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.

Step 1	$O_3 + NO \xrightarrow{K_1} NO_2 + O_2$	$V_1 = K_1[O_3][NO]$
Step 2	$NO_2 + O^* \xrightarrow{K_2} NO + O_2$	$V_2 = K_2[NO_2][O]$
Net	$O_3 + O^* \xrightarrow{NO_x} 2O_2$	

- 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*

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

- 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

$$A + B + M \xrightarrow{K} P + M \qquad V = K[A][B][M]$$

  - 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 responsable 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.

$$AB \xrightarrow{h\nu} AB^* \xrightarrow{V_r} \text{ PRODUCTS}$$

- 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