

CH 417 Physical Chemistry for the Life Sciences
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Physical Chemistry for the Chemical & Biological Sciences
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Coverage: Chapters 12-14 & parts of subsequent chapters
 Prerequisites: CH416, College physics and calculus
 Homeworks: Assigned from each chapter. After approximately one week the homework will be collected and worked out solutions to these problems will be available in the chemistry office. Turned-in homeworks will count 15% of the final grade.
 One Midterm Examination: 1/3 homework problems, 1/3 other problems, 1/3 *understanding*, definitions, etc. No makeup examination will be given, if you miss the midterm, the final will determine your grade.
 Final Examination: Standardized Exam multiple choice
 Grading: 15% homework; 40% midterm; 45% final exam.
 Bring to midterm: calculator, lined paper, pencil. Eqns summary provided
 Bring to final: calculator, scratch paper, scantron, etc.

COURSE OUTLINE

Kinetic Theory of Gases, Transport Properties of Gases and Liquids, Centrifugation, Chemical Kinetics, Quantum Chemistry & Spectroscopy
 (equivalent UNITS: molecular: molec $\text{cm}^{-3}\text{s}^{-1}$; molar: mole $\text{l}^{-1}\text{s}^{-1}$;
 $N_a \equiv$ atoms/molecule; gas constant R , Boltzman $k \equiv R/N_o$ ($N_o \equiv$ Avogadro's number)
 units are given for various quantities at the right hand margin)

Energy review: energy \equiv ability to do work, or acquired when work is done
 $E =$ energy per mole, $\epsilon \equiv E/N_o =$ energy per molecule; $m \equiv$ mol.wt $\equiv M/N_o$
 potential energy due to position in a field

gravitational = mgh

electrical = qV

kinetic energy due to motion

linear = $mu^2/2$

rotational = $I\omega^2/2$ $I =$ moment of inertia, $\omega =$ rot. freq.

centrifugal = $mx^2\omega^2/2$ $\omega =$ radians/s = 2π revolutions/s

I. The Equipartition of Energy Principle: $\epsilon = kT/2$ per degree of freedom
 $1/2 mu^2 = 3kT/2$ (brief review from Ch416)

- A. degrees of freedom: x, y, z (3 per atom, $3N_a$ per molec.)
- B. kinetic and potential energy
- C. evidence for equipartition: heat capacity
- D. translation, rotation, vibration, electron energy
- E. temperature dependence of heat capacity

II. Kinetic Theory of Gases

- A. Gas phase collision theory--A collides with B
 $u \equiv$ velocity; reduced mass $\mu_{AB} \equiv [1/m_A + 1/m_B]^{-1}$, $\sigma_{AB} \equiv r_A + r_B$

1. Collision rate: collisions of A with B

$$Z_A = \pi \sigma_{AB}^2 u_{rel}[B], (Z_A \equiv Z \text{ in book}) \quad \text{collisions s}^{-1}$$

a.
b.
c.

2. Bimolecular collision rate:

$$Z_{AB} = \pi \sigma_{AB}^2 u_{rel}[A][B], (Z_{AB} \equiv Z \text{ in book}) \quad \text{collisions cm}^{-3}\text{s}^{-1}$$

- B. Mean Free Path $\lambda \equiv l = \langle u \rangle / Z_A$, distance per collision
- C. Random walk, diffusive transport $\langle x^2 \rangle = 2Dt = Z_A l^2$

cm

D. Distribution of molecular speeds

$$P(u) \equiv \frac{dN}{N_0} = \frac{4\pi}{2\pi kT} \left\{ \frac{m}{2\pi kT} \right\}^{3/2} u^2 \exp\left(-\frac{mu^2}{2kT}\right) du \quad \text{dimensionless}$$

D. Properties of Distribution Functions

1. Normalization, area = constant. $\int P(u) du = 1$
2. average values e.g. $\langle u \rangle = \int u P(u) du = \sqrt{(8kT/\pi m)}$
 $u_{rms} \equiv \sqrt{\langle u^2 \rangle} = \sqrt{(3kT/m)}$, $u_{rel} \equiv u_{AB} = \sqrt{(8kT/\pi \mu_{AB})}$
 note $\langle u \rangle$ does not = $\sqrt{\langle u^2 \rangle}$

III. Statistical distribution of energy levels: the Boltzman distribution

$$P_i = N_i/N = g_i \exp(-E_i/RT) / \sum_i g_i \exp(-E_i/RT)$$

($i \equiv i^{\text{th}}$ state, $g \equiv$ degeneracy)

IV. Reactions and reactivity in the gas phase

A. Hard Sphere Collision Theory

1. Bimolecular collisions A+B
 - a. collision rate Z_{AB} (see above)
 - b. reaction rate $d[C]/dt$

B. Kinetics Definitions

- c.
- d.
1. Reacti
2. Reacti
3. Reacti

4. Reaction Rate Law, based upon mechanism
 - a. Sample mechanism ($\text{Cl}_2 + \text{CH}_2 = \text{CH}_2 \rightarrow \text{CH}_2\text{Cl} - \text{CH}_2\text{Cl}$)
 - b. rate terms
 - c. steady-state approximation
 - d. Rate law, orders, limiting cases
5. Unimolecular processes: collisions, vibrations
6. Termolecular processes

C. Rate constants vs. equilibrium constants;

$$K_{eq} = k_f/k_b; \text{ equilibrium as a dynamic state}$$

$$\text{Approach to equil. e.g. } A \xrightleftharpoons[k_b]{k_f} B \quad \tau_{eq} = 1/(k_f + k_b)$$

D. Reaction orders and their determination; molecularity

1. Integral orders (0, 1, 2, 3)
 - a. Graphical solutions
 - b. Method of initial rates
 - c. Limiting reagents
 - d. Pseudo reaction orders; method of isolation
2. Half-lives $t_{1/2}$ and life-times τ
 - a. zero order: rate independent of concentration
 $\tau = t/t_{1/2}$

b.

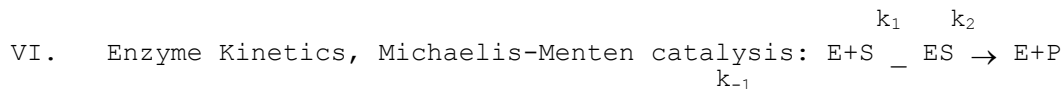
- c. 2nd order: $1/c = 1/c_0 + kt$, $\tau = 1/k[c]$

3. Non-integral orders, or no defined order

E. Energy and other Requirements in Chemical Rxns.

1. Energy barriers--activation energy, Arrhenius equation $k = A \exp(-E_a/RT)$
 - a. Arrhenius plots $\ln k$ vs. $1/T$
 - b. curvature in Arrhenius plots
 - c. negative activation energies/pre-equilibrium steps

2. Orientation requirements: steric factor p , activation entropy S_a
3. pressu
- F. TST thermodynamic rate constant
 $k = RT/h \exp(\Delta S^\ddagger/R) \exp(\Delta H^\ddagger/RT)$
- G. Activation energy E_a vs. enthalpy H_a
 1. gases vs. condensed phases; $RT\Delta n^\ddagger$
 2. detailed temperature dependence, ΔC_p^\ddagger
- H. S_a : units and point of reference
- V. Solution Phase Reactions and Reactivity
- A. Collision rate in solution
 1. solvent cage
 2. collisions $k_{\text{collision}} = RT/h$
 3. encounters $k_{\text{encounter}}$
 4. diffusion coefficient and elemental jumps
 5. temperature dependence of diffusion
- B. Reaction, gradients, diffusion
 1. Smoluchowski Equation $A+B \rightarrow \text{prod}$
 $k_{\text{encounter}} = 4\pi\sigma_{AB}D_{AB}$
 2. time dependent and time independent gradients
 3. comparison of upper-limit kinetic rates in gases and in solution
- C. Transition state theory in solution
 $\text{rate} = kT/h K_\ddagger (\gamma_A\gamma_B/\gamma^\ddagger) [A][B]$
- D. Influence of the solvent, ionic strength
 $\log k = \log k_{\infty\text{dilution}} + 2z_A z_B (0.509) \sqrt{I} / (1 + \sqrt{I})$
 $I = 0.5 \sum_i c_i z_i^2$



1. Michaelis-Menten Eqn.
$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m + [S]}$$

$$K_m \equiv (k_{-1} + k_2) / k_1$$
2. algebraic approaches/limiting cases, data analysis
 - a. initial rate v_0
 - b. maximum rate $v_{max} = k_2 E_0$
 - c. turnover number k_2
 - d. graphical methods
3. more complicated mechanisms, several intermediates, etc.

4. Comp.

reduces to M-M eqn with $K'_M = K_M(1 + [I]/K_I)$

5. A closer look at enzyme catalysis
 - a. the enzyme binds to (stabilizes) the *transition state*, not the substrate!
 - b. accurate reaction coordinate diagram

VII. Diffusion, Flux J

- A. Fick's first and second laws

$$J = -D \frac{d[C]}{dx}, \quad \frac{d[C]}{dt} = D \frac{d^2[C]}{dx^2}$$

1. concen
2. flux,
3. diffus

- a. gases $D = \lambda u / 2 \approx 1 \text{ cm}^2 \text{ s}^{-1}$ (@STP)
 $\lambda = (\sqrt{2} n \sigma^2 [C])^{-1}$
- b. liquids $D = kt / f = kT / 6\pi\eta r \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
4. diffusion dist. $\langle x^2 \rangle = \text{no.steps } l^2 = Z_A l^2 = \langle u \rangle^2 / Z_A$
 in terms of diffusion coeff, $\langle x^2 \rangle = 2Dt$
5. one solution to Fick's 2nd law:

VIII. Duality of light/matter w/ wave & particle nature

- A. Wave behavior:

1. repetitive behavior: sines, cosines, etc.
2. wavelength, frequency and velocity $c = \lambda v$
3. constructive and destructive interference
 - a. frequency analysis
 - b. double slit diffraction
 - c. x-ray diffraction-Bragg equation
4. Bohr's model of the atom; Rydberg equation
 radial acceleration force = coulombic force

$$\mu v^2 / r = ze^2 / 4\pi\epsilon_0 r^2$$

- B. Energy and matter
- $E = mc^2$
- (Einstein),

- C. Electromagnetic radiation (light)

1. wave nature $c = \lambda v$
2. particle nature $E = hv$

- D. Molecular behavior in Coulombic Fields
- $F = -q_1 q_2 / 4\pi\epsilon_0 r^2$
- ,
- $E = q_1 q_2 / 4\pi\epsilon_0 r$
-
- translation, rotation, vibration, polarization,
- $\epsilon \equiv$
- dielectric const

IX. Absorption and emission of light: ions and dipole moments

- A. molecular rotations: microwave region, Raman
- B. molecular vibrations: infrared region, Raman
- C. electronic orbitals: visible and ultraviolet
- D. uncertainty Principle: $\Delta p \Delta x = h / 4\pi$, $\Delta E \Delta t = h / 4\pi$

- E. DeBroglie wavelength $\lambda=h/p$ (wave nature of matter)
 origin of DeBroglie wavelength $E=mc_2=hv$
- F. time dependent or time independent (standing wave)
 Schrodinger Equation $H\psi=E\psi$, $H\equiv$ Hamiltonian Operator

$$H \equiv \frac{-\hbar^2}{4\pi^2m} \frac{d^2}{dx^2} + U \quad (U\equiv\text{Potential Energy PE})$$

$$(E\equiv\text{Total Energy}=\text{KE}+\text{PE})$$
1. wave function $\psi=f(x,y,z,t)$ or $f(r,\theta,\psi,t)$
 2. ψ^2 gives probability of finding the object (wave) in any region of space i.e. Probability = $\int \psi^2 dx dy dz$
 3. ψ not a function of time for a standing wave or equilibrium electron orbital
- X. Fundamental solutions to Schroedinger's equation: energy levels of atoms and molecules expressed in terms of waves: translation, rotation, vibration, electronic
- A. Translation: particle in the box; boundary conditions,
1. wavefunctions or eigenfunctions: $\psi_n=(2/a)^{1/2}\sin(n\pi x/a)$
 2. potential barrier problems, tunneling
 3. energies or eigenvalues: $E=n^2\hbar^2/8ma^2$; quantum number $n=1,2,3\dots$
 4. sample application: conjugated π systems
- B. Rotation, the rigid rotor: diatomic molecule A-B
1. energy levels and energy spacings $J(J+1)\hbar^2/4\pi^2\mu_{AB}r^2$ $J=0,1,2\dots$
 $E_J=B J(J+1)$, moment of inertia $I=\mu_{AB}r^2$
 2. angular momentum
 - a. space quantization ($g=2J+1$)
 - b. selection rules: $\Delta J=+1$ because photon has angular momentum, and molecule must have a dipole moment
 - c. energy spacings $h\nu=2B(J+1)$ in absorption lines
- C. Vibration: harmonic and anharmonic oscillator: diatomic molec A-B
1. Potential energy functions
 - a. Harmonic Osc. Hooke's Law $F=-k(r-r_0)$, $U=k(r-r_0)^2/2$
 parabola, $k\equiv$ force constant
 - b. Anaharmonic Osc. Morse potential $U=U_0[1-e^{-a(r-r_0)}]^2$
 $U_0\equiv$ depth of potential well
 2. energy levels: kinetic, potential, total & zero point energy
 - a. $E_{\text{harmonic}} = (v+1/2)h\nu_0$, $\nu_0\equiv(k/\mu)^{1/2}/2\pi$
 - b. $E_{\text{Morse}} = (v+1/2)h\nu_0 - [(v+1/2)h\nu_0]^2/4U_0$
 - c. wave functions
 - d. Potential energy diagrams
 - i. electronic states
 - ii. total, kinetic, & potential energies
 - iii. rotation, vibration, electronic energies
 - e. microwave, infrared, visible absorption spectra
 - i. absorption/emission lines $\Delta E=h\nu=hc/\lambda$
 - ii. absorption/emission intensities, Boltzman distribution
- D. Electronic, hydrogen atom: Rydberg and Schrodinger equations
1. Rydberg Equation (obtained experimentally)

$$\frac{1}{c} = \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right); \quad R \equiv \frac{2\pi^2\mu z^4 e^4}{(4\pi\epsilon_0)^2 \hbar^3 c}$$

$$n_1 = 1(\text{Lyman}); = 2(\text{Balmer}); = 3(\text{Paschen})$$

$$E=\text{constant}(1/n_1^2-1/n_2^2)$$
. Difference between two energy levels
 2. Schroedinger Eqn (obtained mathematically)
 - a. quantum numbers: n,l,m (or m_l), s
 - i. n principle quantum number: $K,L,M\dots$ shells
 - ii. l orbital quantum number: $s,p,d,f\dots$ orbitals

- iii. m (m_l) magnetic q.n.: orientation p_x, p_y, p_z
 - iv. s spin quantum number $\pm 1/2$
 - b. Pauli exclusion principle
- E. simple molecules: molecular orbital theory
 - 1. linear combination of atomic orbitals
 - a. bonding, antibonding, and nonbonding orbitals: σ, σ^*
 - b. atomic and molecular term symbols e.g. $^2P_{1/2}, ^1\Sigma_g^+$
 - 2. hybridization
 - 3. diatomic molecular orbitals
- F. Modern (approximate) solutions to Schrodinger's Eq.
 - 1. ab initio calculations (most rigorous)
 - 2. semiempirical calculations (less rigorous)
 - 3. molecular mechanics, force-field calculations (Hooke's Law)

$\pi, \pi^*; n$