Lewis Dot Structures and Curly Arrows

OH^- + CH_3CH_2-Br $\longrightarrow$ Br$^-$ + CH_3CH_2-OH
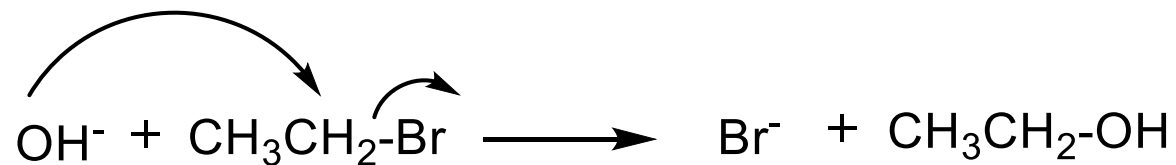
1. Lewis Dot Structures

2. Curly arrows

Gilbert N. Lewis

(*Nominated more than 35 times but never got Nobel prize*)

✓ G. N. Lewis proposed Lewis dot structures to represent the valence shell electronic configuration of molecules

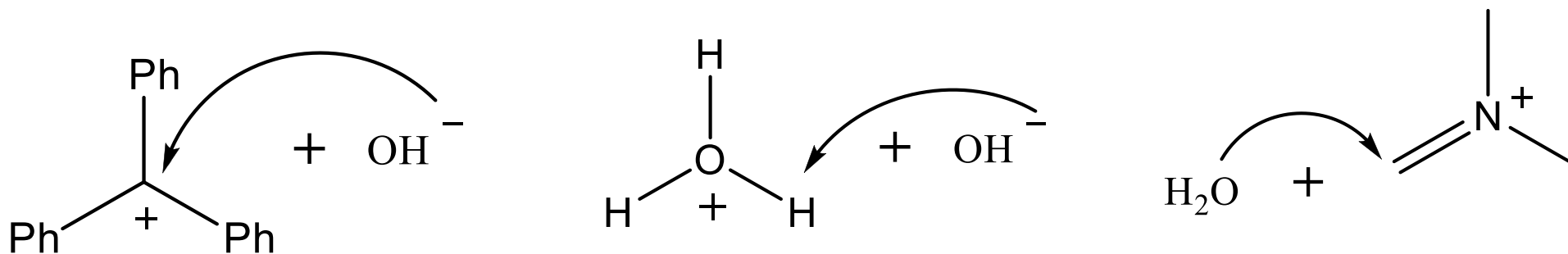✓ This was proposed in 1916 when quantum mechanics was at its nascent state; no idea of orbitals

Formal Charge and Actual Charge Distribution

➢ We often use the formal charges in Lewis Structures to show curly arrow mechanism

➢ Curly arrows to represent coulombic interactions is not a good idea!

➢ Molecular orbitals will give a better indication about writing curly arrow mechanisms

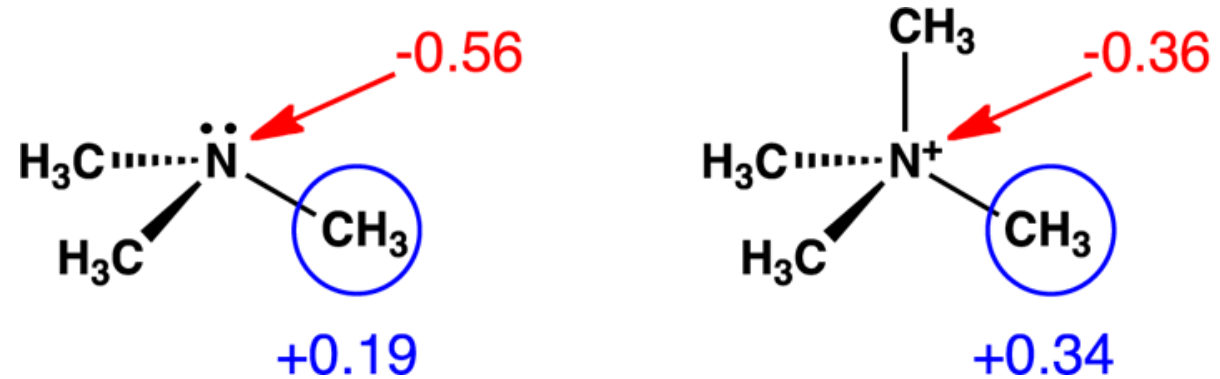*The main problem is that formal charges in Lewis structures often misrepresent the charge distribution in molecules*

Let's consider the following:
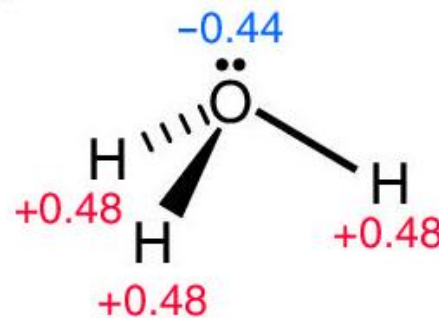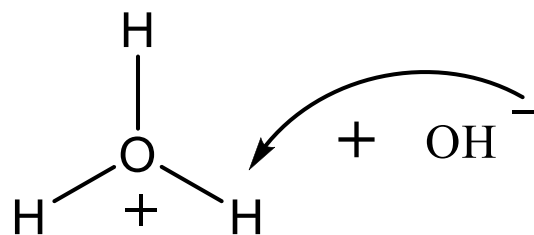
✓ The oxygen still retains a partial negative charge in H_3O^+

✓ The LUMO in H_3O^+ has higher contribution from hydrogen

Another example:

$H_3C \cdots N$ -0.56
H_3C CH_3
+0.19

CH_3
$H_3C \cdots N^+$ -0.36
H_3C CH_3
+0.34

The Nature of Chemical Bond


✓ In 1926, Linus Pauling, then a promising young doctoral candidate, went to Europe to study quantum mechanics with an eye toward applying this new physics to problems in structural chemistry. He did his studies with Arnold Summerfeld in Munich, Niels Bohr in Copenhagen and Erwin Schrödinger in Zurich

✓ Nobel Prize in Chemistry, 1954

✓ Nobel Peace Prize, 1962
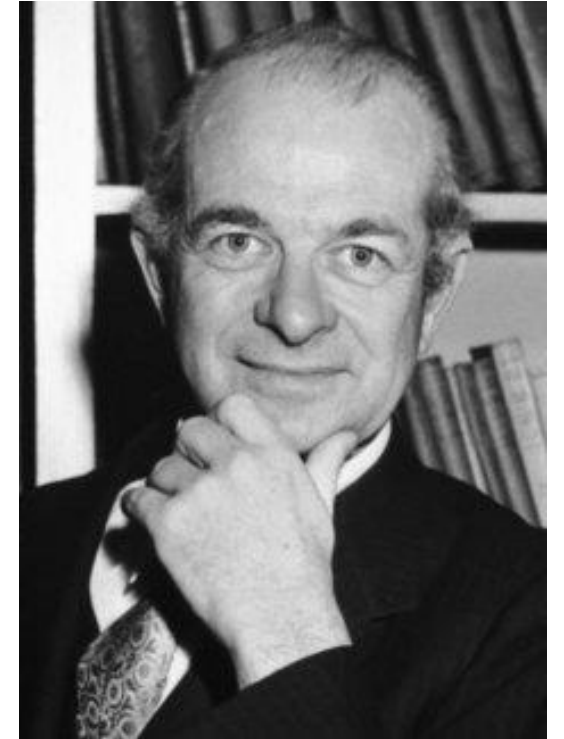
Linus Pauling

Caltech, USA

As two molecules collide, three major forces operate

1. The occupied orbitals of one repel the occupied orbitals of the other

2. Any positive charge on one attracts any negative charge on the other (and repels any positive)

3. The occupied oribitals (especially the HOMOs) of each interact with the unoccupied orbitals (especially the LUMOs) of the other

LUMO
HOMO

LUMO
HOMO

MOs for
reactant A

MOs for
reactant B
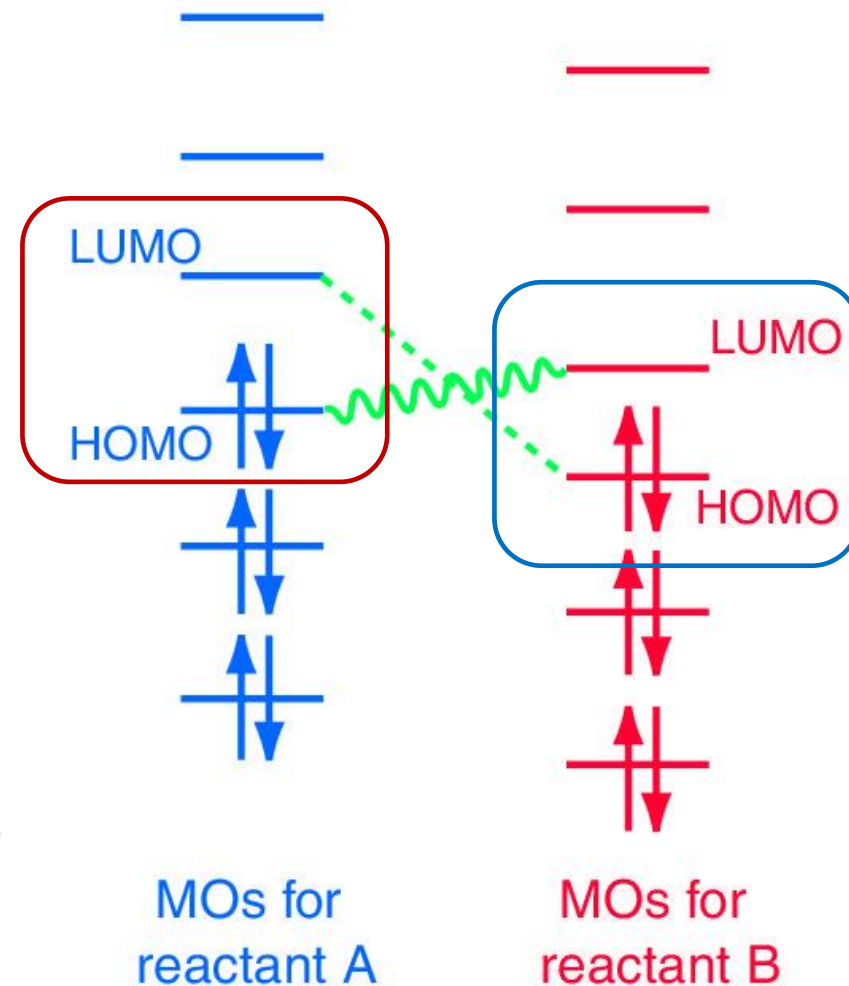
In a chemical reaction, molecular orbitals as well as the charges on the reactants are important

We will use the following form for our analysis:

ΔE (interaction energy) : + Σ sterics − Σ orbital overlap/(E_{LUMO} −E_{HOMO}) + Σ charge interaction

Reactivity

Curly arrows
(Interaction between *frontier molecular orbitals*)

➢ *The more negative is the value of ΔE, the higher is the reactivity*

✓ The energy (ΔE) gained/lost when the orbitals of one reactant overlap with those of another

✓ *HOMO (Nucleophile) and LUMO (Electrophile)/ HOMO (Base) and LUMO (Acid)*

Molecular Orbital Description of the following Reactions:

Nucleophilic Substitution: Unimolecular (S_N1) and Bimolecular (S_N2)

Rate Laws and Rate Limiting Step

➢ The rates of chemical reactions are dependent on concentrations
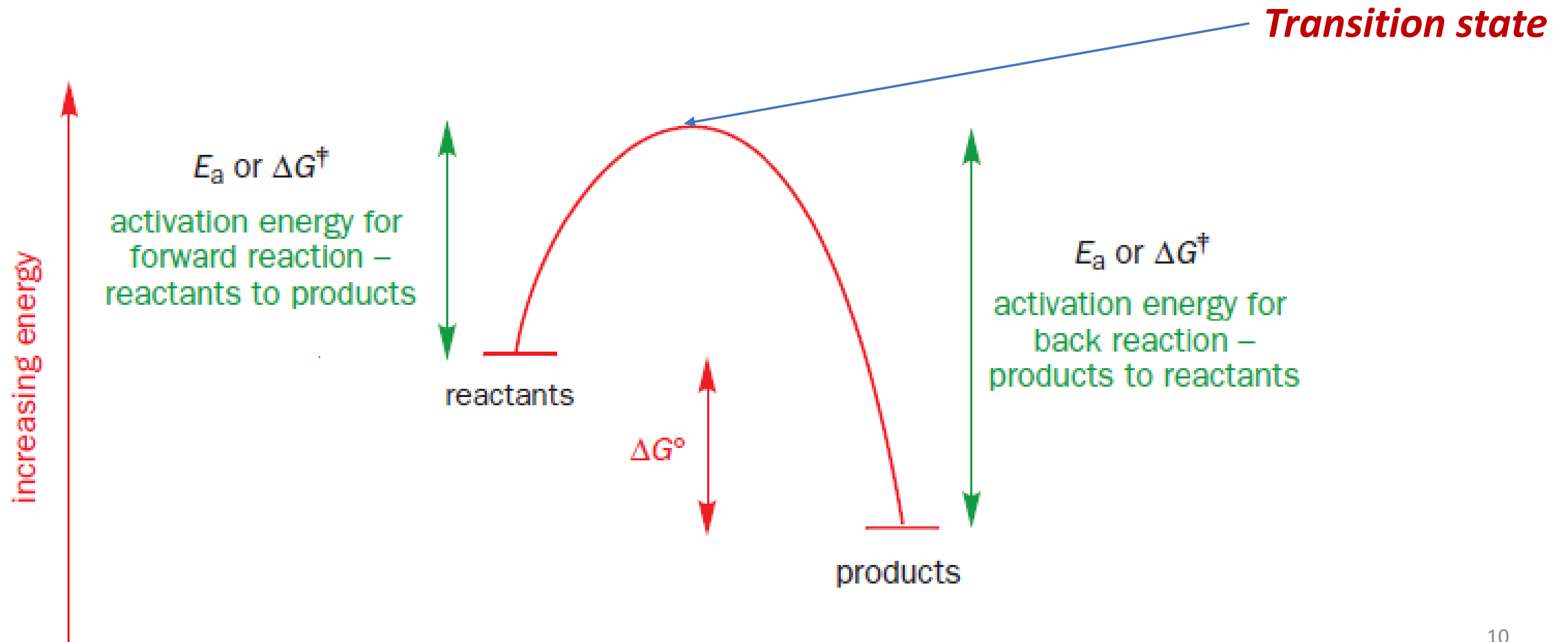
$$\text{Rate} = k [A]^x [B]^y$$

k = Rate Constant

A & B = Reactants

x & y = Reactant orders

➢ If a reaction has several steps, the rate is determined the rate of the slowest step

➢ This step is called rate determining step (rds) or rate limiting step (rls)

$$A \xrightarrow{\text{Slow}} B \xrightarrow{\text{Fast}} C$$

$$A \xrightarrow{\text{Fast}} B \xrightarrow{\text{Slow}} C$$
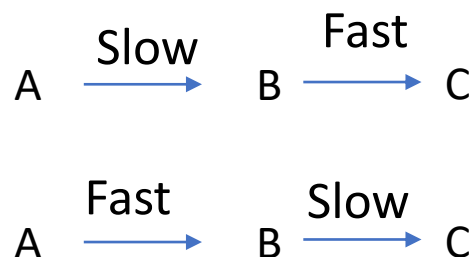
Transition State and Activation Energy

➢ In every reaction, the reactants go through an energy uphill process

➢ An activation energy is required to reach the transition state

Transition state

E_a or $\Delta G^{\dagger}$

activation energy for forward reaction – reactants to products

reactants

increasing energy

E_a or $\Delta G^{\dagger}$

activation energy for back reaction – products to reactants

$\Delta G°$

products

Nucleophilic Substitution at a Saturated Carbon (Tetrahedral) Atom

S_N2

S for Substitution

N for nucleophilic

2: The order of the reaction

S_N1

S for Substitution

N for nucleophilic

1: The order of the reaction

Nucleophilic Substitution Bimolecular (S$_N$2)

$$OH^{\ominus} + CH_3Cl \longrightarrow CH_3OH + Cl^{\ominus}$$

✓ *We are not going to look at every bonding and antibonding MOs in the reactants*

✓ First, we have to identify which bond is being formed and which one is being broken: *only they are the important ones*

✓ C-Cl bond breaks, C-O bond forms

✓ OH⁻ is the nucleophile here and CH_3Cl is the electrophile

✓ We have to identify the HOMO of OH⁻ and the LUMO of CH_3Cl

✓ The C-Cl bond breaking can be visualized as a pair of non-bonding electrons from the HOMO of OH⁻ are donated to the σ* of C-Cl bond and this will make the bond order of the C-Cl bond momentarily zero. Cl⁻ leaves and a new compound is formed having a C-O bond