast are each of the successive reactions?
- Can you control the product ratio?

To answer these questions, we need to:

1. Understand the mechanism of the reaction (arrow-pushing!).

2. Use thermodynamics and kinetics to analyze the reaction.

1. Mechanism of Radical Chlorination of Methane (Free-Radical Chain Reaction)

Free-radical chain reactions have three distinct mechanistic steps:

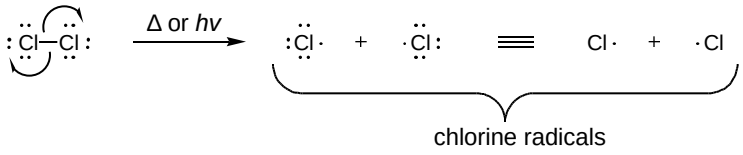
- **initiation step:** generates reactive intermediate

- **propagation steps:** reactive intermediates react with stable molecules to generate other reactive intermediates (allows chain to continue)

- **termination step:** side-reactions that slow the reaction; usually combination of two reactive intermediates into one stable molecule

Initiation Step: Cl_2 absorbs energy and the bond is homolytically cleaved.

(Remember to use fishhook arrows!)



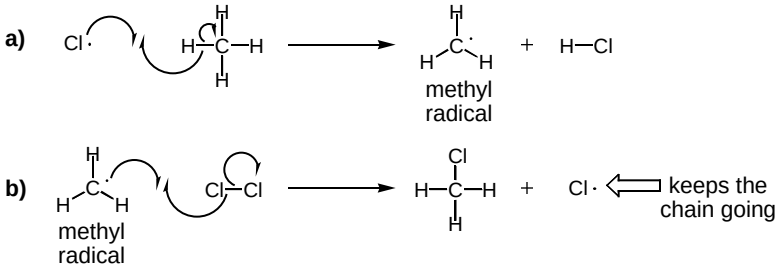
- The first-formed reactive intermediate is a chlorine radical.

reactive intermediate: short-lived species that reacts quickly as it is formed

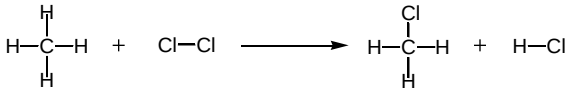
radical: species with an unpaired electron (usually just draw the unpaired electron)

Propagation Steps: The Meat of the Reaction

a) Chlorine radical abstracts a hydrogen from methane to form a methyl radical.
b) Methyl radical abstracts a chlorine from Cl_2 to form product and another chlorine radical



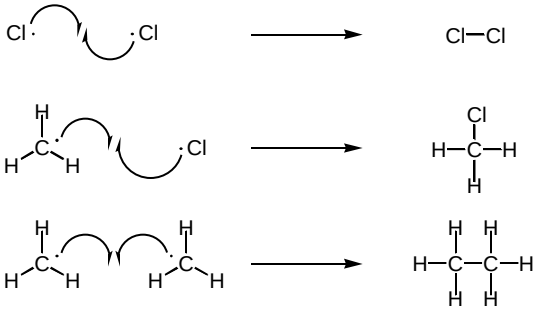
Sum:



- The sum of the propagation steps is the overall chlorination reaction.

Termination Steps: Unproductive Steps

- Consumption of reactive intermediates (radicals) without generation of new ones.



- Termination steps slow down and eventually stop the chain reaction.
- Termination reactions become most important at the end of a reaction, when there are very few reactant molecules left.

Before we investigate the energetics of this particular reaction, let's review some general thermodynamics and kinetics.

B. Thermodynamics: energy changes that accompany chemical and physical transformations

- **Thermodynamics** are used to describe systems that are in their **equilibrium** state

A $\rightleftharpoons$ **B**

Equilibrium Constant: $K_{eq} = \frac{[products]}{[reactants]} = \frac{[B]}{[A]}$

Gibbs Free Energy: $\Delta G = \Delta H - T\Delta S = -RT(\ln K_{eq})$

R = 1.987 cal/K·mol **T = temperature (K)**

Gibbs Free Energy: $\Delta G = \Delta H - T\Delta S = -RT(\ln K_{eq})$

entropy (ΔS): disorder or freedom of motion; an increase in entropy ($\Delta S > 0$) is favorable

enthalpy (ΔH): the amount of heat evolved or consumed in a reaction (bonds broken/formed)

endothermic: $\Delta H > 0$; need to put energy into the reaction (uphill)

exothermic: $\Delta H < 0$; energy given off by the reaction (downhill)

- In the Gibbs Free Energy equation, the enthalpy term (ΔH) is generally much larger than the entropy term ($T\Delta S$). In other words, the change in enthalpy (bond breaking/bond formation) usually governs the favorability of a reaction.

Standard Gibbs Free Energy: $\Delta G° = \Delta G$ at 298K and 1 atm

The 1.4 Rule: At 25 °C (298 K), every **1.4 kcal/mol change in $\Delta G°$** results in a **factor of 10 difference in K_{eq}** (useful for estimating conversion of a reaction).

conversion: percentage of starting material that is converted to products at equilibrium

[A] ⇌ [B]

$\Delta G°$	K_{eq}	ratio [B] : [A]	conversion [B]/([B] + [A])
–4.2	10^3	1000 : 1	> 99.9%
–2.8	10^2	100 : 1	99%
–1.4	10	10 : 1	91%
0	1	1 : 1	50%
+1.4	10^{-1}	1 : 10	9%
+2.8	10^{-2}	1 : 100	< 1%
+4.2	10^{-3}	1 : 1000	< 0.1%

Note: Similar rules apply at different temperatures: 100 °C (1.7), 50 °C (1.5), 0 °C (1.3), –78 °C (0.9), etc.

C. Kinetics: Reaction Rates

reaction rate: how fast products appear and reactants disappear (measured experimentally)

rate equation: relationship between concentration of reactants and observed reaction rate (determined experimentally and used to deduce reaction mechanisms)

[A] + [B] ⇌ [C] + [D]

observed rate = $-d[A]/dt = d[C]/dt$
$= k_r[A]^a[B]^b$
(k_r = rate constant)

a: order of the reaction with respect to A
b: order of the reaction with respect to B
a + b: overall order of the reaction

} These all depend on the reaction mechanism.

- The rate constant is dependent on the activation energy and the temperature.

Arrhenius Equation: $k_r = Ae^{-Ea/RT}$

***A* = Arrhenius prefactor**

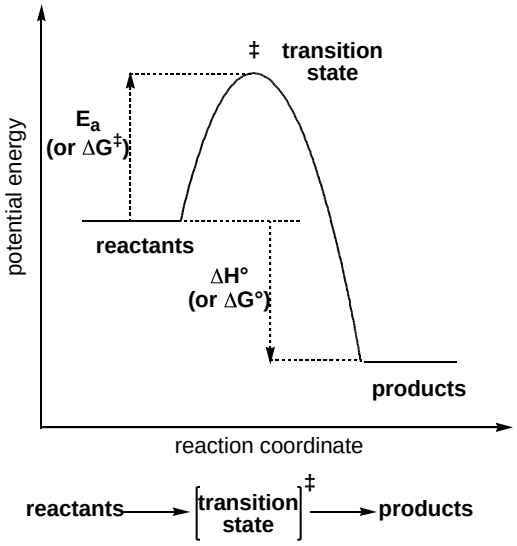
E_a = activation energy (minimum energy the reactants must have for the reaction to occur)

- In this class, we'll also refer to the activation energy of a reaction in terms of $\Delta G^{\ddagger}$ (**free energy of activation**).

Enough equations! Now let's look at pictures!

D. Reaction-Energy Diagrams

- A **reaction-energy diagram** is a plot of the potential energy as reactants are converted to products (also called a **reaction-coordinate diagram**); **very useful for understanding thermodynamics and kinetics!**

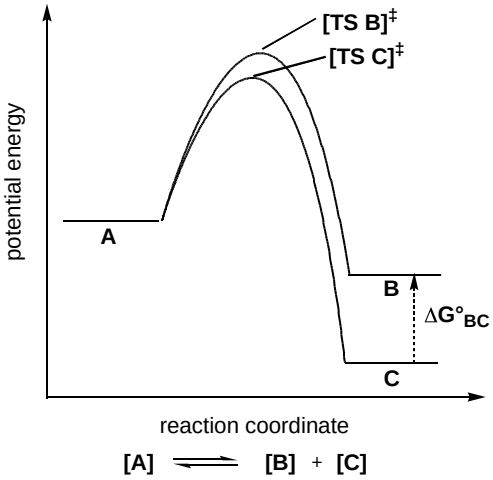


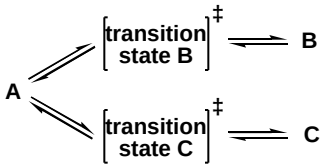
reactants → [transition state]‡ → products

- X-axis is the progress of the reaction.
- Y-axis can be either ΔG or ΔH.
- The **transition state** is state of highest energy between reactants and products.
- Transition states are transient (written in brackets).
- Transition states are unstable, do not have a finite lifetime, and **cannot be isolated**.

If more than one product is formed in a reaction, what determines the ratio of products? It depends on the reaction!

Thermodynamic Control: When the reaction is reversible (reactants and products are in equilibrium), the reaction is said to be under **thermodynamic control**, and the product ratio is determined by the relative energies of the products.

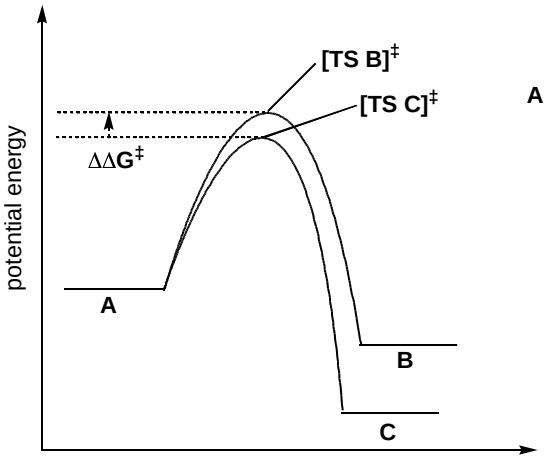


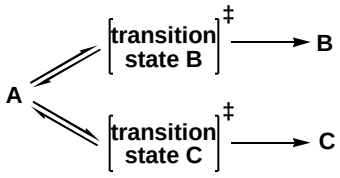


[A] ⇌ **[B]** + **[C]**

$\Delta G°_{BC}$ ($G_B - G_C$)	product ratio ([B] : [C])
+4.2	1 : 1000
+2.8	1 : 100
+1.4	1 : 10
0	1 : 1

Kinetic Control: When the products are formed irreversibly, the reaction is said to be under **kinetic control**, and the product ratio is determined by the difference in the activation energies (the difference in the energies of the transition states ($\Delta\Delta G^{\ddagger}$)).





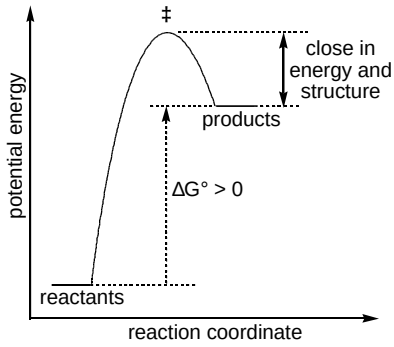
[A] ⟶ **[B]** + **[C]**

$\Delta\Delta G^{\ddagger}$ ($\Delta G^{\ddagger}_B - \Delta G^{\ddagger}_C$)	product ratio ([B] : [C])
+4.2	1 : 1000
+2.8	1 : 100
+1.4	1 : 10
0	1 : 1

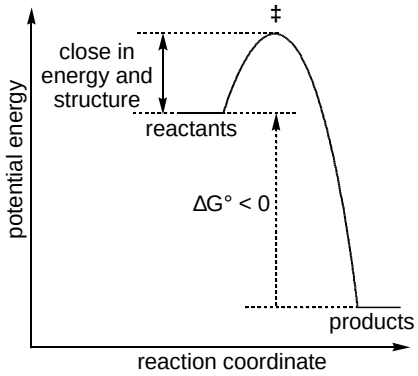
Is there any way to estimate the relative energies of transition states?

Hammond Postulate: Related species that are similar in energy are similar in structure.

The structure of a transition state resembles the structure of the closest stable species.



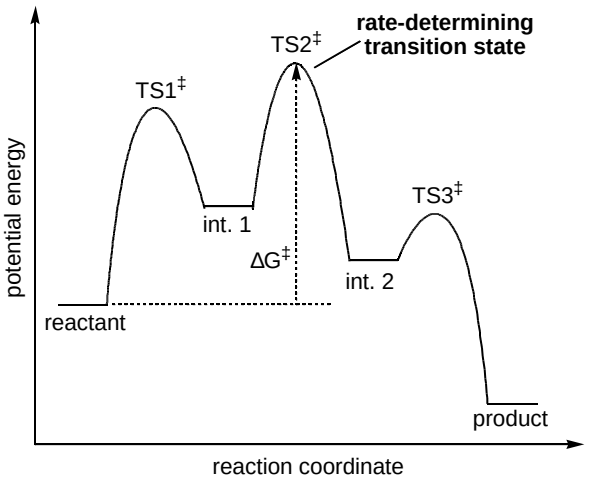
- **Endothermic reactions have late transition states.**
- In an **endothermic** reaction, the transition state is **product-like** (close in energy and structure to the product).
- In an endothermic reaction, anything that changes the energy of the product will also change the energy of the transition state.



- **Exothermic reactions have early transition states.**
- In an **exothermic** reaction, the transition state is **reactant-like** (close in energy and structure to the reactant).
- In an exothermic reaction, anything that changes the energy of the reactant will also change the energy of the transition state.

- This will come in very handy when we start thinking about radical halogenation reactions!

- **Multi-step reactions have more than one transition state.**



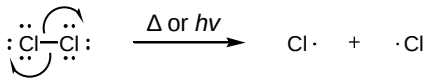
- The local maxima are transition states.
- The local minima are **reactive intermediates** (short-lived species that are never present in high concentration because they react quickly as they are formed).
- The overall reaction rate is determined by the highest energy transition state.
- The **rate-determining step** is the step with the highest energy transition state.

5. Reaction-Energy Diagram for Radical Chorination of Methane

- Now we have the tools to examine the energetics of a free-radical halogenation.
- We can use **bond dissociation energies** to estimate ΔH° for each step (p. 134 in Wade).

bond dissociation energy: amount of energy required to **homolytically** break a bond

initiation step:



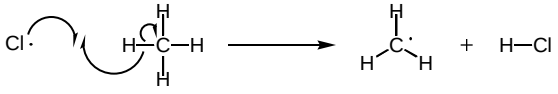
ΔH° = BDE = 58 kcal/mol

- It is important that the initiation step involves cleavage of a fairly weak bond like Cl–Cl.

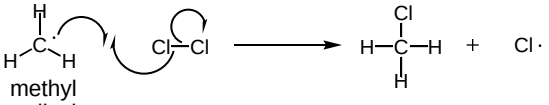
- Other than that, the initiation step is not important in the overall thermodynamics and kinetics of the reaction. This is because one initiation step starts a chain that can go through thousands of propagation cycles.

- The termination steps are also unimportant in the overall energetic picture of the reaction, so let's focus on the propagation steps.

Propagation Steps:

1) 

break $H_3C–H$:	$\Delta H° = +104$ kcal/mol
form H–Cl:	$\Delta H° = -103$ kcal/mol
step 1:	$\Delta H°_1 = +1$ kcal/mol

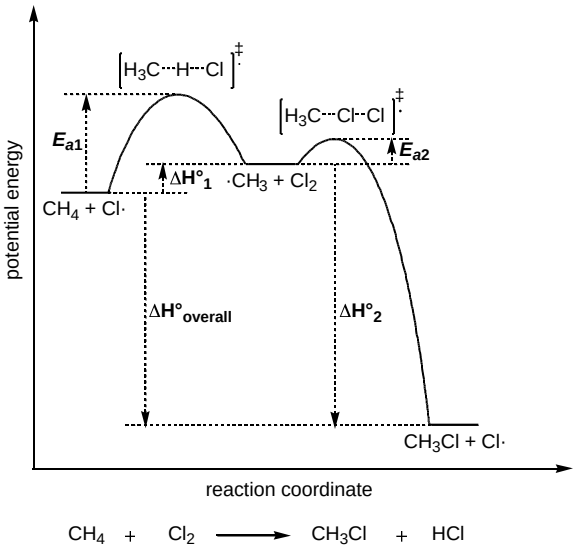
2) 

methyl radical

break Cl–Cl:	$\Delta H° = +58$ kcal/mol
form $H_3C–Cl$:	$\Delta H° = -84$ kcal/mol
step 2:	$\Delta H°_2 = -26$ kcal/mol

overall: $\Delta H°_{overall} = -25$ kcal/mol

Drawing the Reaction-Energy Diagram:



$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

From BDEs (previous slide):

$\Delta H°_1$ = +1 kcal/mol
$\Delta H°_2$ = –26 kcal/mol
$\Delta H°_{overall}$ = –25 kcal/mol

Experimental Values:
(cannot predict)

E_{a1} = +4 kcal/mol
E_{a2} = +1 kcal/mol

From this diagram, we know:

- **The overall reaction is exothermic by 25 kcal/mol.**
- **The rate-determining step is step #1.**