



Chemistry Lecture 2 – Gases, Kinetics and Chemical Equilibrium

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Gases

- STP: 0 degrees C, 1 atm, 22.4 L/mol
- Ideal Gas Law:

$$PV = nRT$$

Assumes molecules have no volume, no intermolecular forces, elastic collisions

- Partial pressure: contribution of one gas to the total pressure

$$P_a = \chi_a P_{total}$$

- Dalton's law of partial pressures:

$$P_{total} = P_a + P_b + \dots$$

- Average molecular kinetic energy:

$$KE_{avg} = \frac{3}{2}kT$$

- Graham's law:

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

Generally used to describe relative velocities. But can also be used for:

- Effusion: gas going through pinhole, $\frac{effrate_1}{effrate_2} = \sqrt{\frac{m_2}{m_1}}$
- Diffusion: gas moving into empty space (i.e. two ends of tube), $\frac{diffrate_1}{diffrate_2} = \sqrt{\frac{m_2}{m_1}}$
- Real gases: when pressure is high or temperature is low
 - Actual volume is greater than ideal volume b/c gas molecules now have volume
 - Actual pressure is less than ideal pressure b/c gas molecules attract each other

Reactions

- Molecules must (1) collide, (2) have total KE > activation energy, (3) are in right orientation
 - Reaction rate increases with temperature b/c more collisions, more KE
- Rate law: rate = $k_f[A]^\alpha[B]^\beta$ – can find with multiple experiments with changing [A], [B]
- Reaction order = sum of exponents
 - Zero order: rate = $k_f[A]$ vs. t has linear slope $-k_f$
 - First order: rate = $k_f[A]$, $\ln[A]$ vs. t has linear slope $-k_f$
 - Second order: rate = $k_f[A]^2$ or rate = $k_f[A][B]$, $\frac{1}{[A]}$ vs. t has linear slope k_f
 - Third order: rate = $k_f[A]^3$, $\frac{1}{2[A]^2}$ vs. t has linear slope k_f
- Multiple-part reactions: overall rate is defined by rate determining step (“slow step”) and all steps PRIOR to it

Catalysts

- Increases rate without being consumed or permanently altered
- Heterogeneous: different phase (usually solids), can enhance rate by increasing surface area
- Homogeneous: same phase, can enhance rate by adding more catalyst



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Equilibrium

- When forward reaction rate = reverse reaction rate

$$K = \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{\text{at equilibrium}} = \left(\frac{\text{products}^{\text{coeffs}}}{\text{reactants}^{\text{coeffs}}} \right)_{\text{at equilibrium}}$$

- When amounts are given in terms of partial pressures, we use the partial pressure equilibrium constant:

$$K_p = K_c (RT)^{\Delta n} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

- Reaction quotient: tells us which direction a reaction will go

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{\text{products}^{\text{coeffs}}}{\text{reactants}^{\text{coeffs}}}$$

If $Q = K$, reaction is at equilibrium

If $Q > K$, there's too many products so reaction will go backwards

If $Q < K$, there's too many reactants so reaction will go forwards

- Le Chatelier's Principle: if we add a stress, it will proceed in a direction to counteract the stress
 - Adding product/reactant
 - Changing pressure of system
 - Heating/cooling the system
- Note that adding a nonreactive gas will not shift the equilibrium b/c it doesn't change partial pressures