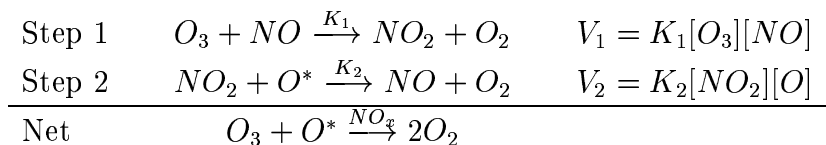


# Basic Chemical Principles

## 1: Reaction Kinetics

*Mechanism* of a reaction is a sequence of basic reactive events (collisions leading to reactions) leading from a set of reactants to a set of products.

Example: Consider the destruction of ozone in the presence of nitric oxide  $NO$ : bimolecular collisions.

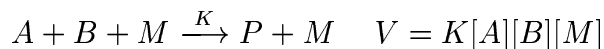


- $K_1$  and  $K_2$  are *rate constants*
- *Rate-determining step*: often one basic step is much slower which simplifies the overall rate law
- *Steady-state approximation*: Intermediates (often *radicals*) very reactive and disappear quickly

What determines the rate constants? Usually well-described by the *Arrhenius law*

$$K_1(T, \rho) \simeq A \exp\left\{-\frac{E_a}{RT}\right\}$$

- $E_a$  is an *activation barrier*
  - High  $T$   $\longrightarrow$  faster rates since rate constants larger
- Prefactor  $A$  depends on rate of collision of reactants  $\longrightarrow$  mobility (masses) and density
  - *Diffusion-controlled* reactions: prefactor  $A$  is the most important factor since  $E_a$  is small.
- \*\*\*\*Key Point\*\*\*\* When many different reaction paths are available, the **rates** determine which dominate.
  - At low densities, trimolecular steps slow since trimolecular collisions very rare



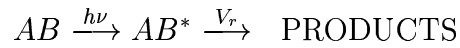
- Concentrations are tiny
- In atmosphere, *photo-chemical reactions* are important: reactions initiated by light

- Interaction of matter with radiation can cause chemical events: bonds broken, molecules excited
- Creation of *radicals*

### Molecular structure, reactivity and interaction with light:

- Valence electrons responsible for chemical activity
- Orbitals come from quantum mechanics: electron has spin states  $\pm 1/2$  (spin up, spin down)
- Pauli principle: If electrons have same spin, cannot be paired in same orbital
- *Electronic ground state*: Lowest energy configuration of electrons in orbitals
- To form chemical bond, combine atomic orbitals to form “molecular orbitals”: Electrons fill these orbitals-singlets, doublets, triplets,...
- A molecule with an unpaired electron is called a **radical**.
  - **Important fact**: Quirk of quantum structure that Oxygen atom *and* molecule  $O_2$  are ground state triplets.
- **Important fact**: Quantum mechanics tell us that
  - singlet and singlet are reactive
  - radical and radical are reactive
  - radical and singlet are *not* reactive: Spin forbidden
- Consequence: Reactions with ground state Oxygen are slow
- Molecules can be excited by absorbing radiation
  - Frequency of absorbed light determined by  $h\nu = \Delta E$ .
  - Absorption maintains spin multiplicity: spin state change must occur through collision with another body
  - Can use thermodynamics to estimate minimum amount of energy required from light for a chemical change
  - Excitation can be lost through many channels:
    1. Fluorescence (light emission)
    2. Collisional deactivation

3. Energy transfer
  4. Reaction (like dissociation)
- Quantum yield: relative importance of pathway
  - Example:  $\phi_r = .9$  means 90% of time excited absorber (chromophore) goes on to react.



- Beer-Lambert Law:  $V_r = I_0(\lambda)A\phi_r$ 
  - $I_0(\lambda)$  is the wavelength (or frequency) dependent intensity of radiation,  $A$  is the absorption efficiency (depends on concentration, path of light through sample and molecular factors)
  - $I_0(\lambda)A$  can be viewed as rate of producing excited chromophore