Chemistry 331
Physical Chemistry
Practice Final Exam

Section ________ Name ____________________________________

1. A researcher has a laser that has a 250 nm wavelength. Which of the metals in the table below can be used to generate electrons? What is the highest energy electron that can be generated?

Metal	Electron Work Function
Al	4.28 eV
Au	5.10 eV
Cu	4.65 eV
In	4.12 eV
Mo	4.60 eV
Ni	5.15 eV
Pt	5.65 eV
Ti	4.33 eV
W	4.55 eV
Zn	4.33 eV

Solution:

The energy of a 250 nm photon is:

$E = hc/\lambda = (6.626 \times 10^{-34}\ \text{Js})(2.99 \times 10^{8}\ \text{m s}^{-1})/(250 \times 10^{-9}\ \text{m}) = 7.924 \times 10^{-19}\ \text{J}$

$= 4.946\ \text{eV}$

The work function of the metal must be less than 4.946 eV. The metals that satisfies this criterion are Zn, W, Ti, Mo, In, Cu and Al.

In can be used to generate the highest energy electron. $1/2mv2 = h\nu - \Phi = 4.946\ \text{eV} - 4.12\ \text{eV} = 0.826\ \text{eV}$

Energy of a 250 nm photon = _______4.946 eV ___________________.

Appropriate metals that satisy criterion = ____ Zn, W, Ti, Mo, In, Cu and Al____.

Highest energy electron that can be generated = ____0.826 eV _________________.

2. A white dwarf collapses and then explodes into a supernova. The peak of the blackbody emission is observed to shift from 400 nm to 300 nm. A. What is the

change in temperature of the surface of star as it becomes a supernova? B. What is the relative increase in radiative emitted power?

Solution:
part A. $T = 2.88 \times 10^6$ nm-K/λ_{max} = 2.88×10^6 nm-K/300 K = 9600 K
part B. $T = 2.88 \times 10^6$ nm-K/λ_{max} = 2.88×10^6 nm-K/400 K = 7200 K
part C. $\rho = \sigma T^4$, $\rho_{hot}/\rho_{cold} = T_{hot}^4/T_{cold}^4 = 9600^4/7200^4 = 3.16$

A. T at 300 nm = ______9600 K ________________________________.
B. T at 400 nm = ______7200 K ________________________________.
C. Relative increase in radiative power = ______3.16_______________.

3. Estimate the electron transition energy and wavelength of dodecene using the particle-in-a-box model. Assume that dodecene is a box of length 17.34 Å that contains 12 electrons.

Solution: The particle-in-a-box model for a polyene assumes that electrons are paired in each quantum level. Thus, 12 electrons will fill the first 6 levels and the first transition will be from level 6 → 7. The ground state quantum number will be $n_g = 6$ and the excited state quantum number will be $n_e = 7$.
$\Delta E = h^2/8ma^2(n_e^2 - n_g^2) = (6.626 \times 10\text{-}34 \text{ Js})^2/8/9.1 \times 10^{-31} \text{ kg}/(17.34 \times 10^{-10} \text{ m})^2 (7^2 - 6^2) = 2.61 \times 10^{-19} \text{ J} = 1.61 \text{ eV} = 12{,}981 \text{ cm}^{-1}$.
The wavelength can be obtained from $\Delta E = hc/\lambda$ or $\lambda = hc/\Delta E = (6.626 \times 10^{-34} \text{ Js})(2.99 \times 10^8 \text{ m})/(2.61 \times 10^{-19} \text{ J}) = 770$ nm.

Transition energy = 2.61×10^{-19} J = 1.2 eV = 12,981 cm^{-1}.
Transition wavelength = 7.7×10^{-5} m = 770 nm.

4. A. The molecule Integrafor has a fluorescence quantum yield of 0.75 and an observed decay lifetime of 50 ns. Please determine the fluorescence rate constant (k_f) and the internal conversion (or non-radiative decay) rate constant (k_{IC}).

Solution:
$k_{obs} = 1/20 \text{ ns} = 5 \times 10^7 \text{ s}^{-1}$
$k_f = \Phi_f k_{obs} = 4 \times 10^7 \text{ s}^{-1}$
$k_{IC} = k_{obs} - k_f = 10^7 \text{ s}^{-1}$.

k_f = ___________________________ k_{IC} = _____________________

B. A scientist synthesizes the molecule bromo-Integrafor with a fluorescence quantum yield of 0.1. The bromine causes a spin transition (singlet → triplet) because of the heavy atom effect. Assuming that k_f and k_{IC} are unchanged and that the origin of this effect is a third process is a rate constant for intersystem crossing k_{ISC}. Calculate the expected observed fluorescence lifetime for bromo-Integrafor. Please calculate the phosphorescence quantum yield (i.e. the quantum yield for emission from the triplet state Φ_{ISC}).

Solution: The quantum under quenching conditions becomes

$$\Phi_f = \frac{k_f}{k_f + k_{IC} + k_{quench}}$$

We know the Φ_f = 0.1 and k_f and k_{IC} are unchanged. We can solve for k_{pseudo}.

Under these conditions the observed fluorescence lifetime is:

$$t_{obs} = \frac{1}{k_f + k_{IC} + k_{quench}} = \frac{1}{8 \times 10^7\ s^{-1}} = 1.25 \times 10^{-8}\ s = 12.5\ ns$$

τ_{obs} = ____.

Φ_{ISC} = ____.

5. An enzyme that follows Michaelis-Menten kinetics has a K_m of 100 µM. The initial velocity is 0.1 µM min^{-1} at a substrate concentration of 100 µM. What is the initial velocity when [S] is equal to (a) 1 µM or (b) 1 mM? (10 points)

Solution: First determine V_{max} using the Michaelis-Menton equation.

$$V = \frac{[S]V_{max}}{K_M + [S]}$$

$$V_{max} = \frac{V(K_M + [S])}{[S]} = \frac{(0.1\ mM / \min)(1\ mM + 100\ mM)}{100\ mM}$$

$$= 0.101\ mM/\min$$

(a) V = V_{max}/2 = 0.05 mM min^{-1}

$$k_{quench} = \frac{k_f}{\Phi_f} - k_f - k_{IC} = k_f\left(\frac{1}{\Phi_f} - 1\right) - k_{IC}$$

$$= 4 \times 10^7 s^{-1} - 10^7 s^{-1}$$

$$= 3 \times 10^7\ s^{-1}$$

(b) V = V_{max} = 0.1 mM min^{-1}

V = __________________________________. [S] = 1 µM

V = __________________________________. [S] = 1 mM

6. The binding constant of a drug at 310 K is 10^4 M^{-1} and at 330 K it is 5 x 10^3 M^{-1}. Calculate the standard enthalpy and entropy change for the binding process.

Solution: Use the van't Hoff equation.

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

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

$$\Delta H^o = \frac{R\ln\left(\frac{K_2}{K_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{RT_1T_2\ln\left(\frac{K_2}{K_1}\right)}{(T_2 - T_1)}$$

Plugging in numbers we obtain:

$$\Delta H^o = \frac{(8.31\ J/mol\text{–}K)(300\ K)(320\ K)\ln\left(\frac{5\times 10^4}{10^5}\right)}{20\ K} = -27.65\ kJ/mol$$

At 300 K, ΔG^o = -RT ln K = -(8.31 J/mol-K)(300 K) ln(10^5) = -28.7 kJ/mol
ΔS^o = (ΔH^o - ΔG^o)/T = (-27650 - (-28700)) J/mol /300 K = 3.5 J/mol-K.

ΔH^o =___________-27.65 kJ/mol______________________________.
ΔS^o =___________3.5 J/mol-K ______________________________.

7. A. Calculate the energy of the transition series 6p → 2s, 5p → 2s, 4p → 2s in the hydrogen atom. B. Calculate the wavelength of light emitted for the 6p → 2s, 5p → 2s and 4p → 2s emission processes. C. What part of the electromagnetic spectrum is emitted by hydrogen in this series?

Solution: A. Use the Rydberg constant R = 109,737 cm^{-1} to calculate the energy of the transition.

$$\Delta E = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109737\ cm^{-1}\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 20{,}575\ \ cm^{-1}$$

$$\Delta E = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109737\ cm^{-1}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 23{,}044\ \ cm^{-1}$$

$$\Delta E = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109737\ cm^{-1}\left(\frac{1}{2^2} - \frac{1}{6^2}\right) = 24{,}386\ \ cm^{-1}$$

B. The wavelengths are:

$$\lambda(nm) = \frac{10^7}{\dot{\nu}(cm^{-1})} = \frac{10^7}{20575\ cm^{-1}} = 486\ nm$$

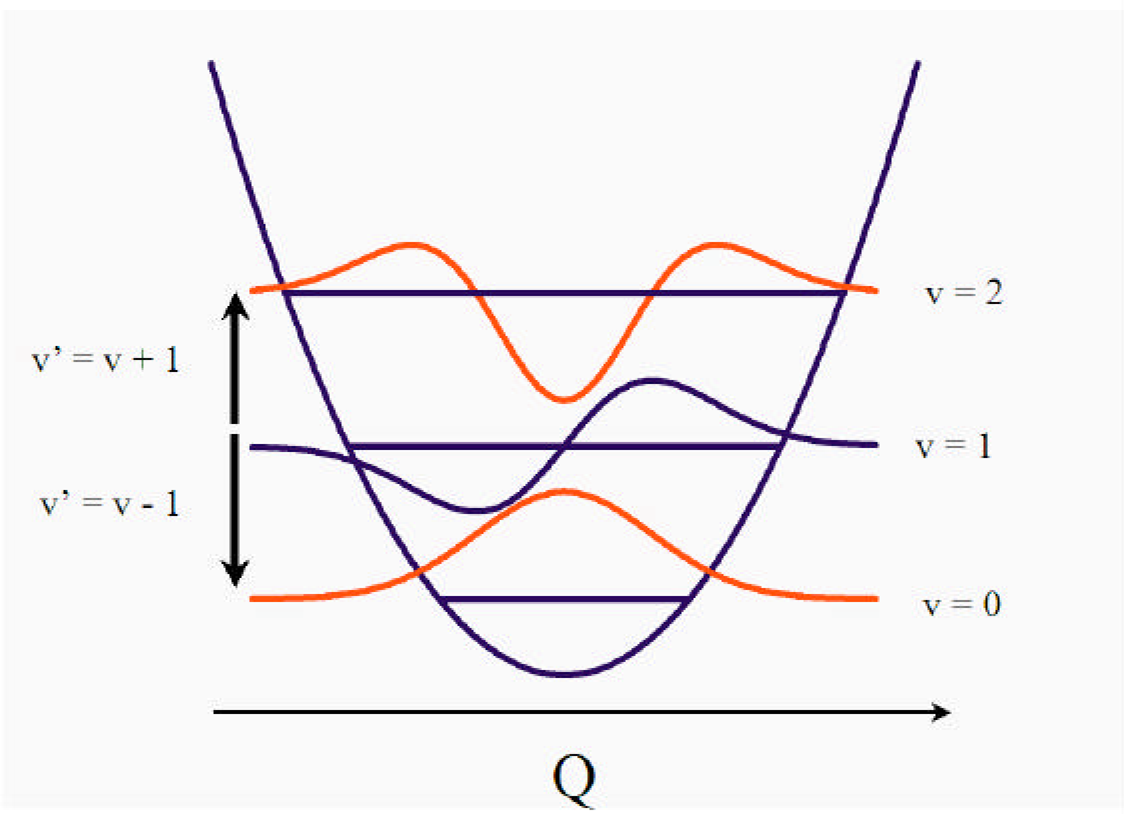
$$\lambda(nm) = \frac{10^7}{\dot{\nu}(cm^{-1})} = \frac{10^7}{20575\ cm^{-1}} = 434\ nm$$

$$\lambda(nm) = \frac{10^7}{\dot{\nu}(cm^{-1})} = \frac{10^7}{24386\ cm^{-1}} = 410\ nm$$

ΔE (6p → 2s) = ____.
ΔE (5p → 2s) = ____.
ΔE (4p → 2s) = ____.
λ (6p → 2s) = ____.
λ (5p → 2s) = ____.
λ (4p → 2s) = ____.
Part of electromagnetic spectrum _____Visible________________________.

8. Please provide the following descriptions regarding vibrational and rotational energy levels and transitions.

   A. Sketch the potential energy function and first two wavefunctions for the vibrational solutions of the Schrödinger equation for N_2.



B. Write a formula for the energy levels of vibration. Discuss the significance of the lowest vibrational level. What does the harmonic oscillator tell us about the motion of atoms at T = 0 K?

Answer: The solutions to the quantum mechanical harmonic oscillator form a set of energy levels with constant spacing. The quantized energies are:

$$E_v = (v + \frac{1}{2})h\nu$$

The lowest energy level is not zero, but is 1/2hν. This energy is called the zero-point vibrational energy. It represents that energy of vibration that is present even at absolute zero. This is required for the wave-like properties of matter to be satisfied. The Uncertainty principle states that one cannot simultaneously know the position and momentum of a particle. If the nuclei in a crystal were completely motionless (i.e. if E = 0) then we would know both position and momentum to arbitrary accuracy.

C. Please write down the equation describes the rotational energy levels of N_2. Estimate the spacing of rotational lines in the microwave spectrum of N_2. In other words, derive the rotational constant (in units of Joules) from the difference in the energy levels.

Answer: The solution to the rotational Schrodinger equation provides the energy expression:

$$E = \frac{h}{8\pi^2 \mu R^2} J(J+1)$$

The difference in energy levels is proportional to 2J.

$$\Delta E = \frac{h}{8\pi^2 \mu R^2} 2J$$

And therefore the line spacing is:

$$Line\ spacing = \frac{h}{8\pi^2 \mu R^2}$$

9. The rotational constant of $H^{79}Br$ is 8.46 cm^{-1}. Calculate the bond length of the molecule.

R = 1.414 Å

$$R = \sqrt{\frac{(1.054 \times 10^{-34} Js)}{4 \times \pi \times 1(79)/(1+79) \times (1.67 \times 10^{-27}\ kg)(3 \times 10^{10} cm/s)(8.46\ cm^{-1})}}$$

10. The fundamental vibrational frequency of $H^{79}Br$ is 2649 cm^{-1}. Calculate the force constant of stretching vibration of this diatomic molecule in Newtons per meter.

$$\hbar\omega = hc\tilde{\nu} \text{ or } \omega = 2\pi c\tilde{\nu}$$

$k = \mu\omega^2 = 79/80(1.67 \times 10^{-27}\text{ kg})4\pi^2 (3 \times 10^{10}\text{ cm/s})^2(2649\text{ cm}^{-1})^2 = 411.1\text{ N/m}$

11. Given the diagram below fill in the occupancy of the electrons in diatomic O_2 (Z=8).

A. What is the spin multiplicity of the ground state? $2S + 1 = 2(1) + 1 = 3$ S=1 since there are two unpaired spins.

B. Assign the lowest energy transition in diatomic oxygen using the molecular orbitals in the diagram.

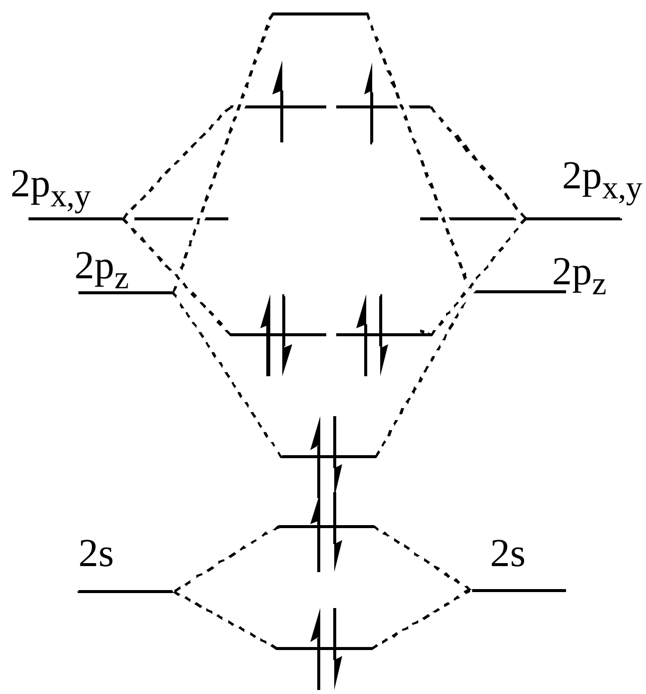
$2\pi^* \rightarrow 4\sigma^*$

C. Give the bond order in the ground state.

Bond order = ½(8 bonding – 4 anti-bonding) = 2

D. Give the bond order of O_2^-.

Bond order = ½(8 bonding – 5 anti-bonding) = 1.5



13. The catabolism (break-down) of glucose is an important source of energy for all cells. It begins with the following transformation which is the first step of the glycolytic pathway:

Glucose → Glucose-6-Phosphate

Theoretically, the cell could phosphorylate glucose directly with inorganic phosphate (Pi) like so:

Glucose + Pi → Glucose-6-Phosphate + H_2O $\Delta G^o = +3.3$ kcal/mol I

a) Calculate the equilibrium constant for this reaction (include correct units).

$K = \exp\{-\Delta G^o/RT\} = \exp\{-3300 \text{ cal/mol}/(1.986 \text{ cal/mol-K})/310 \text{ K}\}$
$= 0.0047$ (no units)

b) Is it favorable under standard conditions? Why or why not?

The reaction is not favorable since the equilibrium constant is less than one.
The reactant concentrations will be higher than the product concentrations

c) In a typical cell, glucose and phosphate are maintained at 4.8 mM each. (1 mM = 10^{-3} M) What would be the equilibrium concentration of Glucose-6-Phosphate if the cells used the reaction as written above to make it?

Glucose	Pi	Glucose-6-Phosphate	H_2O
0.0048 –x	0.0048 –x	x	x

$K = x^2/(0.0048 - x)^2$
$K(0.0048 - x)^2 - x^2 = 0$
$0.000023K - 0.0096Kx + (K-1)x^2 = 0$
$1 \times 10^{-7} - 0.00045\, x - 0.953\, x^2 = 0$

$$x = -\frac{0.00045 \pm \sqrt{0.00045^2 + 4(0.953)1 \times 10^{-7}}}{2(0.953)}$$

x = 0.000165 = 0.165 mM

d) Does this direct phosphorylation of glucose represent a reasonable route for the catabolism of glucose? Explain briefly.

At steady state only 3% of the glucose is phosphorylated. This is not sufficient for catabolism of glucose.

The cell actually accomplishes the phosphorylation of glucose by coupling it to the hydrolysis of ATP in a reaction catalyzed by the enzyme hexokinase:

ATP + H_2O → ADP + Pi ΔG^o = -7.3 kcal/mol   II

e) Write a balanced equation for the coupled reactions showing the ΔG^o for the net reaction.

Glucose + ATP → Glucose-6-Phosphate + ADP

$\Delta G^o = \Delta G^o$ (I) + ΔG^o (II) = 3.3 kcal/mol -7.3 kcal/mol
= -4.0 kcal/mol

14. A. Calculate the molar entropy change for a **reversible** expansion of an ideal gas from 1 L to 10 L to achieve a final pressure of 1 atm at 298 K.
B. Calculate the molar entropy change for an **irreversible** expansion of an ideal gas from 1 L to 10 L against an external pressure of 1 atm at 298 K.

Solution: A. For the reversible expansion $\Delta S_{sys} = nR \ln(V_2/V_1)$ and you will need calculate n using n = PV/RT = (10 atm)(1 L)/(0.08206 L-atm/mol-K)(298 K) = 0.408 moles.
$\Delta S_{sys} = nR \ln(V_2/V_1)$ = (0.408 mol)(8.31 J/mol-K) ln(10/1) = 7.80 J/K
We also calculate the entropy change in the surroundings along a reversible path so
$\Delta S_{surr} = - nR \ln(V_2/V_1) = - \Delta S_{sys}$
and therefore
$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 0$

B. For the irreversible expansion $\Delta S_{surr} = - P_{ext}(V_2 - V_1)/T$ = - (1 atm)(10 L – 1 L)/298 K(101.32 J/L-atm) = - 3.06 J/K
$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$ = 7.8 J/K – 3.06 J/K = 4.74 J/K

15. If the xylem in a tree has an effective diameter of 0.1 mm calculate the height to which water can be transported by capillary action alone.

Solution: $\Delta P = 2\gamma/r$ where g is the surface tension and r is the capillary tube radius.
The hydrostatic pressure is ρgh and so the height is
$h = 2\gamma/r\rho g = 2(0.072\ J/m^2)/(10^{-4}\ m)(1000\ kg/m^3)(9.8\ m/s^2) = 0.149\ m$

16. An engineer is asked to design a novel cylinder for an engine. What advice would you give the engineer regarding the paths for expansion and compression in the cylinder? Please write down formulae that justify your argument.

Answer: The expansion should be a close as possible to a reversible expansion. The energy that can be extracted will be a maximum for a reversible expansion.
$W_{rev} = -nRT \ln(V_2/V_1)$
$W_{irrev} = -P_{ext} (V_2 – V_1)$
The single-step irreversible path (or any multistep irreversible path) will have less area on a pressure-volume plot (i.e. less work will be extracted).

17. Use as many formulae as possible to justify the following statement. “Trees over 10 meters tall must use osmotic pressure and capillary action to facilitate transport of water from the roots to the top of the tree.”

Answer: Without some other mechanism (such as capillary action or osmosis) a column of water under vacuum (i.e. maximum suction by transpiration and any other processes in a tree) can be approximately 10 m high according to $P = \rho g h$ or $h = P/\rho g = (10^5 \text{ Pa}/1000 \text{ kg/m}^3)(10 \text{ m/s}^2)$.

18. It takes longer to cook soup at high elevation. Please provide the correct formula to justify your answer.

Answer: The Clausius-Clapeyron equation provides the dependence of the temperature of phase transition (in this case boiling) as a function of the pressure.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{trs} H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$