Physical Chemistry (Chem 132A)

Lecture 26
Wednesday, December 8

Homework 9 (last homework) Due on Saturday, December 9
Last homework of the quarter

Reminder: FINAL EXAM, DEC. 15,

8—10AM

Please Complete the Course Evaluations

Final Exam Logistics

Final exam: Friday, December 15, 8Am

The Exam will cover Chapters 1—6, 19, 20, 21a,b

- **there will be a seating chart**

- **same procedures as the midterms**
  1 page notes allowed (use both sides)
  bring calculator

- **arrive by 8Am**

Material Covered Before Midterm 1

- **Important definitions**
  extensive, intensive, state functions, equation of state, closed system, open system, isolated system, reversible, adiabatic, etc.

- **Heat(q) and work(w): sign of w**

- **$\Delta U = q + w$, $dU = dq + dw$**

- **First Law: internal energy of an isolated system is constant**

- **Heat capacity** $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ $\quad C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$ $\quad q_v = C_v \Delta T$

- **$H = U + pV$**

$$\Delta_r H^0 = \sum_{\mathrm{Products}} \nu \Delta_f H^0 - \sum_{\mathrm{Reactants}} \nu \Delta_f H^0$$

Material Covered before Midterm 1—page 2

- **Joule-Thompson expansions**
- $$dS = \frac{dq_{reversible}}{T}$$
- $$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$
- **Second Law: "The Entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{total} > 0$"**
- **for a phase transition:** $\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$
- $$\Delta A = \Delta U - T\Delta S$$

  For constant V&T ΔA negative is spontaneous

Material Covered Before Midterm 1—page 3

- $\Delta G = \Delta H - T\Delta S$

  For constant P&T ΔG negative is spontaneous

Note: quantities are for the SYSTEM

- Maxwell's relations
- fugacity
- phase boundaries in single component phase diagrams
- phase rule: $F = 3 - P$ (for single component system
- definition of 1st order and 2nd order phase transitions
  - $\ln\left(\frac{p}{p^*}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$ Clausius–Clapeyron Equation T dependence of vapor pressure

Important Topics Up to Midterm 2 (slide 1)

- **Mixtures: Limited to Binary mixtures**

  Phase rule: F = C–P+2

  partial molar quantities:

$$V_j = \left(\frac{\partial V}{\partial n_j}\right)_{p,T,n'}$$

Gibbs-Duhem equation: $$d\mu_B = -\frac{n_A}{n_B}d\mu_A$$

Mixing (for an ideal gas mixing is driven by delta S_{mix})

for non-Ideal systems enthalpy may play a role

Roult's Law: $p_A = x_A p_A^*$

Non-ideal behavior: Henry's Law: $p_B = x_B K_B$ B is solute

Important Topics Up to Midterm 2 (slide 2)

Mixtures (continued)

- Colligative Properties
  - freezing point depression
  - boiling point elevation
- Phase Diagrams for Binary Mixtures
  - distallations
  - azeotropes

Liquid-solid phase diagrams

- cooling curves
- eutectic mixtures

Non-ideal behavior

- fugacity
- activities:

$$a_A = \gamma_A x_A$$

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$

Important Topics Up to Midterm 2 (slide 3)

- **Ionic Solutions**

  Debye-Huckel Law

$$\log\gamma_{\pm} = -0.509\left|z_+ z_-\right| I^{1/2}$$

$$I = \frac{1}{2}\sum_i z_i^2\left(\frac{b_i}{b^0}\right)$$

I is the Ionic Strength

- **Equilibrium Constants and Reaction Quotients**

$$\Delta_r G = \Delta_r G^0 + RT\ln\left(Q\right)$$

$$\mathbf{\Delta G^0 = -RT\ln K}$$

$$K = \frac{a_C a_D}{a_A a_B}$$

$$a_A = \gamma_A x_A$$

$$K = K_\gamma K_b$$

Important Topics Up to Midterm 2 (slide 4)

- **Electrochemical Cells**
  - **Half reactions**
  - **Balancing Redox reactions**
  - **Standard cell potentials**

- **Nernst Equation:**

$$E_{cell} = E^0_{cell} - \frac{RT}{\nu F}\ln Q$$

$$E^0_{cell} = \frac{RT}{\nu F}\ln K$$

Important Topics Up to Midterm 2 (slide 5)

- **Temperature Dependence of K**

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- **Le Chatelier's Principle**

- **Boltzmann Speed Distribution**

$$\left\langle v^n \right\rangle = \int_0^\infty v^n f(v)\,dv$$

$$v_{mean} = \int_0^\infty v f(v)\,dv = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$v_{rms} = \left(\int_0^\infty v^2 f(v)\,dv\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

Important Topics Up to Midterm 2 (slide 6)

- **Collision cross sections**
- **Mean free path**

- **Flux**

$$J(matter) = -D\frac{dN}{dz}$$

$$J(thermalenergy) = -\kappa\frac{dT}{dz}$$

Important Topics Up to Midterm 2 (slide 7)

$D = (1/3)\lambda v_{mean}$ **Diffusion coefficient**

$\kappa = (1/3)\nu v_{mean}\,\lambda N k$ **Thermal conductivity**

$\eta = (1/3)v_{mean}\,\lambda m N$ **Viscosity**

These expressions provide reasonable approximations for the transport coefficients.

Important Topics Up to Midterm 2 (slide 8)

- **Ion Mobilities**

  S = uE

  E = applied field

  u is the mobility

- **Diffusion Equation**

$$F = -\left(\frac{\partial \mu}{\partial x}\right)_{T,p}$$

$$F = -RT\left(\frac{\partial \ln a}{\partial x}\right)_{T,p} = -RT\left(\frac{\partial \ln c}{\partial x}\right)_{T,p} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p}$$

In One dimension:

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial^2 x}$$

Important Topics Since Midterm 2 (slide 1)

- **Kinetics**

  Rate Laws
  - **Stoichiometry**
  - **Elementary Steps**
  - **Slow steps control the rate**
  - **Pre-equilibrium followed by slow step**
  - **Steady-State Approximation**
  - **Determine the rate law from initial rate data**

  Integrated Rate Laws
  - **First Order, Second Order, Zeroth Order**
  - **Half Lifes**

  Arrhenius Equation (Activation Energy, A factor)

Important Topics Since Midterm 2 (slide 2)

- **Catalyis**
  can increase A or decrease E_a
  does not change the thermodynamics!!

- **Unimolecular Reactions**
  Looks first order except at low concentration

- **Collision Theory Model**

$$k \sim P\, \sigma\, (T/M)^{1/2}\, e^{-E'/RT}$$

Steric factor **encounter rate** **collision energy dependence**

Important Topics Since Midterm 2 (slide 3)

- **Collision Theory Model for the Rate Constant**

$$k_r = \left(\frac{8}{\pi\mu kT}\right)^{1/2}\left(\frac{1}{kT}\right)\int_{E_a}^{\infty} E\sigma(E)e^{-E/kT}\,dE$$

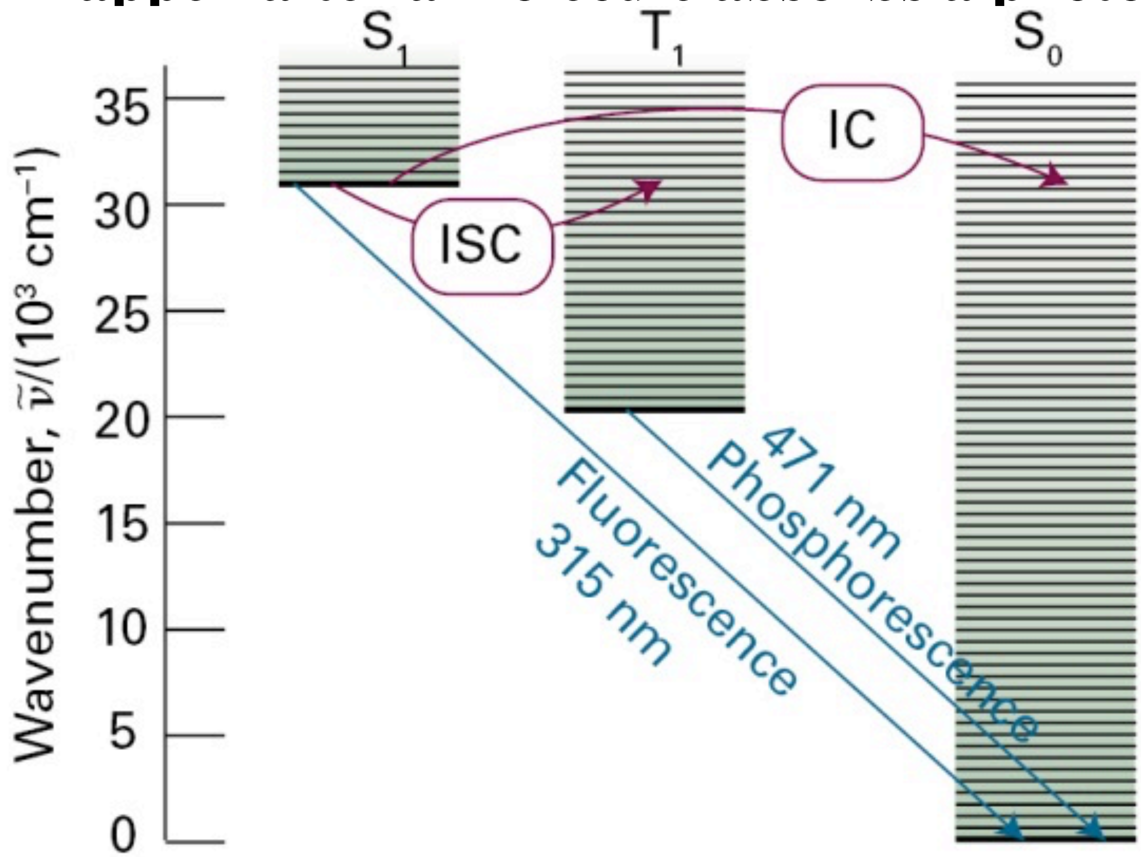
$$k_r = P\sigma N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_a/kT}$$

- **Diffusion Controlled Reactions**

Important Topics Since Midterm 2 (slide 4)

- **Photochemistry**

  What can happen after a molecule absorbs a photon?



- **Quantum yields**

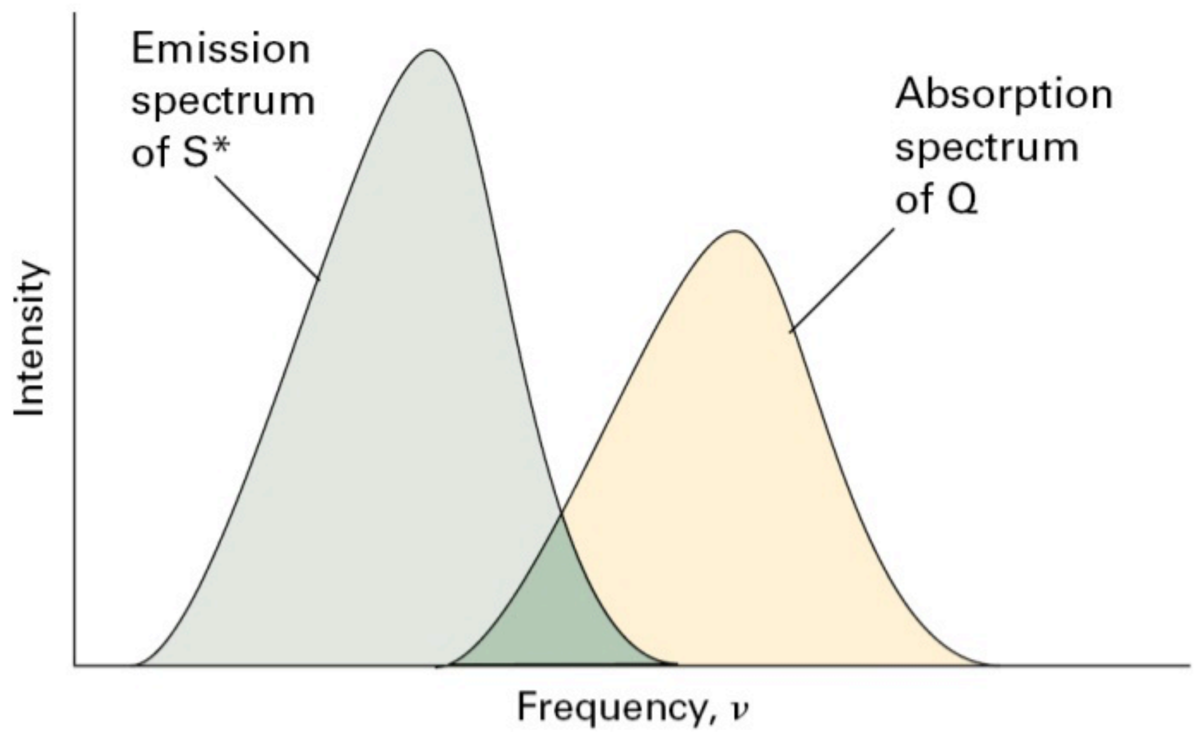
Important Topics Since Midterm 2 (slide 5)

- **Forster Energy Tranfer**
  A molecular ruler

$$\eta_T = 1 - \frac{\phi_f}{\phi_{F,0}}$$

$$S^* + Q \longrightarrow S + Q^*$$

$$\eta_T = \frac{R_0^6}{R_0^6 + R^6}$$



Things to Review Prior to the Final

Everything covered this quarter

Review the midterms (answers are on the canvas site)

Discussion Section Problems

WebAssign Homework Problems

THE END

SEE YOU AT THE FINAL EXAM

FRIDAY, DECEMBER 15
8AM—10AM