Name: _______________________________________

Instructions:

Please do not start working on the exam until you are told to begin. Check the exam to make sure that it contains exactly 6 different pages, including this one and a periodic table.

Some useful constants and equations:

\[ R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \]
\[ h = 6.63 \times 10^{-34} \text{ J s} \quad c = 3.00 \times 10^8 \text{ m s}^{-1} \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \]
\[ \lambda \nu = c \quad \nu = 1/\lambda \quad E = h \nu \]

3N-6 (nonlinear molecule) or 3N-5 (linear molecule) vibrational modes
\[ \nu = (k/\mu)^{1/2}/2\pi \] (vibrational frequency)
\[ \mu = m_A m_B/(m_A+m_B) \] (reduced mass) \[ 1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg} \]
\[ \Delta E = h/4\pi \Delta t \] (Energy uncertainty)
\[ P_1/P_2 = e^{-(E_1-E_2)/RT} \] (Boltzmann equation)
\[ A = - \log(I/I_0) = \varepsilon b c \] (Beer-Lambert law)
\[ \alpha = 180^\circ(n_L - n_R)/\lambda \] (Angle of rotation)
\[ [\alpha]_\lambda^T = \alpha/lc \] (Specific Rotation)
Part 1. Write the letter of the answer which best satisfies each statement or question in the blank at the left. *Please check your answers. Credit will only be given for the letter written in the blank* (3 points each).

A. 1. Which of the following interactions is favored more by entropy than enthalpy? (A) hydrophobic (B) covalent (C) dipole-dipole (D) ion-induced dipole

A. 2. Which of the following is *not* a Lennard-Jones (L-J) interaction (L-J interaction varies as \(1/r^6\))? (A) hydrogen bond (B) dipole-dipole (C) dispersion (D) dipole-induced dipole

C. 3. Transitions between electronic states are caused by light in which region of the electromagnetic spectrum? (A) microwave (B) infrared (C) ultraviolet (D) radio wave

A. 4. How many vibrational modes does benzene \((\text{C}_6\text{H}_6)\) have? (A) 30 (B) 31 (C) 35 (D) 36

D. 5. Tryptophan emits light 6 ns after absorption of UV light. The light emission is (A) phosphorescence (B) stimulated emission (C) IR radiation (D) fluorescence

A. 6. Which of the following octahedral complexes absorbs photons of light of the longest wave length? (A) high-spin complex with \(d^5\) electron configuration (B) low-spin complex with \(d^5\) configuration (C) \(d^6\) complex (D) complex with \(d^6\) configuration and strong field ligands attached

D. 7. Which pair of molecules forms the weakest hydrogen bond? (A) HF-HF (B) \text{NH}_3-\text{NH}_3 (C) \text{H}_2\text{O}-\text{NH}_3 (D) \text{CH}_4-\text{H}_2\text{O}

B. 8. Which of the following is a diamagnetic compound? (A) low-spin octahedral \(d^5\) complex (B) octahedral \(d^{10}\) complex (C) octahedral \(d^6\) complex (D) \(\text{H}_2^+\)

B. 9. For a molecule to be optically active, it must *not* possess which symmetry element? (A) identity element, \(E\) (B) plane of symmetry, \(\sigma\) (C) proper rotation, \(C_1\) (D) proper rotation, \(C_2\)

A. 10. If a three-level laser emits light in the visible region, optical pumping can be done in which region of the electromagnetic spectrum? (A) UV (B) IR (C) microwave (D) radio wave
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. The optical rotation of a sample of α-D-glucose is +112.2˚ and that of β-D-glucose is +18.7˚. A mixture of these two sugars has an optical rotation of +46.8˚. Calculate the percentage of each isomer in the mixture.

\[ x_{\alpha}(+112.2˚) + (1-x_{\alpha})(+18.7˚) = +46.8˚ \]

\[ x_{\alpha} = 0.30 \]

So 30% of α-D-glucose and 70% of β-D-glucose

2. The molar absorptivity of a certain compound of molecular weight 142.0 g mol\(^{-1}\) is 1.2 x 10\(^3\) L mol\(^{-1}\) cm\(^{-1}\) at 322 nm. Calculate the fraction of incoming light intensity that is transmitted when light of that wavelength passes through a 2.0-cm cell containing a 1.3 x 10\(^{-2}\) g L\(^{-1}\) solution of this compound.

\[ A = (1.2 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1})(2.0 \text{ cm})(1.3 \times 10^{-2} \text{ g L}^{-1}/142.0 \text{ g mol}^{-1}) = 0.22 \]

\[ A = \log_{10}(I/I_0) \]

\[ I/I_0 = 0.60 \]

3. In a three-level laser system, optical pumping is at 1.35 x 10\(^{15}\) Hz, and nonradiative decay is 8.40 x 10\(^{-20}\) J. What is the frequency of the emitted light?

\[ \nu = 1.35 \times 10^{15} \text{ Hz} - (8.40 \times 10^{-20} \text{ J})/(6.626 \times 10^{-34} \text{ J s}) \]

\[ \nu = 1.22 \times 10^{15} \text{ Hz} \]
Part III. Write your answer to the problems below in the space provided. Please show all work. Partial credit will be given based on work shown.

(17 points each)

1. The line width, $\Delta \nu$, due to the Doppler effect $\Delta \nu = \nu(v/c)$ and can be related to temperature, $T$ (in Kelvin), since the speed of the atom or molecule that is studied is $v = (3RT/m)^{1/2}$, where $m$ is the molar mass of the atom or molecule, $c$ is the speed of light and $\nu$ is its frequency. The sun emits a spectral line at $\nu = 4.43 \times 10^{14}$ Hz due to the presence of an ionized $^{57}$Fe atom (molar mass = 0.0569 kg mol$^{-1}$) at the sun’s surface. If the line-width is $2.12 \times 10^9$ Hz, what is the temperature of the sun’s surface?

\[ \Delta \nu = \nu((3RT/m)^{1/2}/c) \]

\[ T = (\Delta \nu)^2c^2m/3R\nu^2 \]

\[ T = ((2.12 \times 10^9 \text{ Hz})^2(3.00 \times 10^8 \text{ m/s})^2(0.0569 \text{ kg/mol})/3(8.314 \text{ J/K mol})(4.43 \times 10^{14} \text{ Hz})^2 \]

\[ T = 4.70 \times 10^3 \text{ K} \]
2. An IR spectrum for carbon monoxide (CO) shows a line at 2143.3 cm\(^{-1}\). (a) Calculate the force constant, k, for the carbon-oxygen bond. (10 points)

\[ \nu = (3.00 \times 10^{10} \text{ cm/s}) (2143.3 \text{ cm}^{-1}) = 6.43 \times 10^{13} \text{ Hz} \]

\[ \nu = (1/2\pi)(k/\mu)^{1/2} \]

\[ k = 4\pi^2 \nu^2 \mu \]

\[ \mu = \frac{(12.01)(16.00)}{(28.01)} \text{ amu} (1.66 \times 10^{-27} \text{ kg/amu}) = 1.14 \times 10^{-26} \text{ kg} \]

\[ k = 1.86 \times 10^3 \text{ N m}^{-1} \]

(b) Calculate the ratio of the population of CO molecules in the first excited vibrational level to the population of CO in the ground vibrational level at 300 K. (7 points)

\[ P_1/P_0 = \exp\left(-\frac{(6.63 \times 10^{-34} \text{ J s})(6.43 \times 10^{13} \text{ Hz})(6.02 \times 10^{23} \text{ mol}^{-1})}{(8.314 \text{ J/K mol})(300 \text{ K})}\right) \]

\[ P_1/P_0 = 3.37 \times 10^{-5} \]

I___________ II___________ III___________ Total___________