The final exam is on **Tues, Dec 12, 4-5:50 PM** in the usual lecture room. A piece of **8 x 11 paper (both sides)** may be used for notes. In addition, the table A.1 will be provided in addition to the usual tables.

Objectives will be the **same** as for the **4 midterm exams, except:**

**New objectives for Final:**
1. Know all **5** (instead of 3) of the quantum concepts and equations below.

**Some Quantum Concepts and their main equation** (same as for Exam 4; the extra words are for your enjoyment)

a. **Quantization of energy:** \( \Delta E = h \nu \)
   
   Can observe only discrete energy levels of particles localized by a force; light of frequency \( \nu \) can give up energy only in bundles having energy \( \Delta E = h \nu = \text{photon energy} \).

b. **Particle nature of light:** momentum = mass \( x \) velocity = \( p = h/\lambda \)
   
   Photons of light with short wavelengths will impart momentum to an electron during scattering. When a constant, very low light level (e.g., candle 1 mile distant) is detected, the signal is not constant, but will be a stream of randomly spaced pulses, each marking the observation of one photon.

c. **Wave nature of particles:** \( \lambda = h/p \)
   
   Electrons can be diffracted just like light, even if one electron at a time passes through the grating (crystal).

d. **Quantization of angular momentum, \( L \):** Total square of angular momentum, \( L^2 = \ell (\ell + 1)(h/2\pi)^2 \); \( \ell = 0, 1, 2 \ldots \) or \( \ell \) can be positive half-integers for certain nuclear spin; a component, \( L_z = m (h/2\pi) \), \( m = -\ell, -\ell + 1, -\ell + 2, \ldots \ell - 1, \ell \) (i.e., always \( 2\ell + 1 \) values ).

e. **Concept of zero point energy and uncertainty principle:**
   
   **Heisenberg:** \( \Delta x \Delta p \geq h \), i.e., product of uncertainty in \( x \) and uncertainty in momentum is about \( = h \). Confinement in a small place leads to zero point kinetic energy, which is, for example, why electrons cannot be pulled to the nucleus.

**Zero point kinetic energy** is \( \approx h^2 / (m\Delta x^2) \), where \( h = \text{Planck's constant} \), \( m = \text{mass} \), and \( \Delta x \) is the length of the region to which the particle is confined. For example, as a nucleus pulls an electron close, the zero-point energy increases and the electron will not fall to the nucleus. (It is as if the small things like electrons "refuse" to be localized.) The \( \Delta H \) of a chemical reaction is mainly due to change in electronic zero-point energy. Note that this effect is apparent only if \( m \) and \( \Delta x \) are very small, for example electrons in atoms, and nuclei in bonds.

2. **Schrödinger Equation:**
   
   Know the following 4 things about the Schrödinger Equation:
   
   (a) that **orbitals are wavefunctions** which are solutions of the Schrödinger Eq.;
   
   (b) that the **square of a particle's wavefunction gives the probability density** (probability per unit volume) of finding the particle in a small volume element.

   This means that the **probability** of finding the particle in a small volume \( \Delta V \) near \( x,y,z = \Psi(x,y,z)^2\Delta V \);
(c) that the average curvature, i.e., the average 2nd derivative, of the wavefunction gives the kinetic energy in quantum mechanics.

(d) that the Schrödinger Equation has never (yet) failed to agree with experiment.

3. Know how spectra (not spectrums) of black body radiation change with temperature and that the temperature dependence is from the Boltzmann ratio for probability to be in an excited state: 

\[ \frac{N_{\text{excited}}}{N_{\text{ground}}} = \exp\left(-\frac{\Delta E}{k_B T}\right) \]  
where \( \Delta E = \frac{hc}{\lambda} = E_{\text{excited}} - E_{\text{ground}} \).

4. Why the sky is blue, sunsets are red, and the sun viewed near mid-day appears white.

**End of new objectives.**

****************************************

**General**

The final will be comprehensive; (all objectives for midterms apply). However, the final will be more concerned with your knowledge and grasp of the main principles we have learned. Ample time will be provided to do more thinking, and continued emphasis will be on avoiding outrageous answers, i.e., unphysical numbers in terms of sign or magnitude or violations of Le Chatelier's principle. All problems will be on typical real-world systems that have been encountered several times during the Course. Therefore, all numerical answers to problems should make sense. If you are computing energies, velocities, rates, molecular weights, times, etc., be aware of what is reasonable answer and what is impossible. If you are unable to find a mistake you know must be there, estimate the answer and justify. If you do not, up to 25% may be deducted from your score on a problem if the answer is outrageous, even if worked perfectly except for a unit or sign error. Note that unreasonable does not necessarily mean very small or very large, e.g., the probability of a molecule being in an electronically excited state at room temperature is around 1x10^-30 (from the Boltzmann distribution).

**But in the case of the Boltzmann distribution, 50% will be deducted if the sign is wrong**

Emphasis will be on the more important and widely used concepts such as Gibbs free energy and its relation to spontaneity and non-expansion work, chemical potential, activity, standard states, equilibrium constant*, and the concept of coupling of reactions (wherein a process with positive \( \Delta G \) is driven by one with a large negative \( \Delta G \)). Of course, use of Hess's Law and other examples of exploiting the path independence of state functions is expected.

* You should see that the expression \( K = e^{\Delta G_0/RT} \) is just a general form of the Boltzmann distribution:

\[ \frac{N_2}{N_1} = \frac{g_2}{g_1} e^{\Delta U/RT} \]  
because \( \frac{g_2}{g_1} = e^{\Delta S/R} \). Here we said that \( \Delta H \cong \Delta U \), which is virtually true in solution, and only slightly off in vapor phase.

You should know the three Laws of Thermodynamics and definitions of heat, work, system, surroundings, and important terms like heat capacity, isothermal, adiabatic, reversible, irreversible.

Throughout the course there has been emphasis on the relation of \( \Delta G \) (with \( p = p_{\text{ext}} \), T constant) to the 2nd Law:

\[ \Delta G = -T \Delta S_{\text{universe}} + w_{\text{useful}} \]  
where \( w_{\text{useful}} \) is all work that is NOT obligatory -\( p_{\text{ext}} \Delta V \) work against or by the atmosphere due to the fact the system changes volume during the process. Examples of \( w_{\text{useful}} \) are electrical, pV work that done by expanding hot gas in an engine that moves a vehicle, work of making ATP from \( H^+ \) ions moving from low pH to high pH …
You are expected to know the restrictions of validity for using the important equations.

You will be provided table A.1

****************************************************

Other Hints and Suggestions

1. Put units on all numbers, while you are calculating the number. Be very careful when combining J and kJ. Know which constants are per molecule and which are per mol. Exponents (arguments of logarithms) must be dimensionless. You will usually get an outrageous result if an exponent has units.

2. Rates, rate constants, equilibrium constants, and concentrations cannot be negative. Minus signs appear in rate equations only when the rate is expressed as the rate of change of something that is disappearing (concentration or amount decreases).

First order rates of increase (e.g., growth of bacteria) increase exponentially, i.e., \( f = e^{kt} \), and \( f \) is then a ratio greater than 1 instead of a fraction.

3. Develop scientific "landmarks". Some of mine are: chemical reactions have \( \Delta H \) and \( \Delta G \) values in the range of zero to a few hundred or thousand kJ/mol typically. Chemical bonds have strengths ranging from 100-900 kJ/mol. Diffusion controlled reactions have maximum 2nd order rate constants about \( 10^9 \) - \( 10^{10} \) M\(^{-1}\)s\(^{-1}\) in room temperature water. RT at room temperature is 2.5 kJ/mole (which is equivalent to \( k_B T = 209 \) cm\(^{-1}\)). At room temperature \( e^{-AX/RT} \) changes by a factor of 10 for every 5.7 kJ/mol change in \( \Delta X \), where \( \Delta X \) is usually \( \Delta G^0 \) or \( E_a \); 500 nm (green is 20000 cm\(^{-1}\)) = typical electronic excitation energy. Vibrational quanta are 5-100 times less. Five times higher energy (100 nm) ionizes most molecules.

Below is an example of a favorite problem that thoroughly tests understanding and use of thermodynamic principles.

At constant \( T=300 \) K and \( p = p_{ext} = 1 \) bar, a process with \( \Delta H = -10 \) kJ, \( \Delta S = -20 \) J/K, has initial \( V=100 \) L and final \( V=200 \) L. It is said to do 7 kJ of useful work (\( w_{nonPV} \) or \( w_{other} \)) on the surroundings, i.e., \( w_{useful} = -7 \) kJ. What is the heat absorbed? Is this process possible, or does it violate the 2nd Law?

**Answer:** Because there is useful work done, (called \( w_{other} \) or non-PV work in the text) you cannot use the sign of \( \Delta G \) to see if the process is spontaneous. You must calculate \( \Delta S_{universe} = \Delta S + \Delta S_{surr} \) by first calculating \( q \) and using \( \Delta S_{surr} = -q/T \). (You cannot say \( q = \Delta H \) because \( w_{useful} \) is not zero.) Instead, use the First Law:

\[
q = \Delta U - w = (\Delta H - \Delta(pV)) - (-p_{ext} \Delta V) - w_{useful}
\]

\[
= -10,000 \text{ J} - [100\text{Lbar} \times 100\text{J/Lbar}] + [100\text{Lbar} \times 100\text{J/Lbar}] - (-7000 \text{ J})
\]

\[
= -10,000 \text{ J} + 7000 \text{ J} = -3000 \text{ kJ}.
\]

Thus, \( \Delta S_{surr} = -q/T = 3000 \text{ J}/300\text{K} = +10 \text{ J/K} \) and \( \Delta S_{universe} = \Delta S + \Delta S_{surr} = (-20 + 10) = -10 \text{ J/K} \) = negative, a violation of the 2nd Law. The process is not possible.

You can also see that it is not possible by examining \( \Delta G = \Delta H - T\Delta S = -10,000 -300(-20) = -4000 \text{ J} \). Thus system can only do a maximum of 4 kJ of useful work, but the problem stated 7 kJ was done.