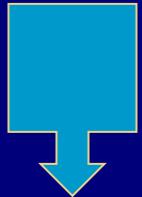


Alkanes, Thermodynamics, And Kinetics

Petroleum!!



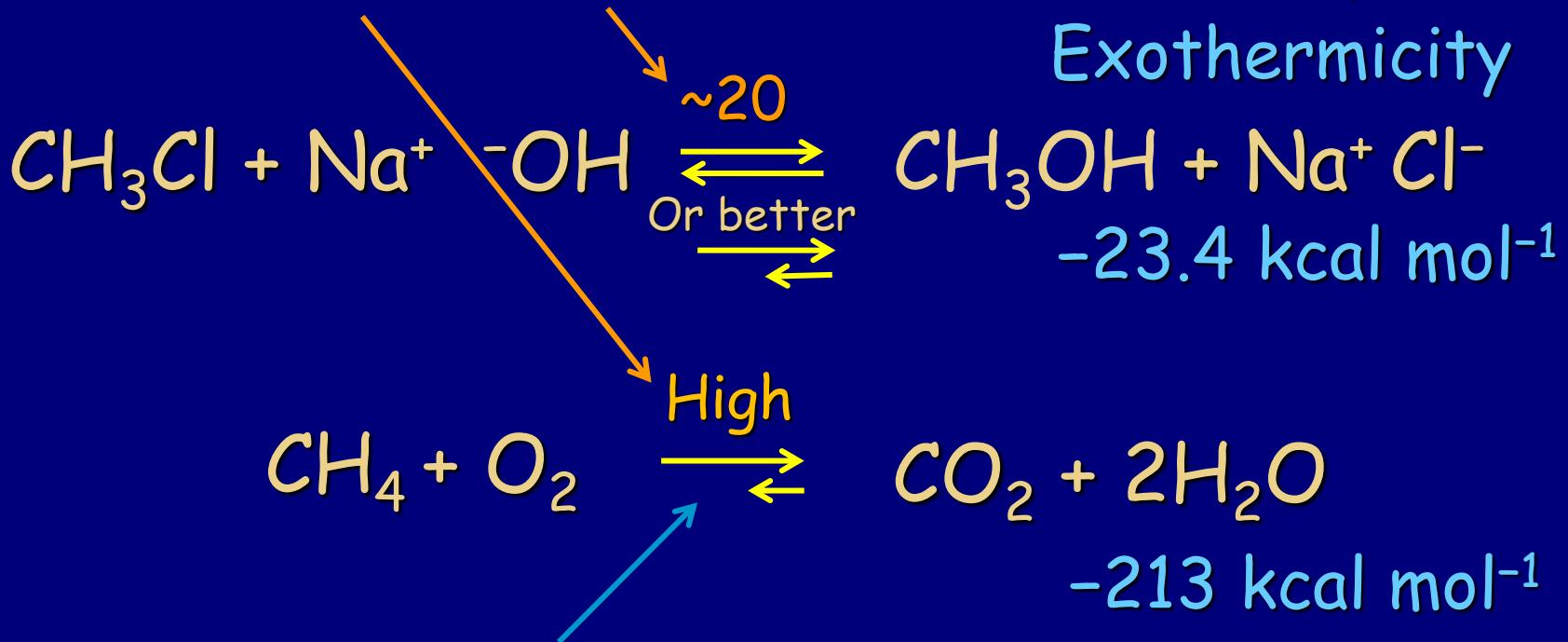
Combustion

How warm? Thermodynamics
How fast? Kinetics



All Reactions Are Equilibria

How fast? "Barrier" kcal mol⁻¹



How warm?
Exothermicity

Equilibrium lies very much to the right.

What governs these equilibria?

Chemical Thermodynamics And Kinetics

1. Chemical Thermodynamics:

Energy changes during reaction, extent of "completion of equilibration/reaction," "to the left/right," "driving force."

2. Chemical Kinetics:

How fast is the reaction or, better, how quickly is equilibrium established - "reactivity"; rates of disappearance of starting materials or appearance of products

The two principles may or may not go in tandem

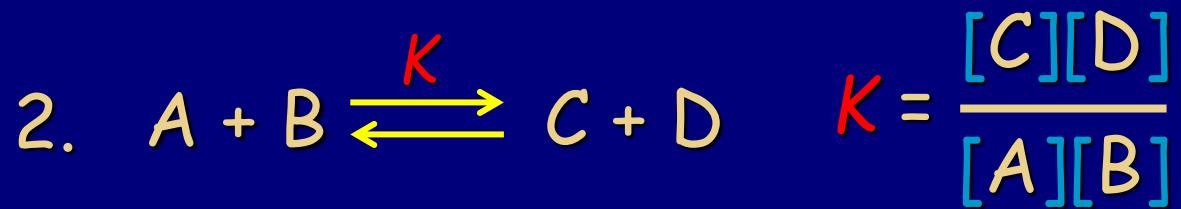
Equilibria

Two typical cases



K = equilibrium constant

[] = concentration in mol L⁻¹



If K large: reaction "complete," "to the right," "downhill."

How do we quantify? Gibbs free energy, ΔG°

Gibbs Free Energy ΔG°

The “°” refers to molecules in their standard states, 1 atm, 25 °C (298 kelvin), 1 M (concentration).

$$\Delta G^\circ = -RT \ln K = -2.3RT \log K$$

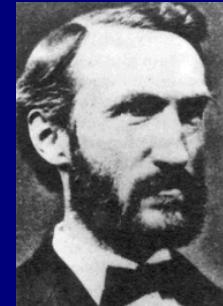
T in kelvin (0 kelvin = -273 °C)

R = gas constant $\sim 2\text{cal deg}^{-1} \text{mol}^{-1}$



At “room temperature”, 25°C (298 kelvin):

$$\Delta G^\circ = -1.36 \log K$$



Josiah Willard
Gibbs
(1839-1903)

Large K : Large negative ΔG° : downhill
(exergonic)

Equilibria And Free Energy

At 25°C (298 kelvin): $\Delta G^\circ = \boxed{-1.36} \log K$

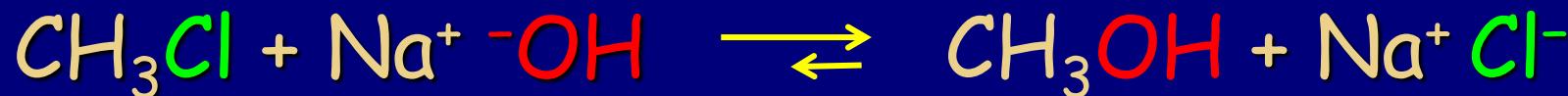
Therefore, for $A \xrightleftharpoons{K} B$

When $K = 1$ ($A/B = 50/50$), then $\log K = 0$ and $\Delta G^\circ = 0 \text{ kcal mol}^{-1}$

$K = 10$, then $\log K = 1$ and $\Delta G^\circ = -1.36 \text{ kcal mol}^{-1}$

$K = 100$, then $\log K = 2$ and $\Delta G^\circ = -2.72 \text{ kcal mol}^{-1}$

$K = 0.1$, then $\log K = -1$ and $\Delta G^\circ = +1.36 \text{ kcal mol}^{-1}$



$$\Delta G^\circ = -23.4 \text{ kcal mol}^{-1}$$

What is order of magnitude of K roughly?

$23.4/1.36 \sim 17$, i.e. $K \sim 10^{17}$ huge!

Enthalpy ΔH° And Entropy ΔS°

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

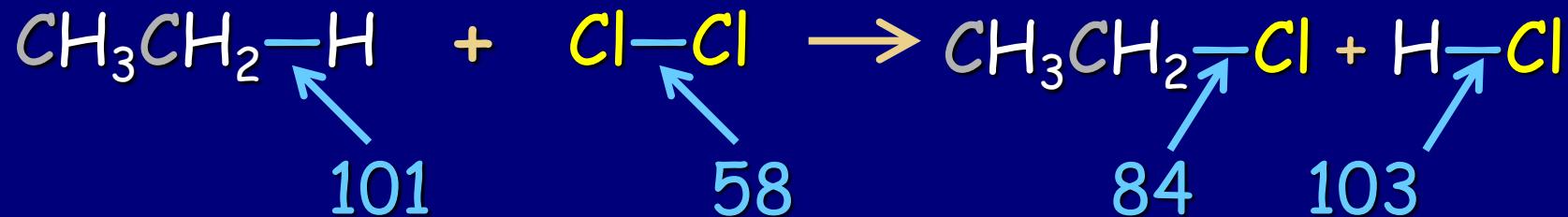
ΔH° units: kcal mol⁻¹
 $T\Delta S^\circ$ units: cal kelvin⁻¹ mol⁻¹ or entropy units (e.u.)

Temperature in kelvin

Enthalpy ΔH° = heat of the reaction, arising mainly from changes in bond strengths:

$$\Delta H^\circ = (\text{sum of strength of bonds broken}) - (\text{sum of strengths of bonds made})$$

Example:



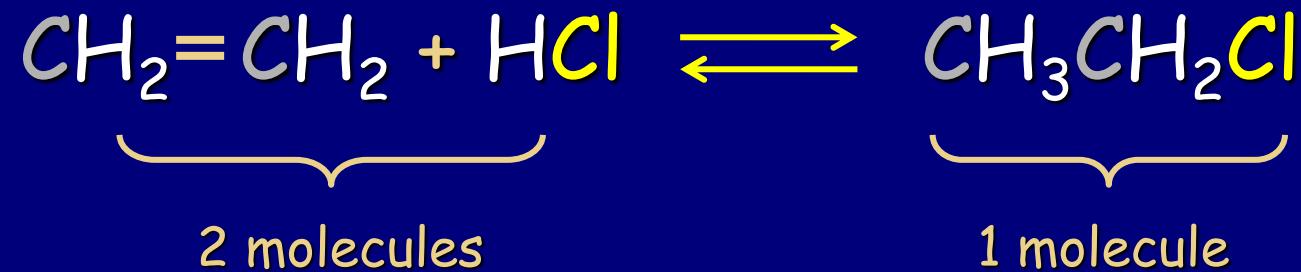
$$\Delta H^\circ = 159 - 187 = -28 \text{ kcal mol}^{-1}$$

ΔH° negative: called "exothermic"
 ΔH° positive: called "endothermic"

Enthropy ΔS°

ΔS° = change in the "order" or "freedom" or "dispersal of energy" in the system. Nature strives for disorder. More disorder = positive ΔS° (makes a negative contribution to ΔG°). More order = negative ΔS° (makes a positive contribution to ΔG°).

Example:



$$\Delta H^\circ = -15.5 \text{ kcal mol}^{-1}$$

$$\Delta S^\circ = -31.3 \text{ e.u.}$$

Negative = makes a positive contribution to ΔG° (at room temperature roughly 10 kcal mol⁻¹)

If # of molecules unchanged, ΔS° small, ΔH° controls (we can estimate value from bond strength tables)

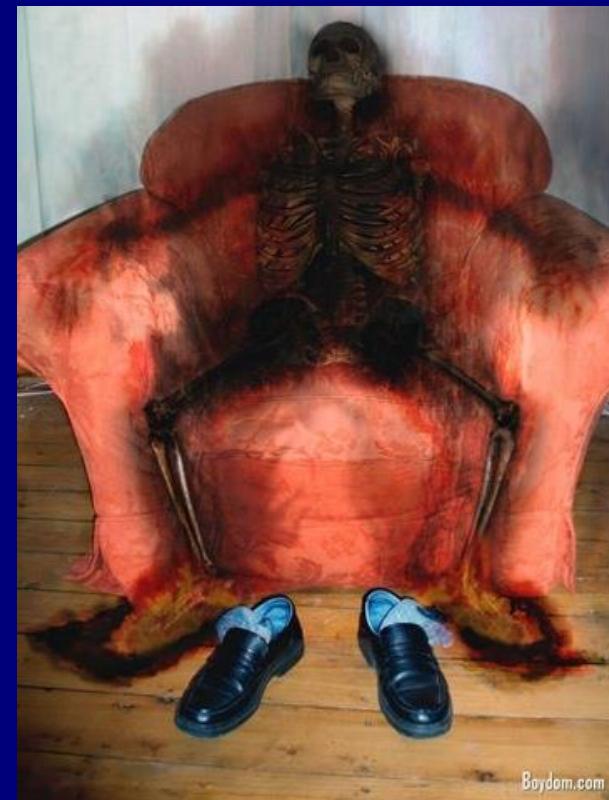
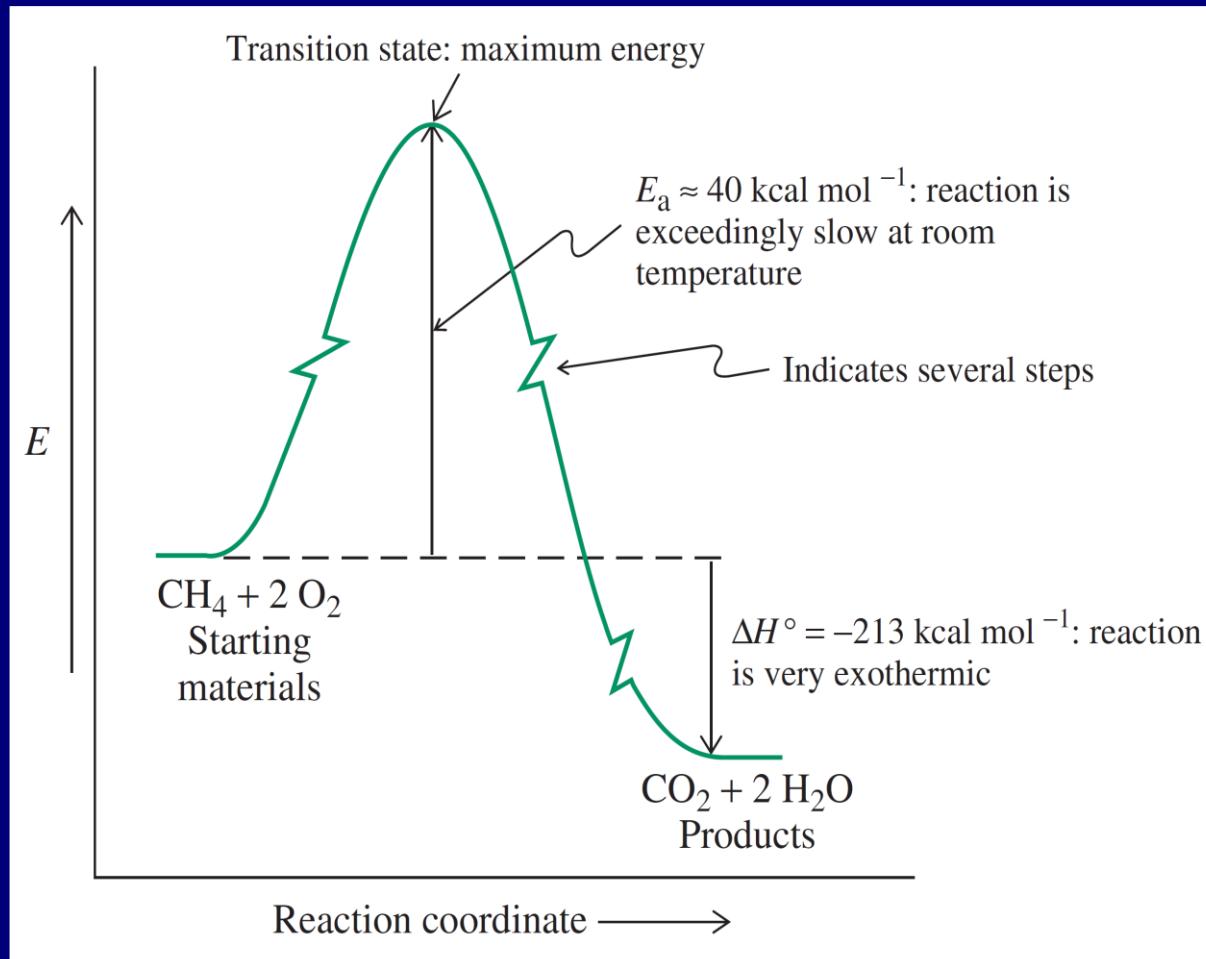


Ice cream makers: "super" cool with ice/NaCl to -20 °C. Dissolution of salt is endothermic (i.e. ΔH° is positive), and the process is driven by entropy (dissolution = positive entropy).



Rates

All processes have "activation barriers" (E_a), otherwise, for example, we and our surroundings would spontaneously combust (burn in our oxygen atmosphere).

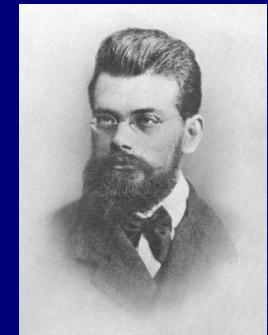
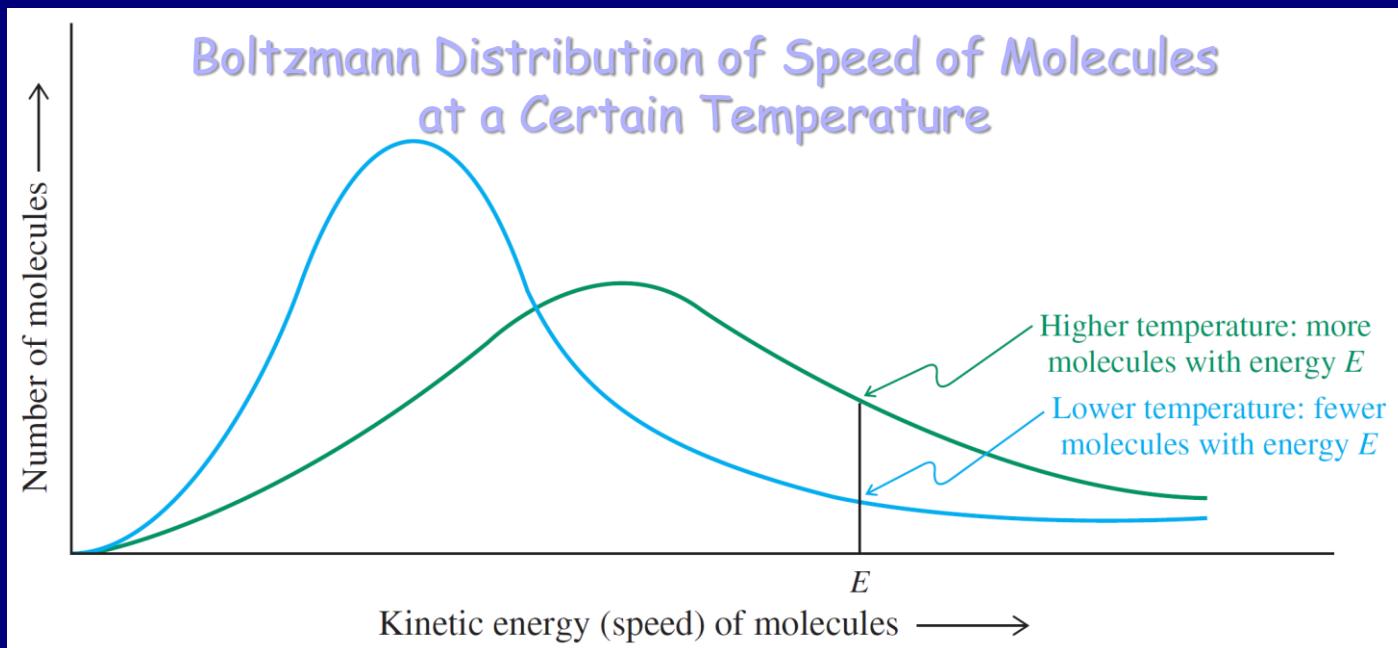


Vollhardt after spontaneous combustion

Rates

Rate of reaction is controlled by:

1. Barrier height (energy of transition state); old bonds have to be loosened, before new bonds are formed
2. T (increased T means faster moving molecules; number of collisions increases; faster reaction)



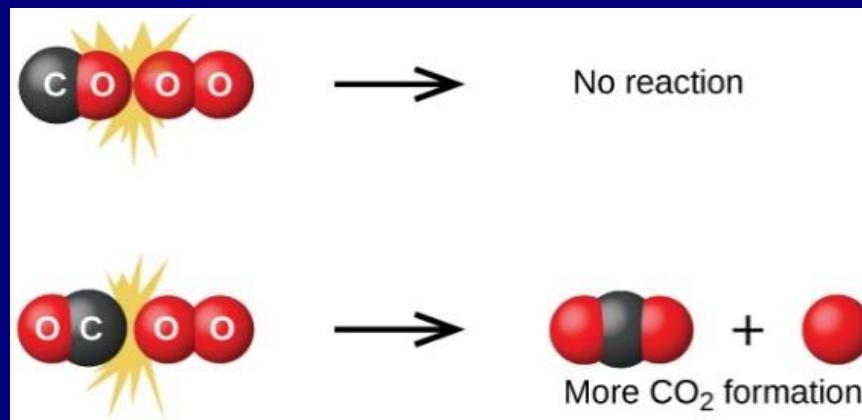
The average kinetic energy of molecules at room temperature is $\sim 0.6 \text{ kcal mol}^{-1}$, enough to overcome $E_a \sim 20 \text{ kcal mol}^{-1}$.

Ludwig Eduard Boltzmann
(1844 -1906)

3. Concentration (the number of collisions increases with concentration)



4. "Probability" factor (how likely is a collision to lead to reaction; depends on sterics, electronics, angle of approach)



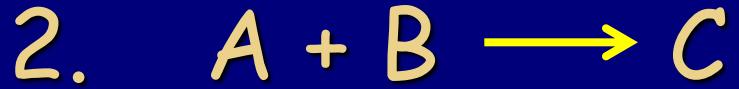
Rate Laws

Rate measurements lead to Rate Laws, which tell us something about nature of the transition state.
Very common:



If rate = $k [A]$ \longrightarrow 1st order
rate law

Unimolecular reaction (TS involves only A)



If rate = $k [A][B]$ \longrightarrow 2nd order
rate law

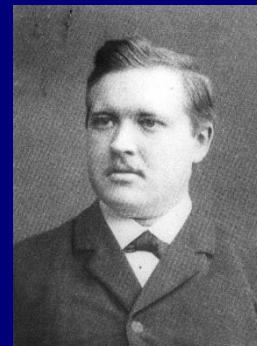
Bimolecular reaction (TS involves both A and B).

How do we measure barriers ?

Energy of activation from (empirical)
Arrhenius equation:

$$k = A e^{\frac{-E_a}{RT}}$$

at high T, $k = A$,
"maximum rate"



Svante
Arrhenius
(1859-1927)

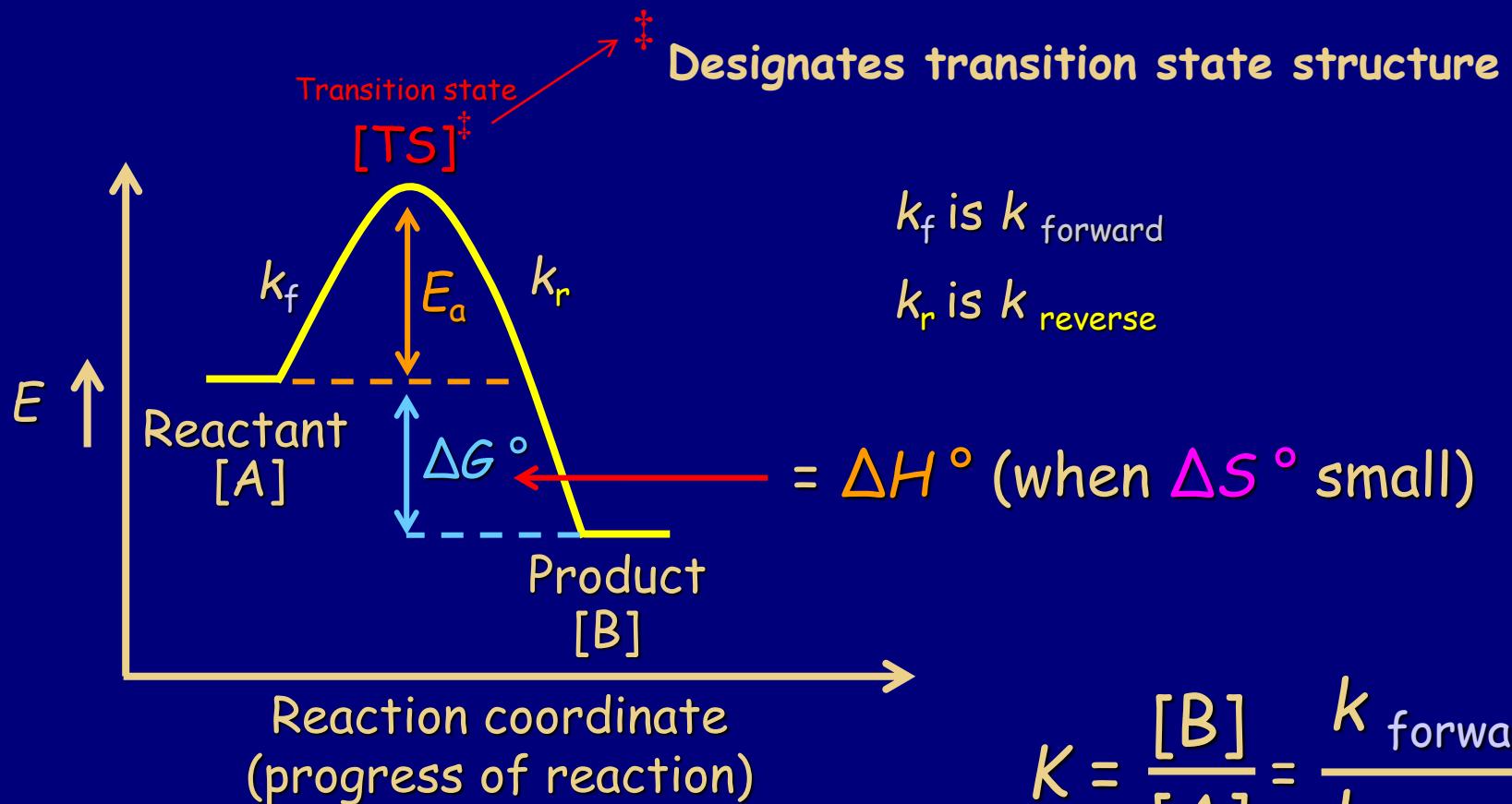
If E_a large \rightarrow reaction slow

Increasing temperature \rightarrow reaction speeds up



Rule of thumb: every +10 °C \sim 2-3 x rate

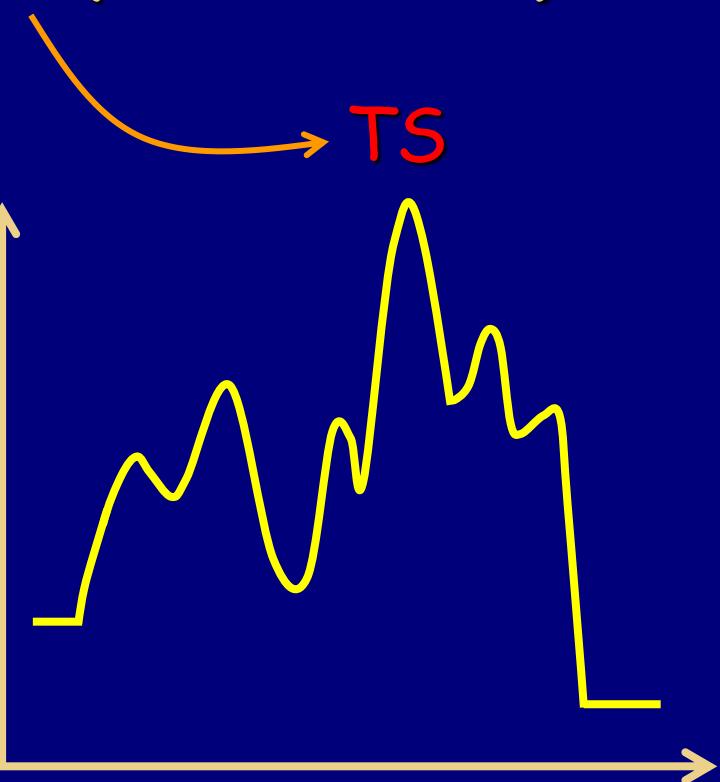
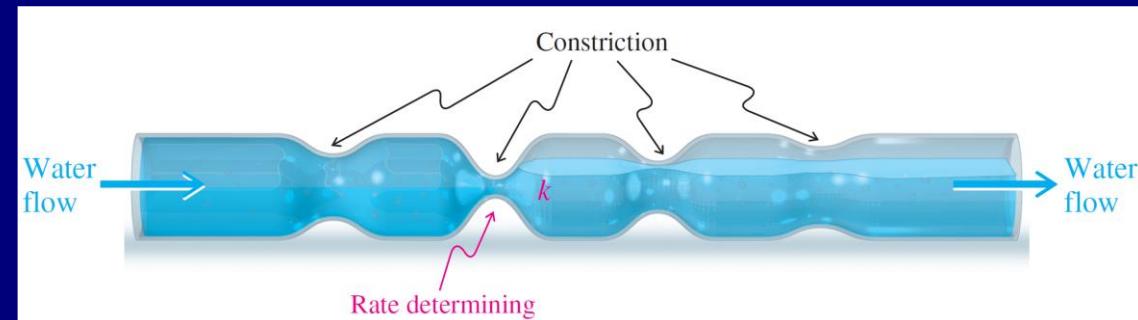
Potential Energy Diagrams



$$K = \frac{[B]}{[A]} = \frac{k_{\text{forward}}}{k_{\text{reverse}}}$$

Rate Determining Transition State

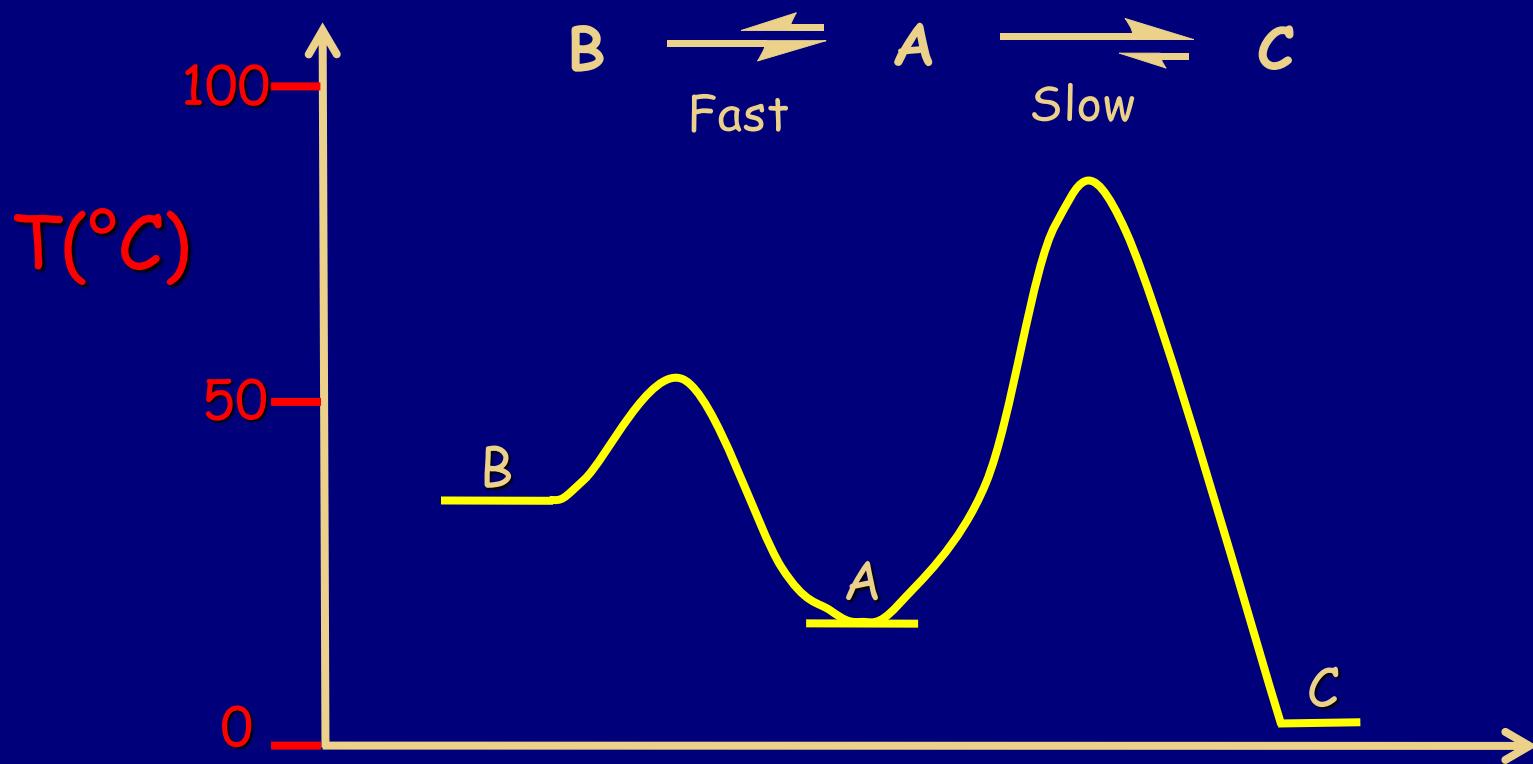
Many reactions have many steps, but there is always a **rate determining TS** (bottleneck).



Problem:

Which is right: On heating to 100°C,

- a. Compound A converts to C directly
- b. It equilibrates first with B and then goes to C
- c. It stays where it is



Using Curved “Electron-Pushing” Arrows To Describe Chemical Reactions

Reaction type 1. *Dissociation of a polar covalent bond into ions*

General case:



Movement of an electron pair converts the A–B covalent bond into a lone pair on atom B

Reaction type 2. *Formation of a covalent bond from ions*

General case:



The reverse of the previous process: A lone pair on B moves toward A, becoming a new covalent bond between A and B

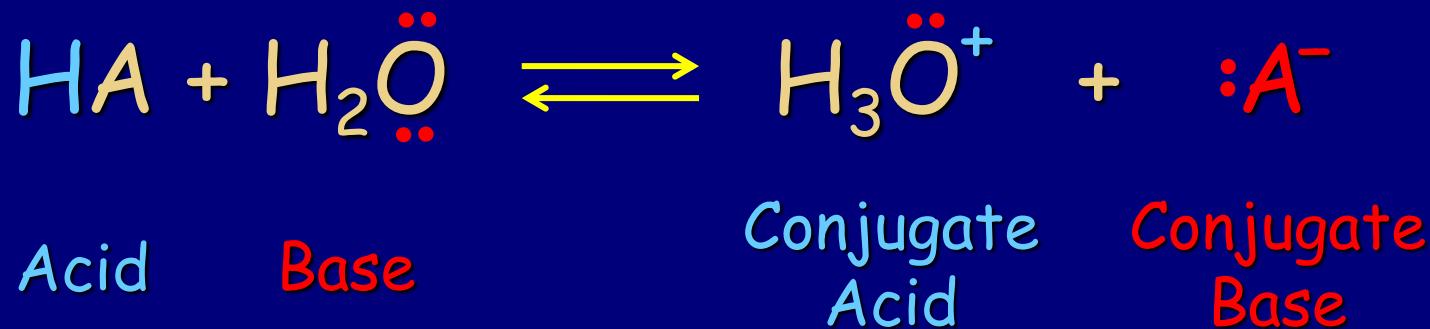
Reaction type 3. *Simultaneous making and breaking of two bonds: substitution reactions*

General case:



Movement of two electron pairs results in substitution of one bond for another

Acid-Base Equilibria



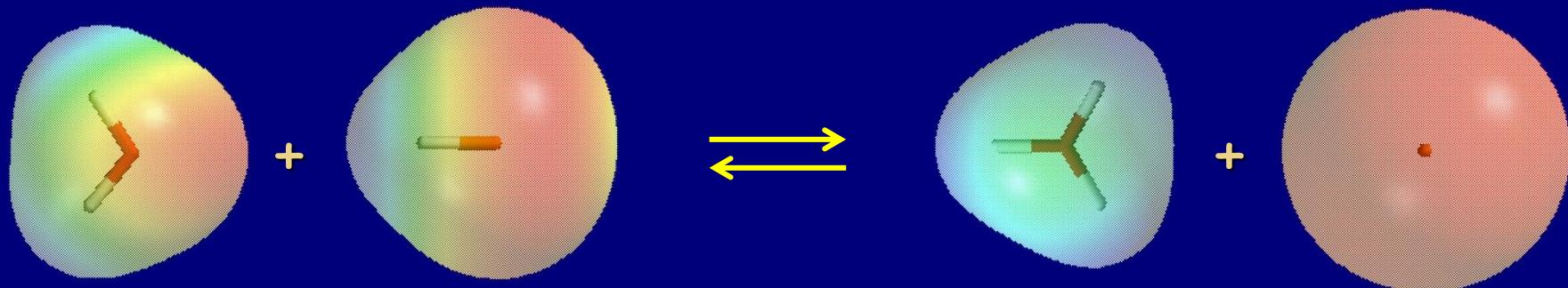
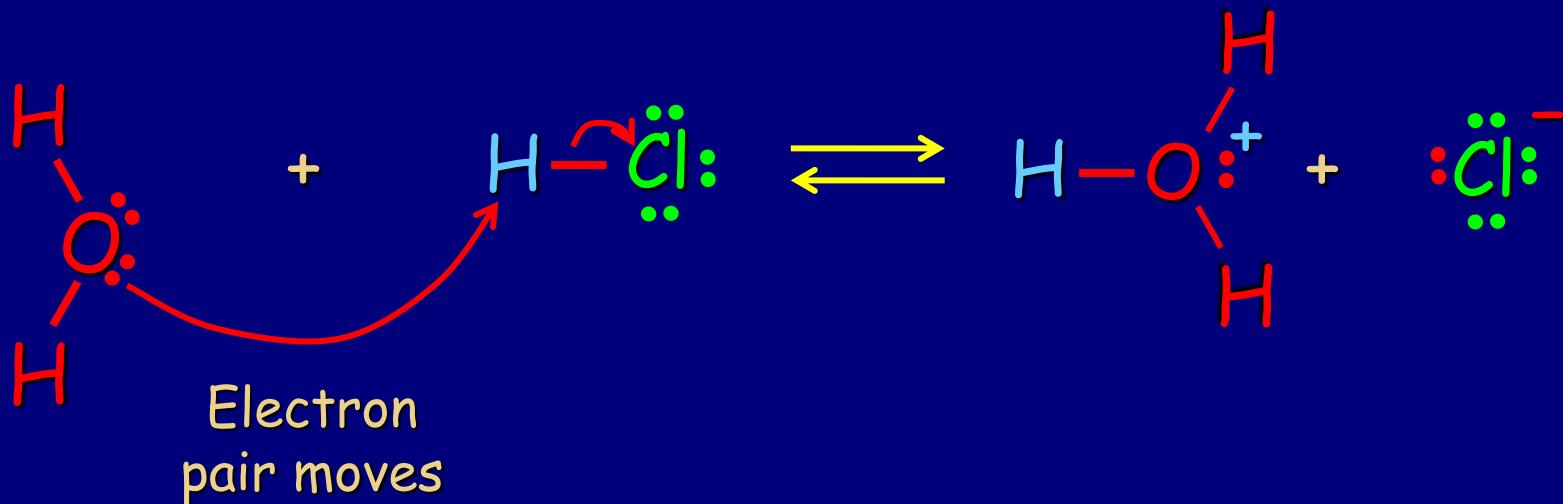
Brønsted and Lowry:

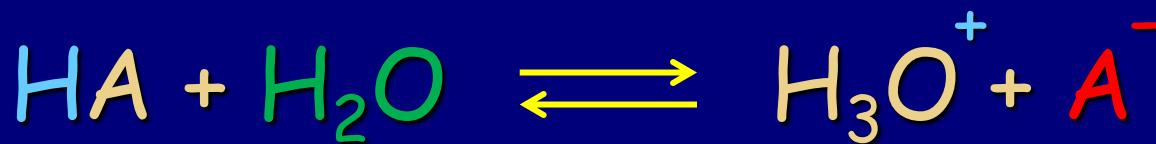
Acid = proton donor

Base = proton acceptor

Acid-Base: Electron “Pushing” And Electrostatics

Electron-pushing arrows





$$pH = -\log [H_3O^+]$$

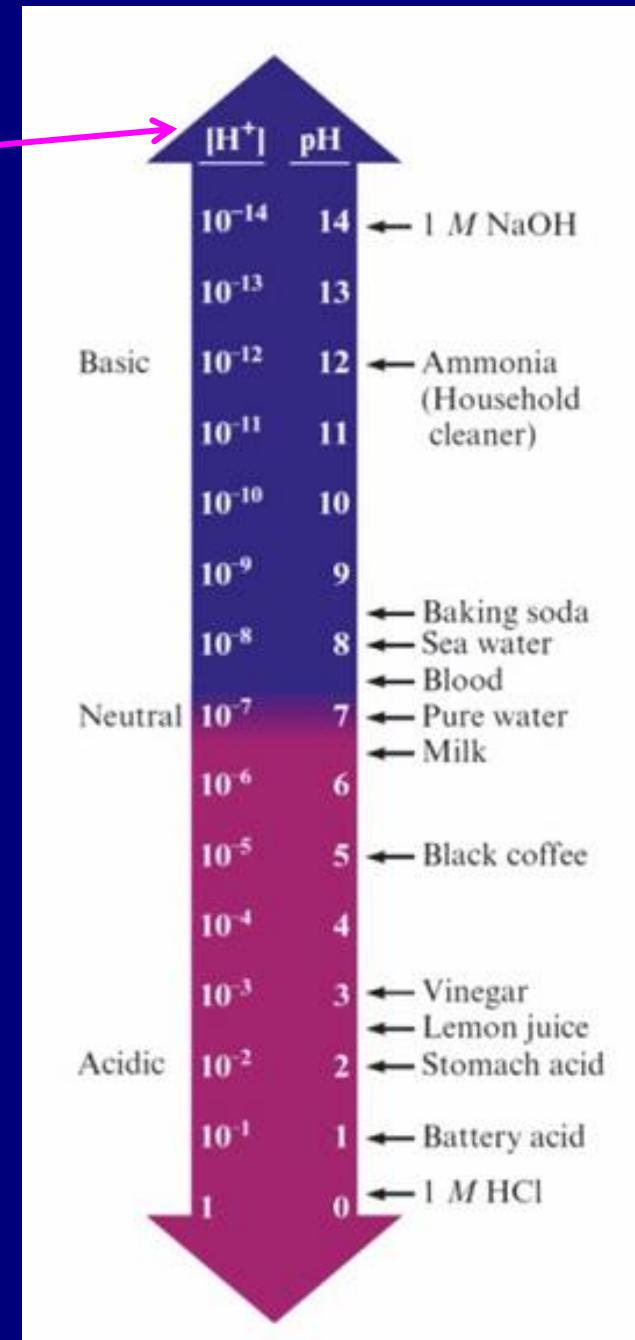
$$K = \frac{[H_3O^+] [A^-]}{[HA] [H_2O]}$$

Solvent 55 mol/L
(~constant)

$$K_a = K \times 55 = \frac{[H_3O^+] [A^-]}{[HA]}$$

Acidity constant

$$pK_a = -\log K_a$$



Acidity

Acidity of HA increases with:

1. Electronegativity of A (moving to the right in PT)

Increasing electronegativity of A



Increasing acidity

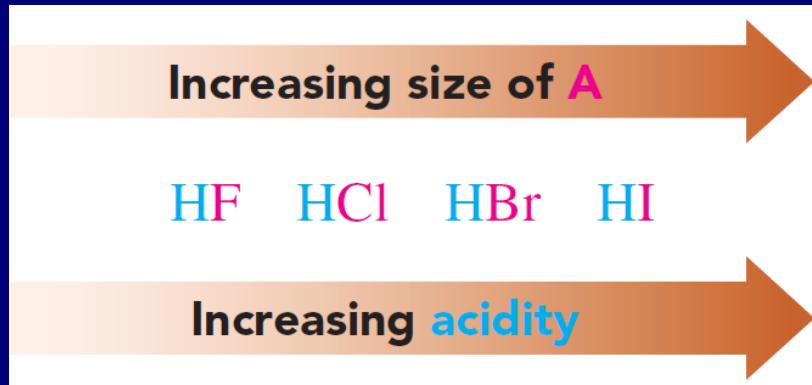
Even though bonds
get stronger
(polar contribution
to bond strength)

Increasing electron-attracting **inductive effect**



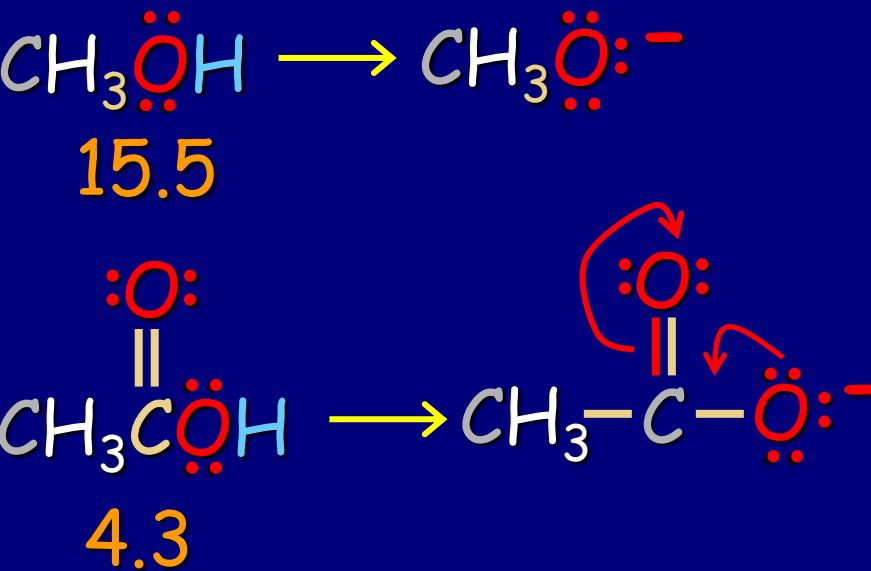
Increasing acidity

2. Increasing size of A ($H \ddot{A}$ gets weaker; Coulombic effect of respective mutual nuclear-electron attraction and bond polarization is diminished; down the PT)

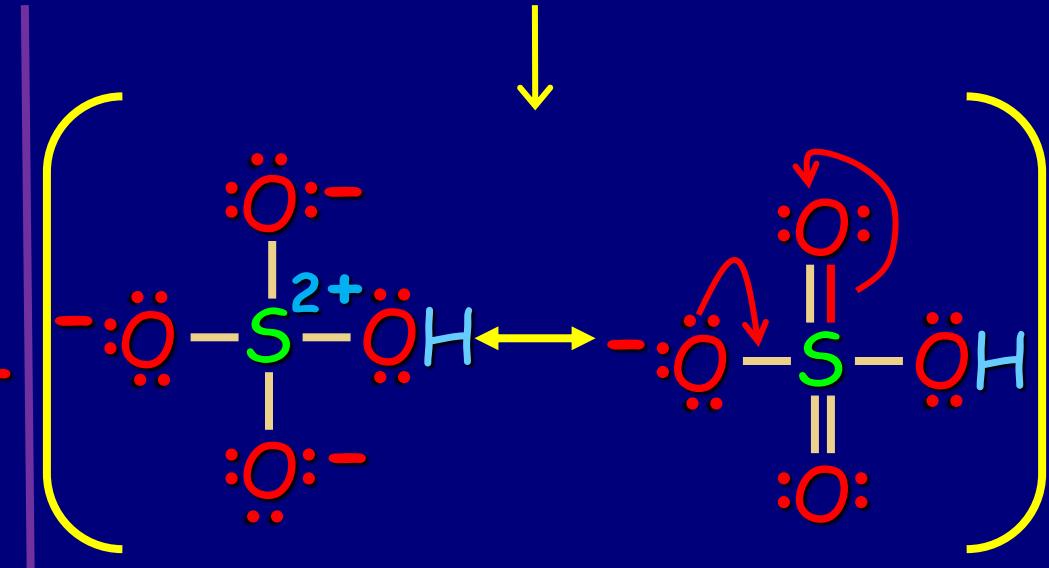


Overrides decreasing electronegativity effect

3. Resonance, e.g., pK_a



$\text{H}_2\text{SO}_4 -3.0$



Relative Acid Strengths

Moving to the right in PT

Moving down in PT

Table 2-2 Relative Acidity of Common Compounds (25°C)

Acid		K_a	pK_a
Hydrogen iodide, HI (strongest acid)	↑↑	$\sim 1.0 \times 10^{10}$	-10.0
Hydrogen bromide, HBr	↑↑	$\sim 1.0 \times 10^9$	-9.0
Hydrogen chloride, HCl	↑↑	$\sim 1.0 \times 10^8$	-8.0
Sulfuric acid, H_2SO_4		$\sim 1.0 \times 10^3$	-3.0 ^a
Hydronium ion, H_3O^+		50	-1.7
Nitric acid, HNO_3		25	-1.4
Methanesulfonic acid, CH_3SO_3H		16	-1.2
Hydrogen fluoride, HF	←	6.3×10^{-4}	3.2
Acetic acid, CH_3COOH	←	2.0×10^{-5}	4.7
Hydrogen cyanide, HCN		6.3×10^{-10}	9.2
Ammonium ion, NH_4^+		5.7×10^{-10}	9.3
Methanethiol, CH_3SH		1.0×10^{-10}	10.0
Methanol, CH_3OH		3.2×10^{-16}	15.5
Water, H_2O	←	2.0×10^{-16}	15.7
Ethyne, $HC\equiv CH$	←	$\sim 1.0 \times 10^{-25}$	~25
Ammonia, NH_3	←	1.0×10^{-35}	35
Ethene, $H_2C=CH_2$		$\sim 1.0 \times 10^{-44}$	~44
Methane, CH_4 (weakest acid)	←	$\sim 1.0 \times 10^{-50}$	~50

Note: $K_a = [H_3O^+][A^-]/[HA]$ mol L⁻¹.

^aFirst dissociation equilibrium



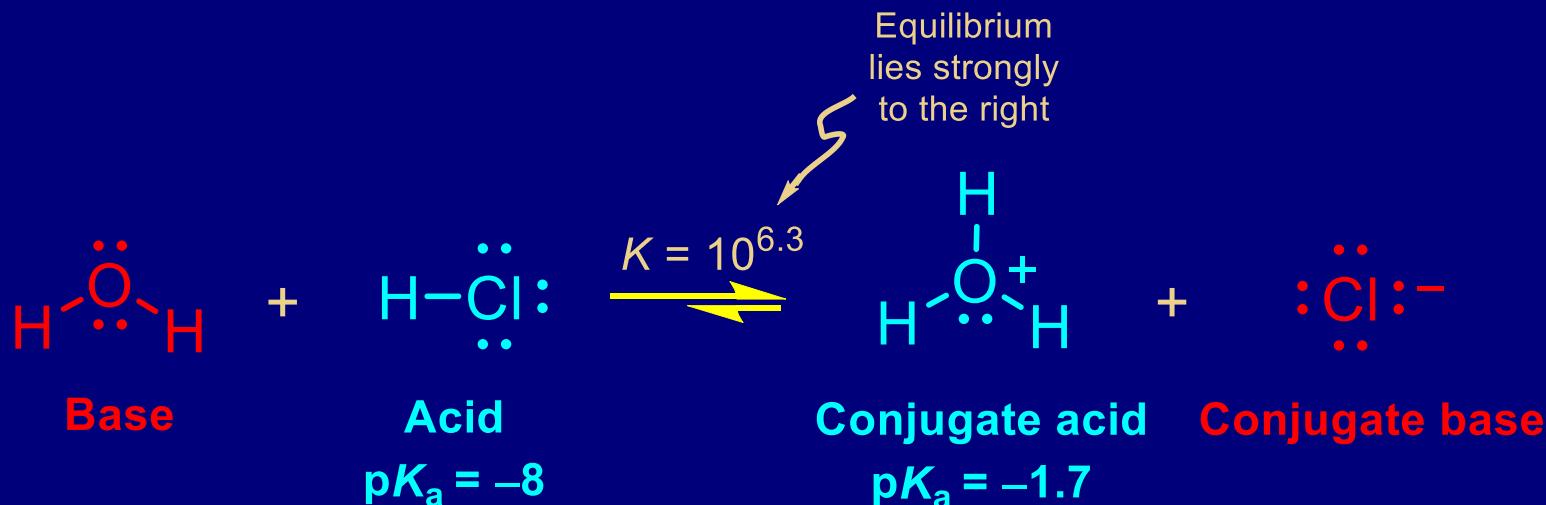
Strong

Weak

Very weak

The Position Of An Acid-Base Equilibrium Using pK_a Data

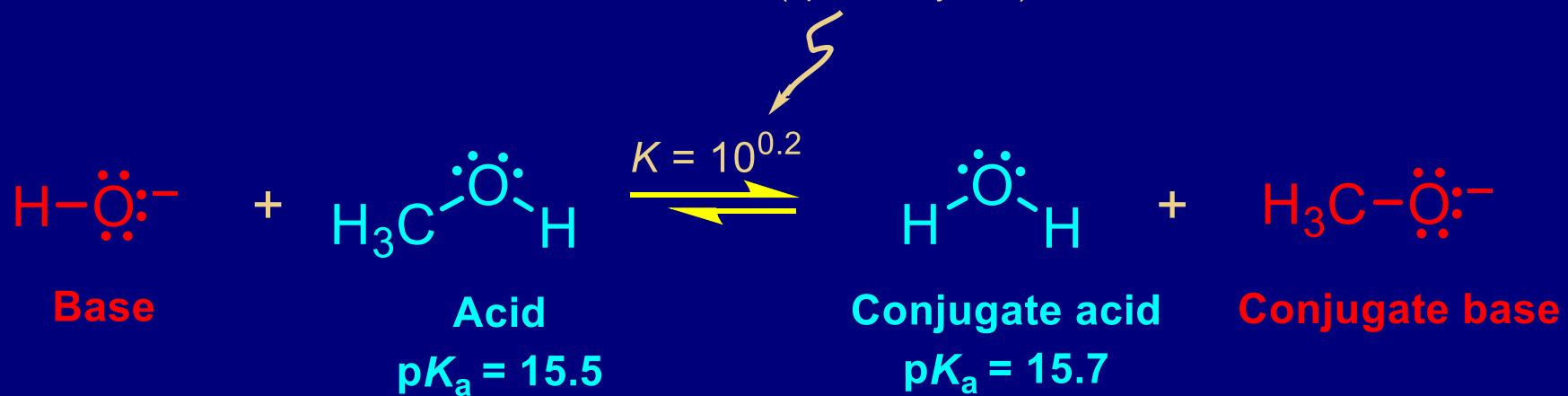
The equilibrium will always lie on the side of the weaker acid, or the acid with a more positive (or less negative) pK_a value.



The equilibrium lies on the right side, because the pK_a of H_3O^+ is less negative than that of HCl .
 $K = 10^{-1.7} - (-8) = 10^{6.3}$

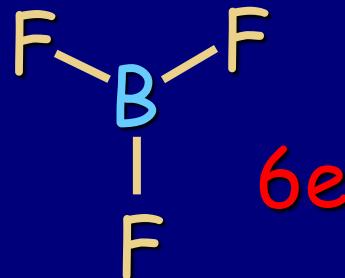
On the other hand, the equilibrium between hydroxide ion and methanol is close to 1:1.

Equilibrium lies slightly
to the right
 $K \geq 1$ (specifically: 1.6)

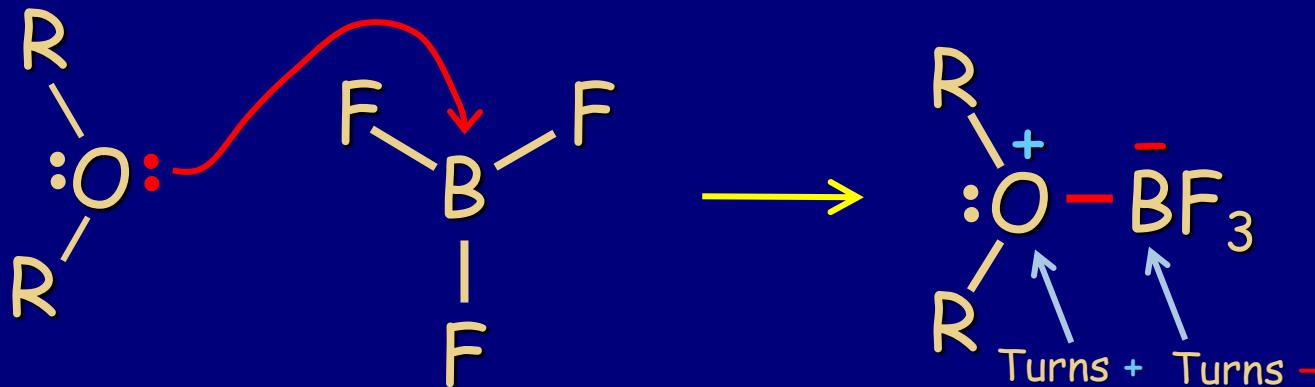
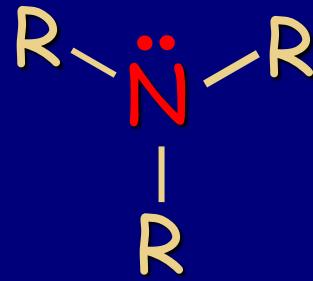
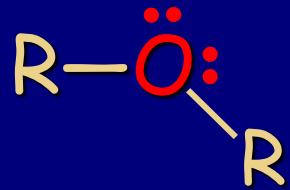


Lewis Acids And Bases

Lewis acids: e-deficient

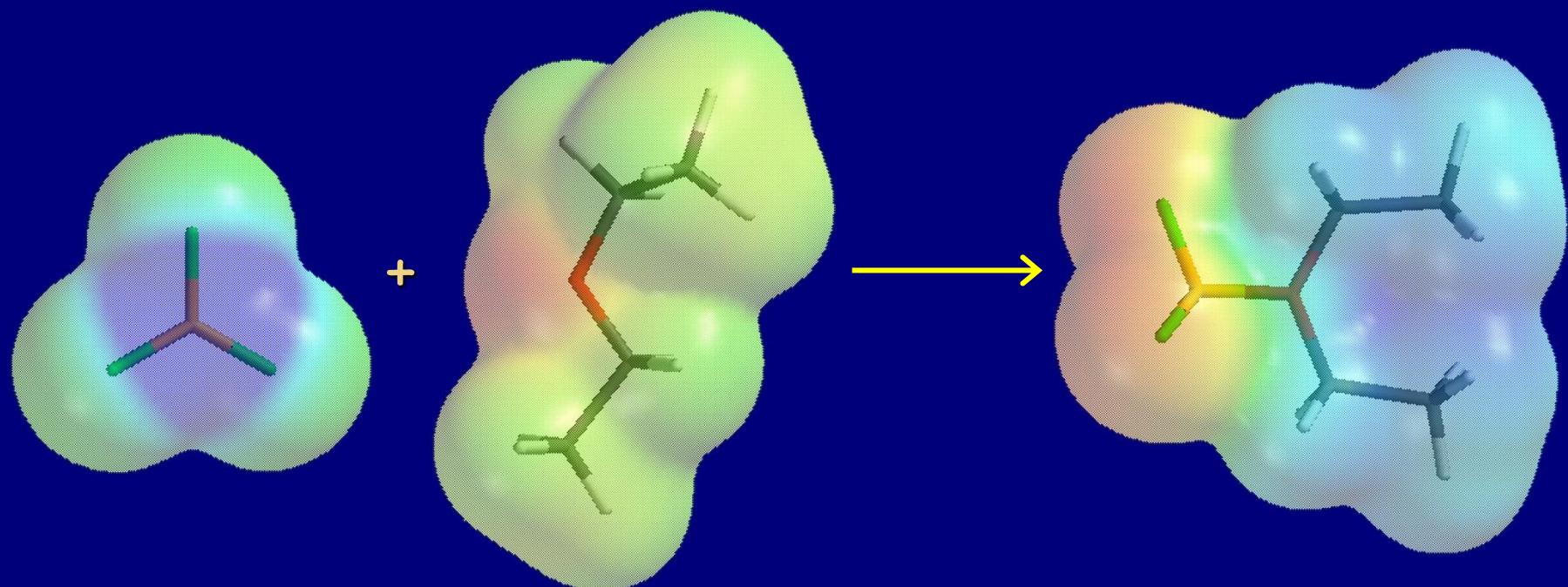
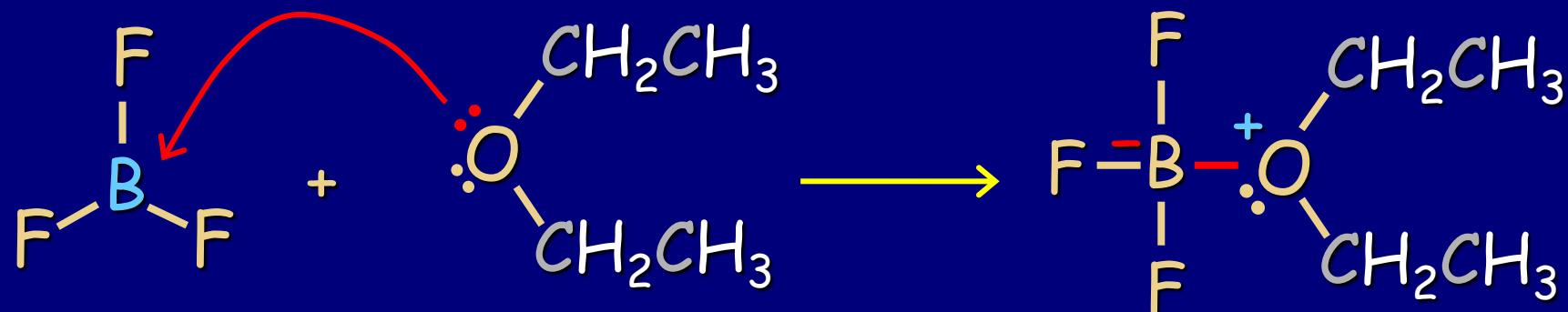


Lewis bases: Lone e-pairs



e-pushing
arrows

Lewis Acid-Base Electrostatics



Alkanes

Hydrocarbons without functional groups

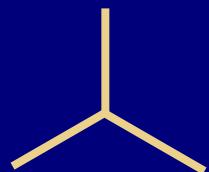
Straight chain: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

Line notation:



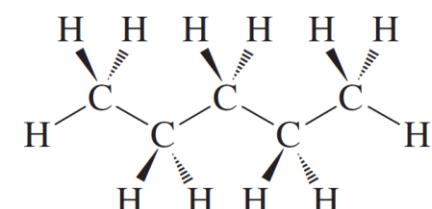
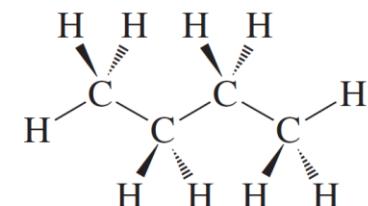
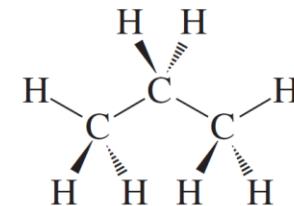
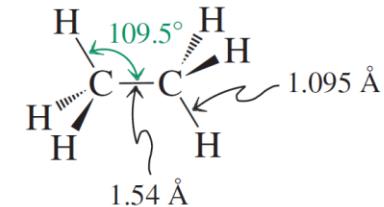
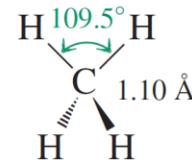
Butane

Branched: $\text{CH}_3-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$



2-Methylpropane

$$1 \text{ \AA} = 10^{-8} \text{ cm}$$





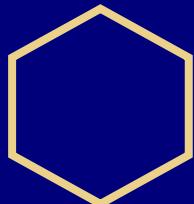
and

are **constitutional isomers**.

Same molecular formula, different connectivity

Cyclic:

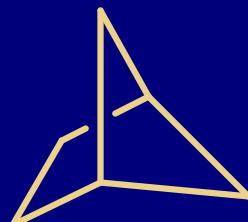
(Chapter 4)



Cyclohexane C_6H_{12}

Bicyclic:

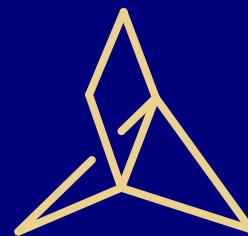
(names not covered)



Bicyclo[2.1.1]hexane C_6H_{10}

Polycyclic

(names not covered)



Tricyclo[2.1.1.0^{1,4}]hexane C_6H_8

Homologous Series

Insert- CH_2- groups into
 C-C bonds

Straight chain
 $\text{CH}_3(\text{CH}_2)_x\text{CH}_3$

General molecular formula
for acyclic systems

For cyclic alkanes: C_nH_{2n}

TABLE 2-4

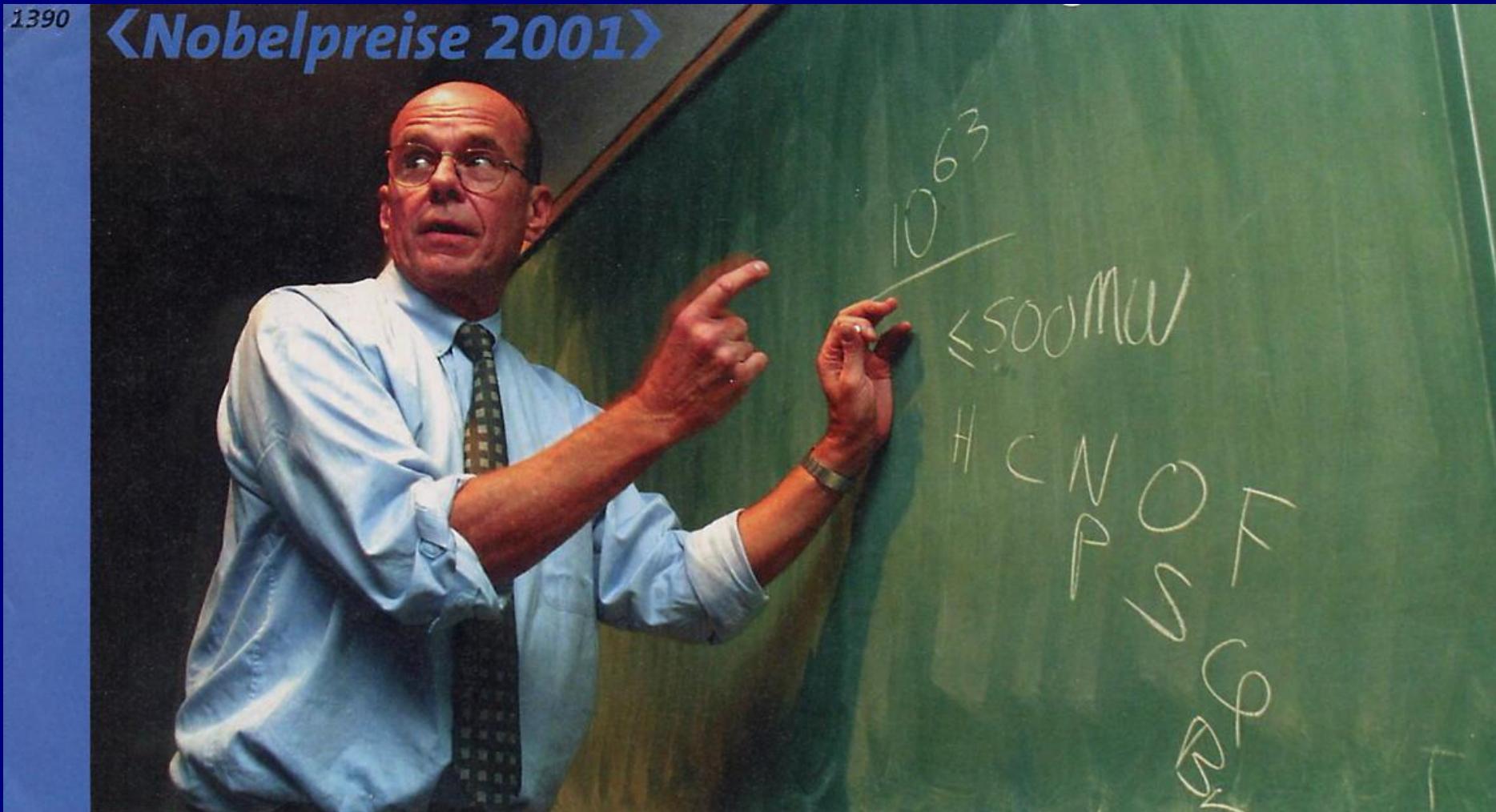
Number of Possible
Isomeric Alkanes,



n	Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319

Early 2020: Chemical Abstracts lists
158 million (10^8) chemical substances

Barry Sharpless (Scripps) NP 2001: estimating chemical “space”



The Names Of Alkanes Are Based On The IUPAC Rules

Table 2-5 Names and Physical Properties of Straight-Chain Alkanes, C_nH_{2n+2}

n	Name	Formula	Boiling point (°C)	Melting point (°C)	Density at 20°C (g mL ⁻¹)
1	Methane	CH ₄	−161.7	−182.5	0.466 (at −164°C)
2	Ethane	CH ₃ CH ₃	−88.6	−183.3	0.572 (at −100°C)
3	Propane	CH ₃ CH ₂ CH ₃	−42.1	−187.7	0.5853 (at −45°C)
4	Butane	CH ₃ CH ₂ CH ₂ CH ₃	−0.5	−138.3	0.5787
5	Pentane	CH ₃ (CH ₂) ₃ CH ₃	36.1	−129.8	0.6262
6	Hexane	CH ₃ (CH ₂) ₄ CH ₃	68.7	−95.3	0.6603
7	Heptane	CH ₃ (CH ₂) ₅ CH ₃	98.4	−90.6	0.6837
8	Octane	CH ₃ (CH ₂) ₆ CH ₃	125.7	−56.8	0.7026
9	Nonane	CH ₃ (CH ₂) ₇ CH ₃	150.8	−53.5	0.7177
10	Decane	CH ₃ (CH ₂) ₈ CH ₃	174.0	−29.7	0.7299
11	Undecane	CH ₃ (CH ₂) ₉ CH ₃	195.8	−25.6	0.7402
12	Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	216.3	−9.6	0.7487
13	Tridecane	CH ₃ (CH ₂) ₁₁ CH ₃	235.4	−5.5	0.7564
14	Tetradecane	CH ₃ (CH ₂) ₁₂ CH ₃	253.7	5.9	0.7628
15	Pentadecane	CH ₃ (CH ₂) ₁₃ CH ₃	270.6	10	0.7685
16	Hexadecane	CH ₃ (CH ₂) ₁₄ CH ₃	287	18.2	0.7733
17	Heptadecane	CH ₃ (CH ₂) ₁₅ CH ₃	301.8	22	0.7780
18	Octadecane	CH ₃ (CH ₂) ₁₆ CH ₃	316.1	28.2	0.7768
19	Nonadecane	CH ₃ (CH ₂) ₁₇ CH ₃	329.7	32.1	0.7855
20	Icosane	CH ₃ (CH ₂) ₁₈ CH ₃	343	36.8	0.7886

Naming Alkyl Substituents

Change ending -ane to -yl, as in

methane → methyl, hexane → hexyl

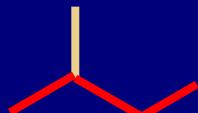
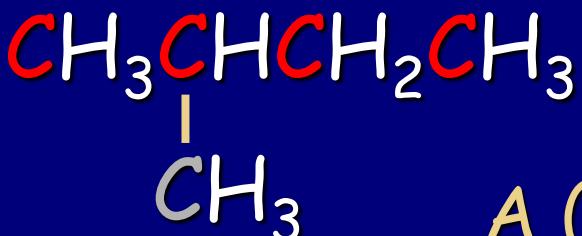
Short notation: alkane R-H → alkyl R-

"Lingo" for groups: RCH_2- "primary"

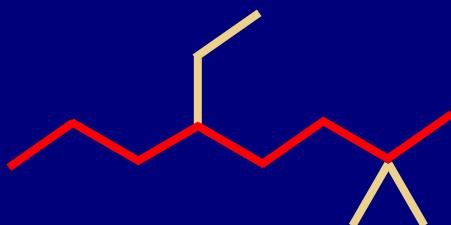


IUPAC Rules

1. Find the longest chain (stem) and name it (Table 2-5)

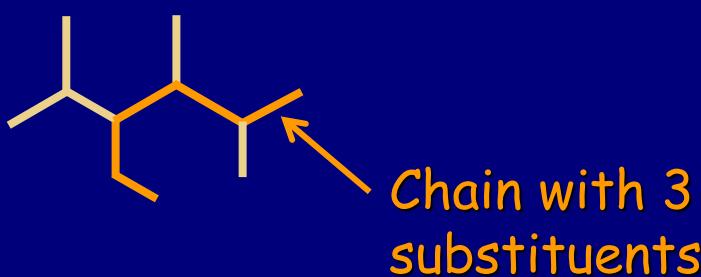
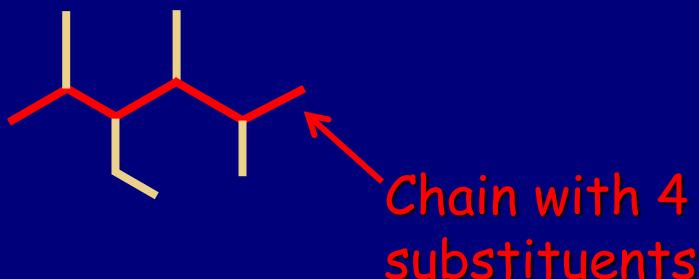


A (methyl-substituted) **butane**



An **octane** (substituted by one ethyl and two methyls)

When there are two equal longest chains,
choose the one with more substituents



2. Name substituents (as alkyl or halo)

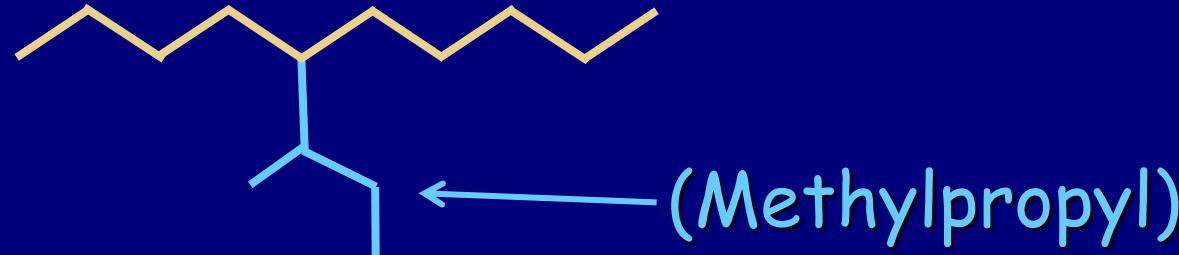
Halo: bromo, fluoro, chloro, iodo

- a. For straight chain R: methyl, ethyl, propyl, etc.
- b. For branched chain R:

- a. Find longest chain (starting from point of attachment)

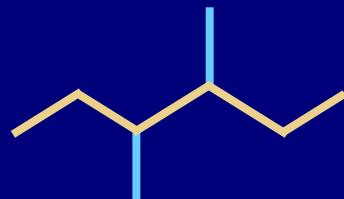
β. Name substituents

Example:



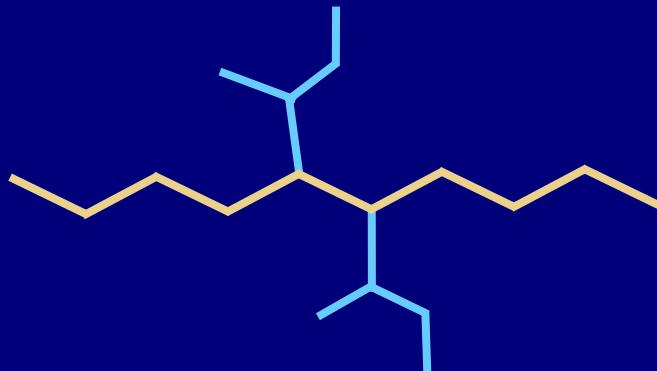
c. Multiple same substituents:

For R = straight, use prefix di-, tri-, tetra-, penta-, etc.:



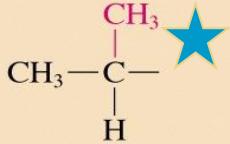
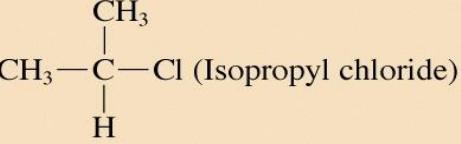
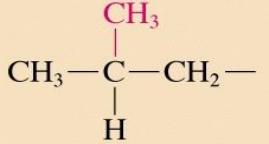
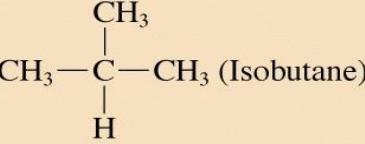
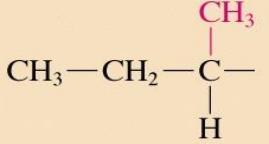
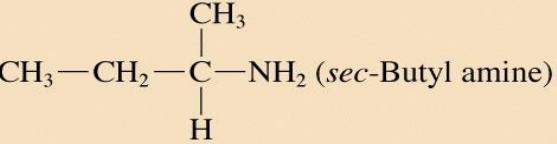
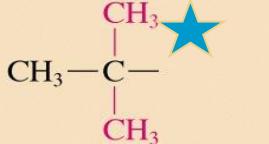
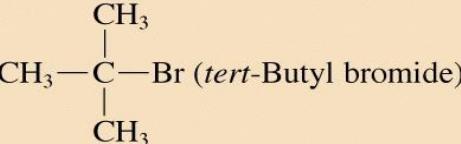
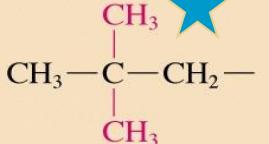
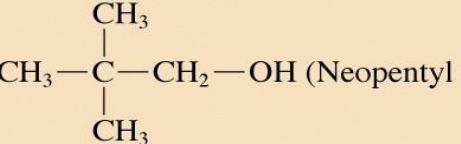
Dimethylhexane

For R = branched, use: bis-, tris-, tetrakis-, etc., and alkyl name in parentheses:



Bis(methylpropyl)

d. Common names: we will use colloquially isopropyl, tert-butyl, neopentyl

Structure	Common name	Example of common name in use	Systematic name	Type of group
	Isopropyl		1-Methylethyl	Secondary
	Isobutyl		2-Methylpropyl	Primary
	sec-Butyl		1-Methylpropyl	Secondary
	tert-Butyl		1,1-Dimethylethyl	Tertiary
	Neopentyl		2,2-Dimethylpropyl	Primary

3. Number stem, starting from the end closest to a substituent:



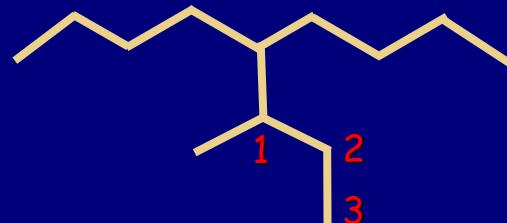
If both ends equidistant to the first substituent, proceed until the first point of difference:



Branched substituents: Number from carbon of attachment (**C1**)



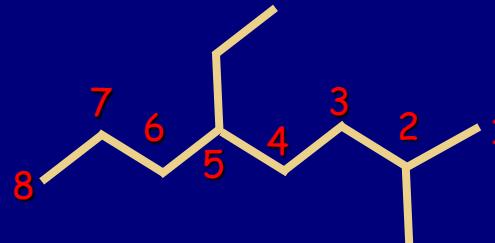
Defined as 1



4. Name the alkane in alphabetical (not numerical) order of substituents, location given by number prefix



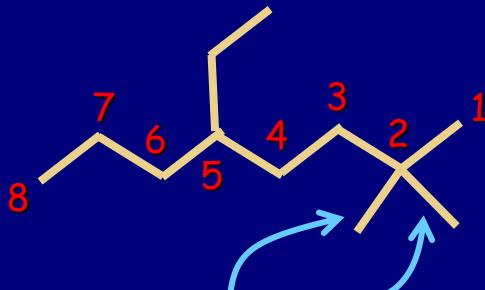
2-Methylbutane



5-Ethyl-2-methyloctane

Alphabet: Di-, tri-, bis-, etc. not counted for main stem R

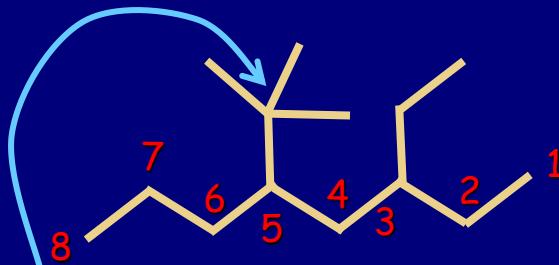
But: Counted when in branched R



5-Ethyl-2,2-di-methyloctane

Not counted

Counted

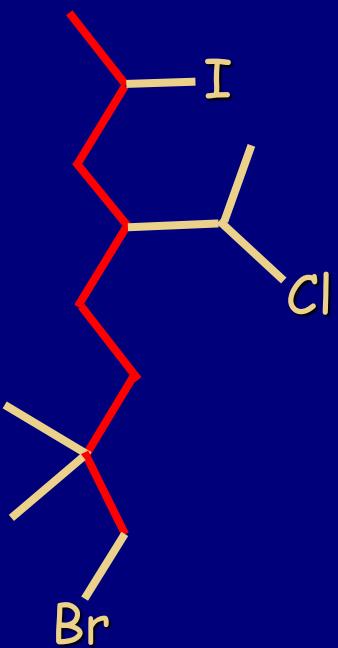


5-(1,1-Dimethylethyl)-
3-ethyl-octane

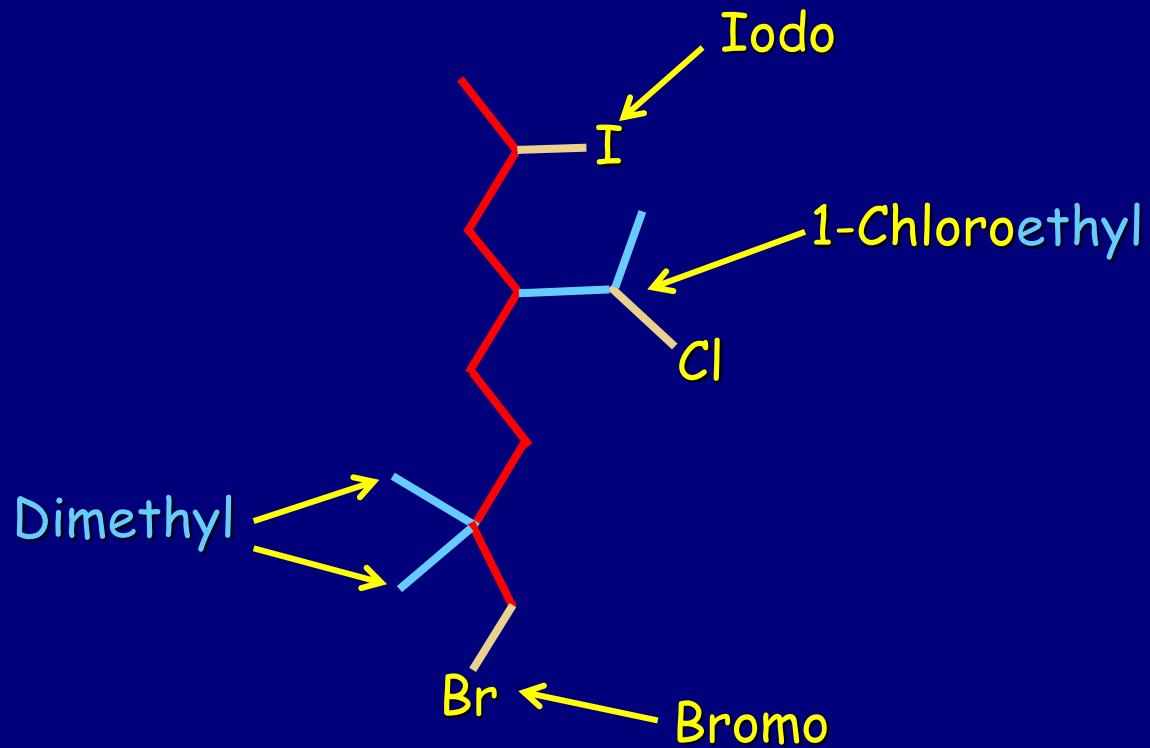
Problem:



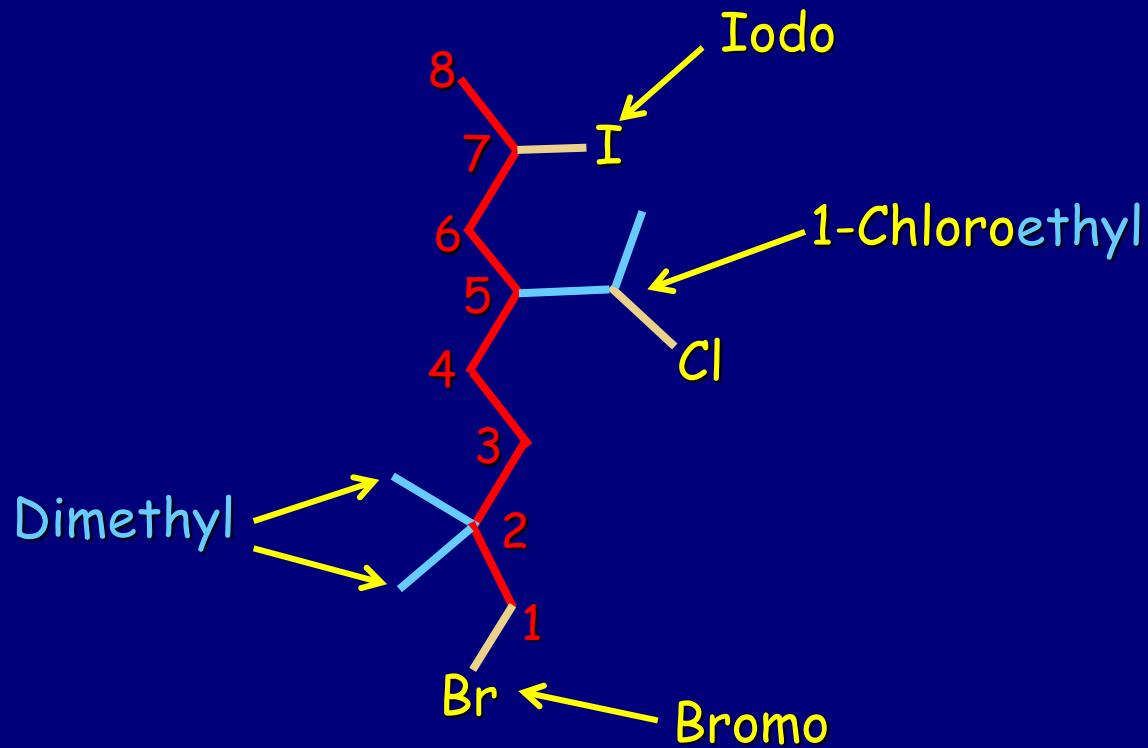
Longest chain?

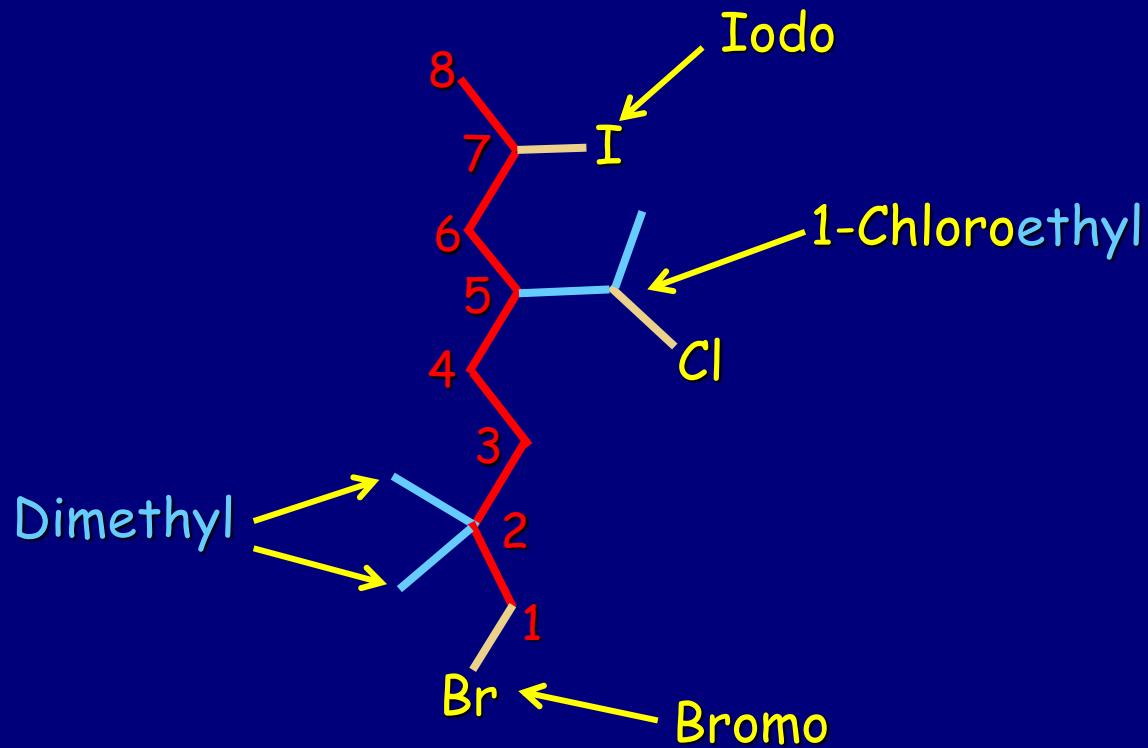


Substituents?



Number stem?

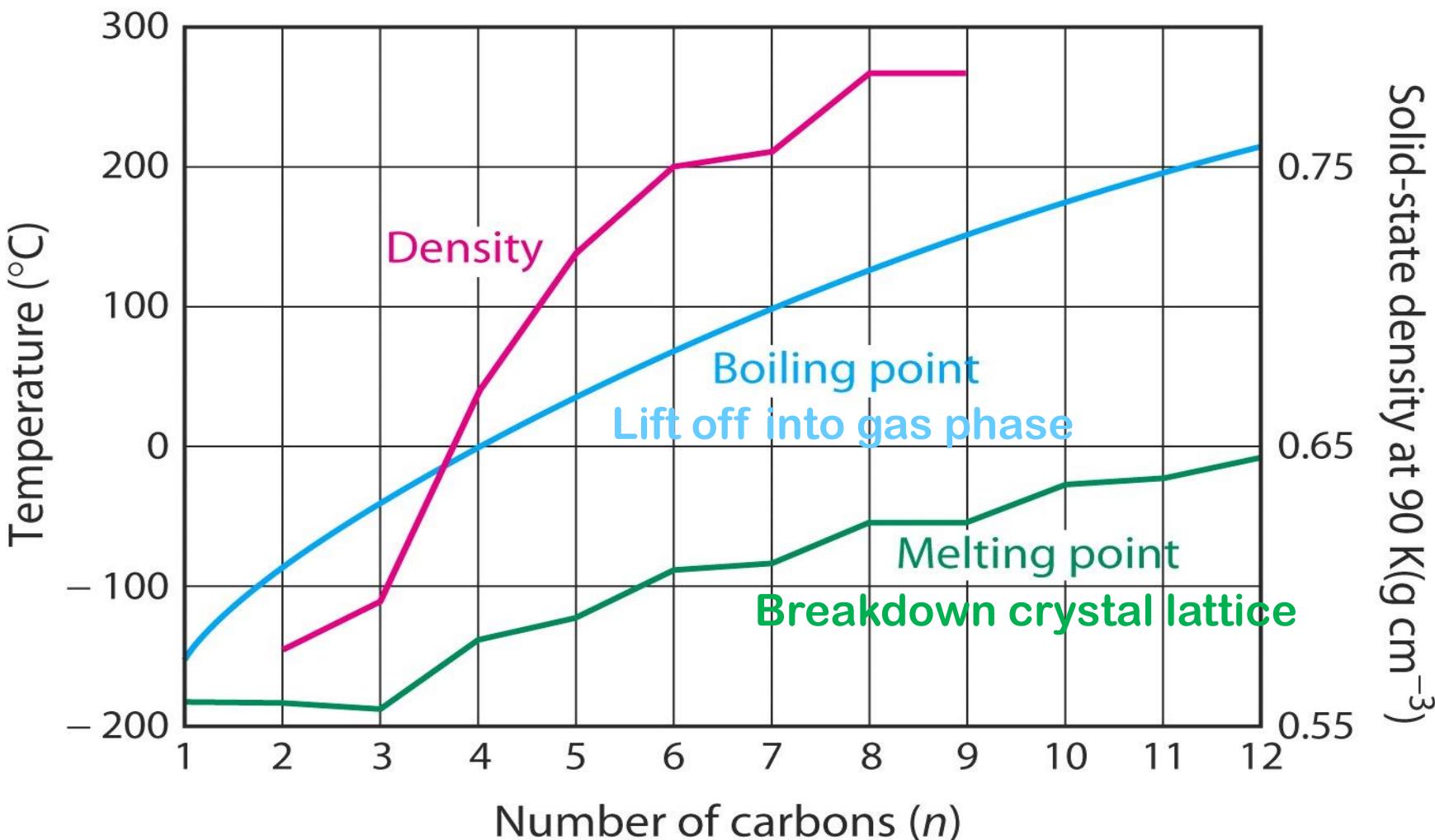




1-Bromo-5-(1-chloroethyl)-7-iodo-2,2-dimethyloctane

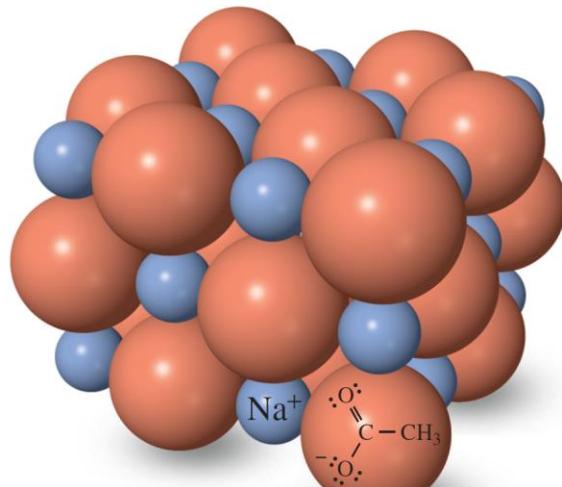
Physical Properties Of Alkanes

Intermolecular Forces Increase With Size



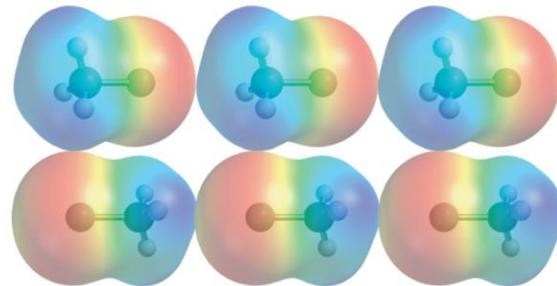
Intermolecular Forces

Ion–Ion Interactions: Full Charges



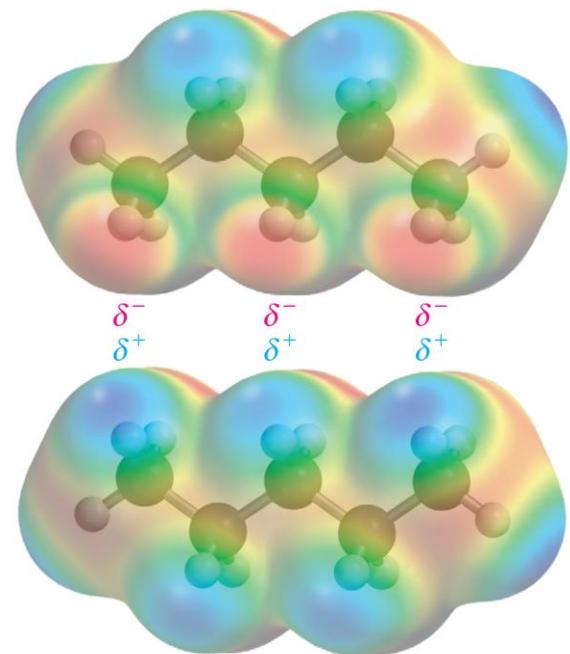
Salts

**Dipole–Dipole Interactions:
Partial Charges**



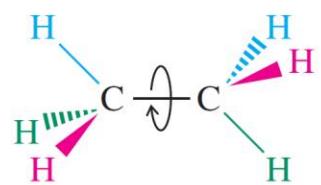
Polar molecules

**London Forces: Unsymmetrical
Charge Distribution**



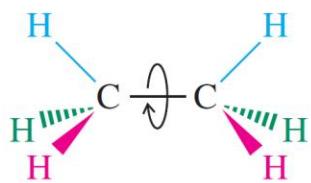
Alkanes (alkyls)

Dynamics: The Rotamers Of Ethane



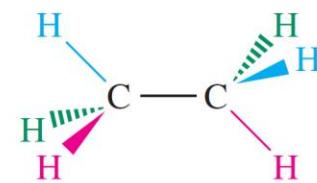
Staggered

60°

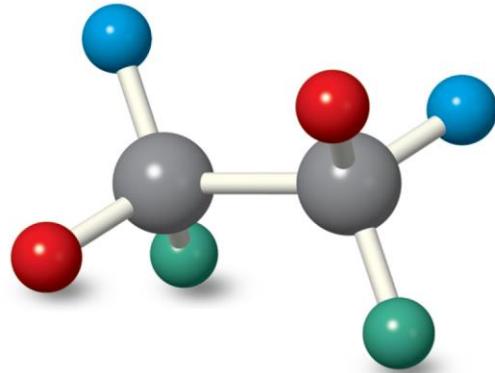


Eclipsed

60°

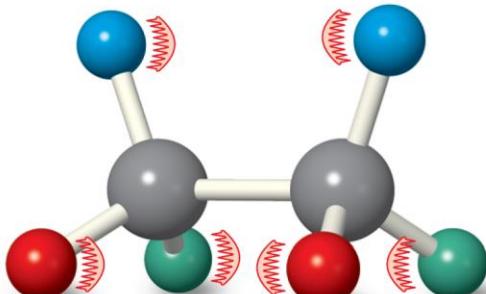


Staggered



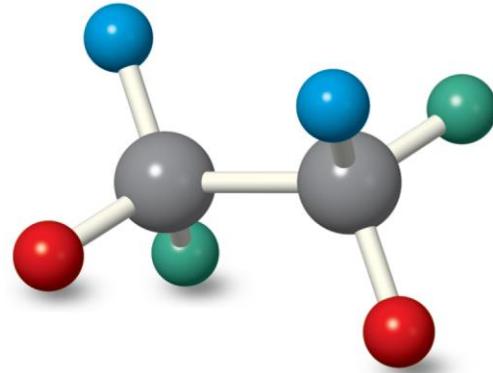
Staggered

60°



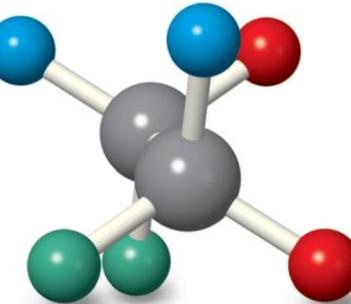
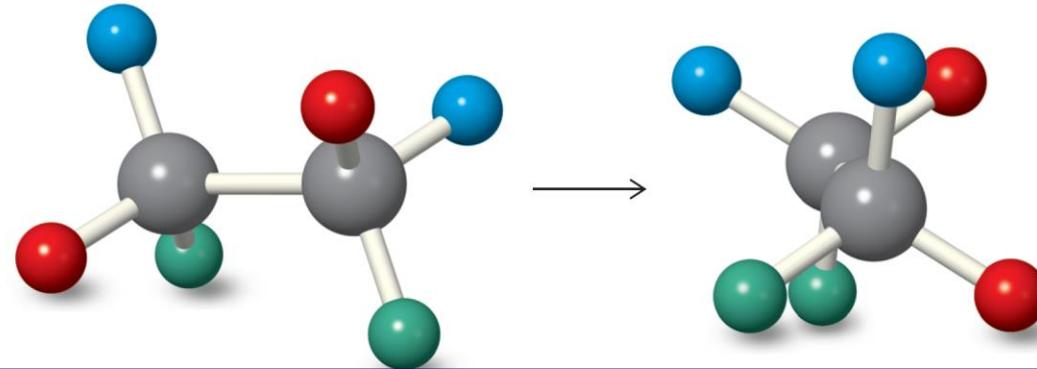
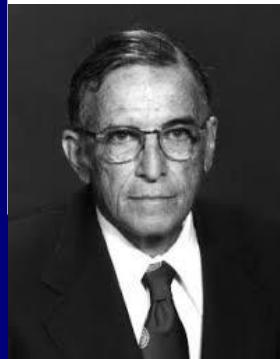
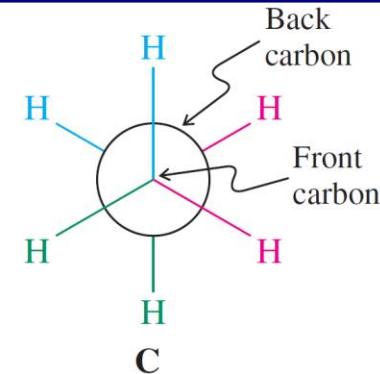
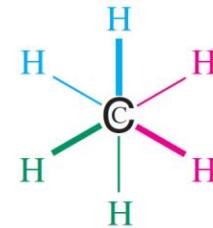
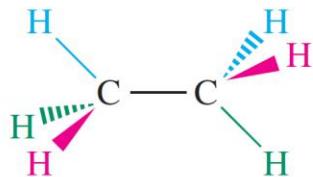
Eclipsed

60°



Staggered

Newman Projections



Note: Any one Newman projection occurs along only one bond.
Everything else is a substituent.

Melvin S.
Newman
(1908-1993)



**STOP THE
BUSH
DEA
MACI**

Organic
Chemists
For Peace!

**STOP TERRORISM
AGAINST
CUBA
FROM
MIAMI**



www.freethefive.org
www.freethefive.org
www.freethefive.org
www.freethefive.org

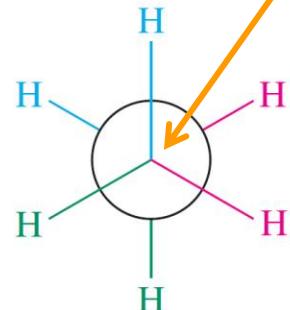
**STOP TERRORISM
AGAINST
CUBA
FROM
MIAMI**



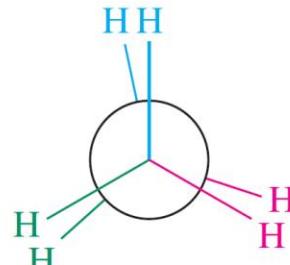
www.freethefive.org

Rotation With Newman Projections

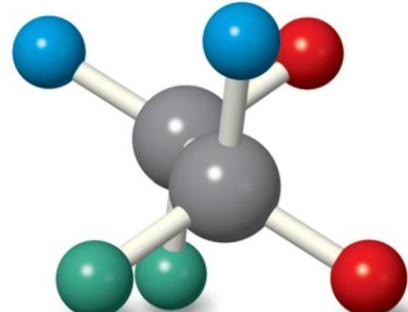
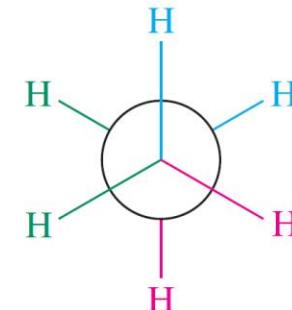
Keep front carbon fixed and
rotate back group



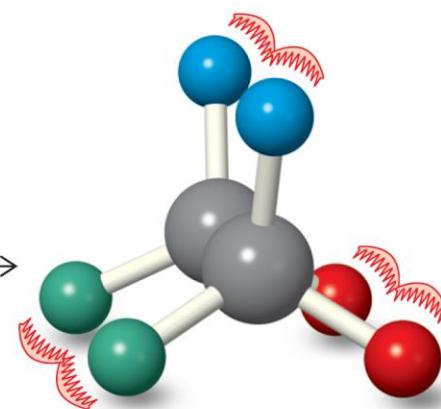
60°



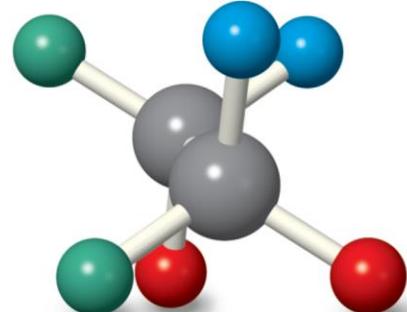
60°



60°



60°



Staggered

Eclipsed

Staggered

Rotation Around Bonds Is Not "Free": Barriers To Rotation

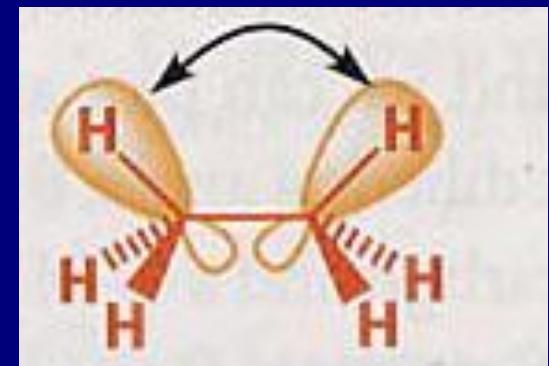
Ethane has barrier to rotation of ~ 3 kcal mol $^{-1}$.
Barrier due to steric and electronic effects.



Most stable rotamer is staggered

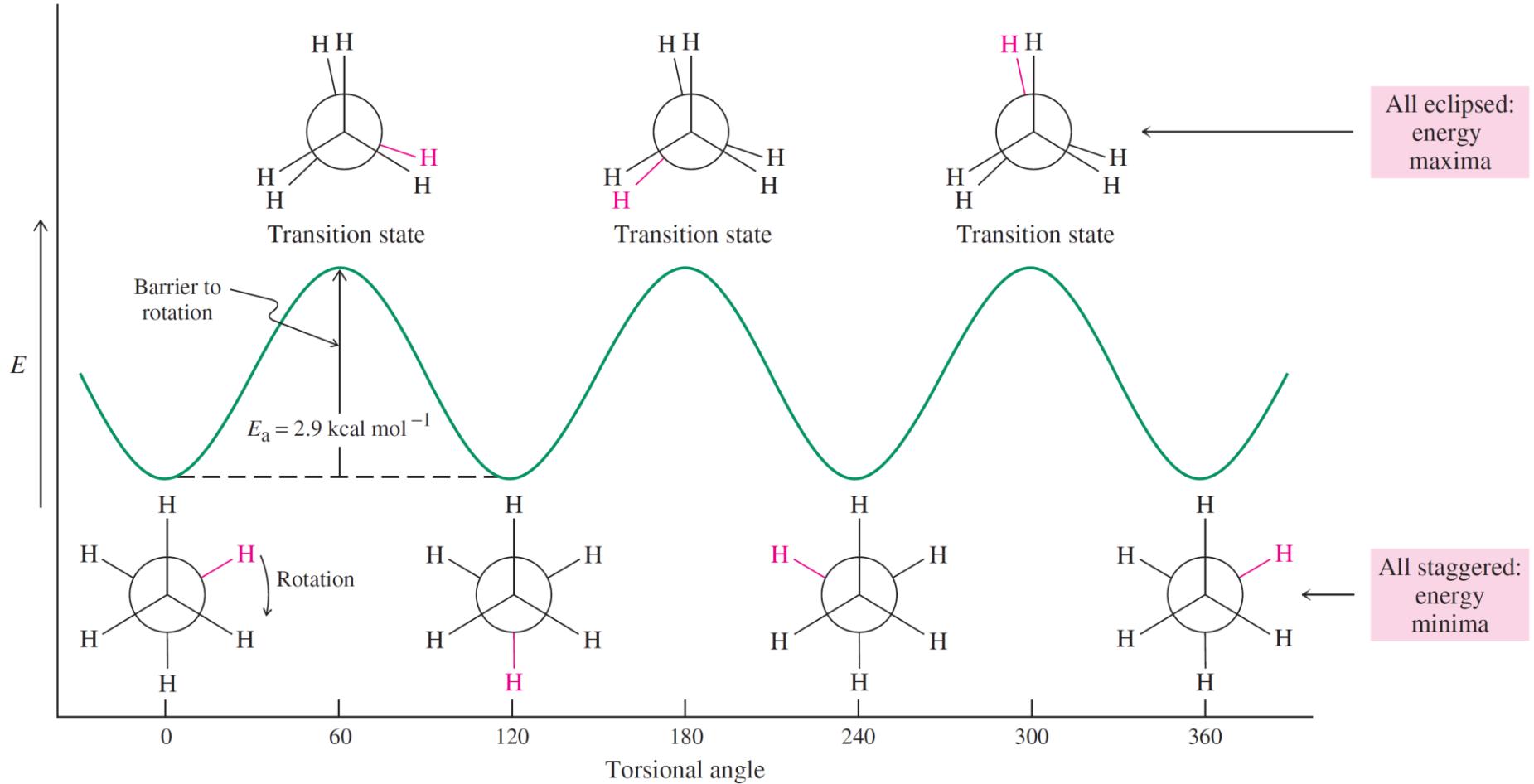


Least stable rotamer is the transition state of rotation and eclipsed

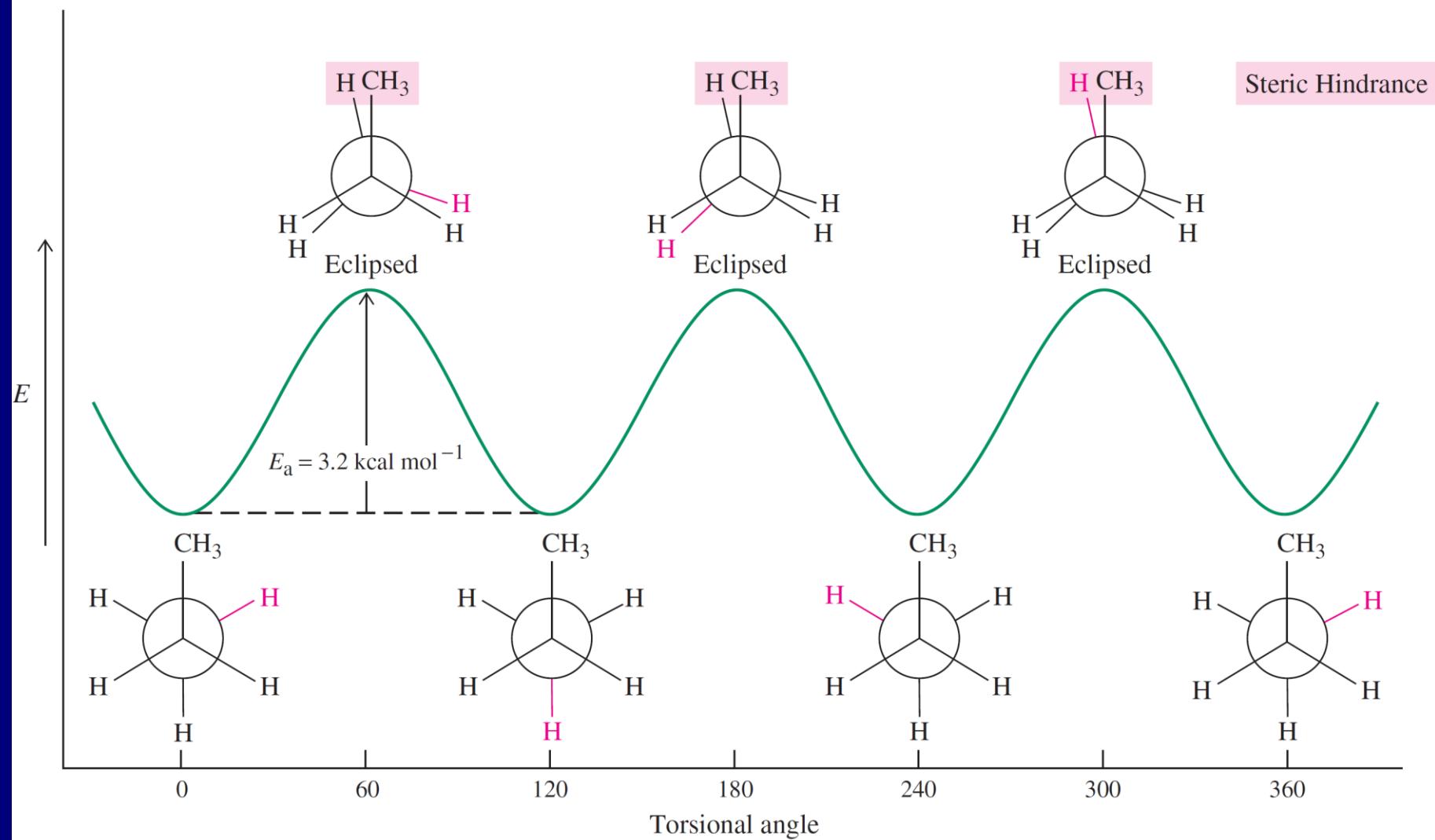


e-Repulsion

Potential Energy Diagrams



Propane: Methyl Increases Barrier



Butane: Staggered And Eclipsed Isomeric Rotamers

