Name: ______________________________

Instructions:

Check the exam to make sure that it contains exactly 10 different pages, including this one and a periodic table at the end.

Some possibly useful equations and constants (continues on next page):

\[
h = 6.626 \times 10^{-34} \text{ J s} \quad (\text{Planck}) \quad k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \quad (\text{Boltzmann})
\]

\[
N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad (\text{Avogadro}) \quad R = N_A k_B = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}
\]

\[
m_e = 9.11 \times 10^{-31} \text{ kg} \quad e^x = 1 + x + \frac{x^2}{2!} + \ldots \quad (1-x)^{-1} = 1 + x + x^2 + \ldots
\]

\[
c = 3.00 \times 10^8 \text{ m s}^{-1} \quad 1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}
\]

\[
\lambda = \frac{h}{p} \quad \Delta E = h c R_H(1/n_i^2 - 1/n_f^2) \quad \ln(N!) \approx N \ln N - N
\]

\[
E_n = \frac{n^2 h^2}{8 m_e a^2}, \quad n = 1, 2, 3, \ldots \quad \psi_n(x) = \sqrt{2/a} \sin(n \pi x / a)
\]

\[
\Delta E = (N+1)\frac{h^2}{8 m_e a^2} \quad \lambda = \frac{8 m_e a^2 c}{(N+1)h}
\]

\[
\lambda \nu = c \quad \tilde{\nu} = 1/\lambda \quad E = h \nu \quad \Delta x \Delta p \geq \hbar / 2
\]

\[
E_{\text{vib}} = (n + \frac{1}{2})h \nu, \quad n = 0, 1, 2, \ldots \quad \nu = (k/\mu)^{1/2}/2\pi \quad (\text{vibrational frequency})
\]

\[
\mu = m_A m_B/(m_A + m_B) \quad (\text{reduced mass})
\]

\[
E_{\text{rot}} = J(J+1)\frac{h^2}{8 \pi^2 I}, \quad J = 0, 1, 2, \ldots \quad (2J+1)-\text{degenerate} \quad I = \mu r_0^2
\]

\[
\psi_n(x) = A \exp \left( -x \sqrt{2m(V_0 - E) / \hbar^2} \right) \quad (A = \text{constant}; \text{particle in barrier})
\]
More possibly useful equations:

\[ \nu = \frac{\gamma B_0}{2\pi} \quad (\gamma = 26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1} \text{ for } ^1\text{H}) \]

\[ A = - \log(T) = \varepsilon b c \]

Bond Order = \( (1/2)[n(\text{bonding}) - n(\text{antibonding})] \)

\[ q = \sum_n g_n e^{-\beta c_n}, \quad p_n = \frac{g_n e^{-\beta c_n}}{q} \]

\[ q_{\text{trans}} = \left( \frac{2\pi n k_B T}{\hbar^2} \right)^{3/2} V \]

\[ q_{\text{rot}} = \frac{8\pi^2 I k_B T}{\sigma h^2} \left( \frac{\hbar}{e^{\frac{kT}{h}} - 1} \right) \]

\[ q_{\text{vib}} = \left( 1 - e^{-\hbar v / k_BT} \right)^{-1} \]

\[ Q = \frac{q^N}{N!} \quad (\text{ideal gas}) \quad \ln(N!) \approx N \ln N - N \]

\[ U_{\text{trans}} = (3/2)N k_B T \quad C_v = \frac{dU}{dT} \quad C_v = \frac{5}{2} N k_B + N k_B \left( \frac{\hbar v}{k_B T} \right)^2 \frac{e^{\frac{kT}{h}}}{e^{\frac{kT}{h}} - 1} \]

\[ \Theta_v = \frac{h v}{k_B} \quad S = k_B \ln Q + \frac{U}{T} \quad S = \frac{nR \ln[(2\pi n k_B T/h^2)^{3/2}(V/N)e^{3/2}]}{\text{mean free path}} \]

\[ z_{11} = \left( \frac{PN_A}{RT} \right)^{1/2} \left( \frac{8RT}{\pi M} \right)^{1/2} \quad \lambda = \frac{1}{\sqrt{2\sigma}} \left( \frac{RT}{PN_A} \right) \]

\[ \nu_{\text{ave}} = \frac{8RT}{\pi M} \quad \nu_{\text{rms}} = \frac{3RT}{M} \quad \nu_{\text{mp}} = \frac{2RT}{M} \quad PV = nRT \]

\[ r_{\text{rms}} = (6Dt)^{1/2} \quad \kappa = \frac{1}{3} \frac{C_{\nu_{\text{mp}}}}{N_A} \nu_{\text{ave}} \frac{1}{\sqrt{2\sigma}} \quad D = \frac{k_B T}{6\pi\eta r} \]
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 (4 points each).

A  1. The constant volume molar heat capacity for Ar(g) at room temperature is
   (A) $3R/2$  (B) $5R/2$  (C) $7R/2$  (D) $9R/2$

B  2. For which of the following is the average speed smallest at standard temperature and pressure?
   (A) He  (B) H$_2$  (C) HD

C  3. Consider $N$ molecules, each with two energy levels.  The lower energy is 0 and the higher energy is $\varepsilon$.  When $k_B T >> \varepsilon$, the average energy of the $N$ molecules is
   (A) 0  (B) $\varepsilon$  (C) $N\varepsilon/2$  (D) $N\varepsilon$

D  4. Which of the following noble gases in a 1.0 m$^3$ container at 298 K has the lowest entropy?
   (A) He  (B) Ne  (C) Ar  (D) Kr

B  5. We use the energy levels of the following system to calculate the rotational partition function for an ideal gas:
   (A) particle-in-a-box  (B) rigid rotor  (C) harmonic oscillator  (D) hydrogen atom

B  6. The root mean square displacement for a diffusing particle is measured to be 14.1 cm after 1000 s.  What is the root mean square displacement for the particle after 10,000 s?
   (A) 141 cm  (B) 44.7 cm  (C) 28.2 cm  (D) 14.1 m

D  7. The energy needed for the hydrogen atom to make a transition from the ground state to first excited state is equal to which of the following?
   (A) $h c R_H$  (B) $3(h c R_H)/4$  (C) $(h c R_H)/4$  (D) $(h c R_H)/9$

D  8. Which of the following functions is an acceptable wave function over the interval $-\infty < x \leq 0$?  ($a$ is a constant)
   (A) $x e^{-2\pi iax}$  (B) $x^{-1} e^{-2\pi iax}$  (C) $\exp(ax^2)$  (D) $\exp(-ax^2)$
9. The wave function for the particle in the box is 0 everywhere outside the box.
This means that
(A) the particle cannot be found outside the box.
(B) the particle is as likely to be found outside the box as inside the box
(C) the particle is most likely in the middle of the box.
(D) the particle is neither inside nor outside the box.

10. To determine the length of a chemical bond in a diatomic molecule, we carry
out spectroscopy in which region of the electromagnetic spectrum?
(A) UV    (B) visible   (C) IR   (D) microwave

11. By increasing the length of a linear polyene from 4 to 6 carbons, the frequency
of light needed to excite the molecule from the ground to first excited state
(A) increases  (B) decreases  (C) remains the same

12. The order of the molecular orbitals from lowest to highest energy for O₂ and
F₂, is as follows: 1σ < 1σ* < 2σ < 2σ* < 3σ < 1π < 1π* < 3σ*. Which of the
following has the greatest bond order?
(A) F₂   (B) O₂   (C) O₂⁻   (D) F₂⁻

13. An electron of the hydrogen atom has angular momentum quantum number
l = 3.
Which of the following is not a possible value of the principle quantum number, n ?
(A) 3    (B) 4    (C) 6    (D) 9

14. Which of the following depicts the shape of the 1σ* molecular orbital of H₂⁻?
The molecule is oriented as H - H.
(A)  (B)  (C)  (D)

15. The partition function is defined as
\[ q = \sum_n g_n e^{-\beta \varepsilon_n} \]. What is \( \beta \)?
(A) \( k_B T \)    (B) \( 1/k_B T \)    (C) \(-1/k_B T^2 \)    (D) \(-k_B T^2 \)
Part II. Short answer: Answer the following in the space provided. (10 points each)

1. The molar extinction coefficient of a certain compound of molecular weight 96.0 g mol\(^{-1}\) is 1.86 \times 10^3 L mol\(^{-1}\) cm\(^{-1}\) at 387 nm. Calculate the percent of incoming light intensity that is transmitted when light at 387 nm passes through a 1.00-cm cell containing a 2.32 \times 10^{-2} g L\(^{-1}\) solution of this compound.

\[ A = \varepsilon bc \]

\[ A = (1.86 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})(2.32 \times 10^{-2} \text{ g L}^{-1}/96.0 \text{ g mol}^{-1}) = 0.450 \]

\[ T = 10^{-A} = 10^{-0.450} \]

\[ T \times 100\% = 35.5\% \]

2. Calculate the rotational partition function for \(^{35}\text{Cl}_2\) \((B = 0.244 \text{ cm}^{-1})\) at 298 K.

\[ q_R = \frac{k_B T}{8\pi \hbar B} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{(2)(6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^{10} \text{ cm/s})(0.244 \text{ cm}^{-1})} = 424 \]

3. Determine the entropy for 1 mole of Ar\((g)\) at 200 K in a volume of 1000 cm\(^3\). Treat Ar as an ideal gas.

The entropy is given by, \( S = nR \ln[(2\pi mk_B T/h^2)^{3/2}(V/N) e^{5/2}] \).

For 1 mole, \( n = 1 \) and \( N = N_A \). \( V = 1000 \text{ cm}^3 = 1.0 \times 10^{-3} \text{ m}^3 \).

\( m_{Ar} = (39.95 \text{ g/mol})(1/6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ g/1000 kg}) = 6.63 \times 10^{-26} \text{ kg} \).

200 K:

\( S = nR \ln[(2\pi mk_B T/h^2)^{3/2}(V/N) e^{5/2}] \)

\( S = (1 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times \ln[(2\pi(6.63 \times 10^{-26} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(200 \text{ K})(6.63 \times 10^{34} \text{ J s}^{-1})^{3/2}] \times (1.0 \times 10^{-3} \text{ m}^3)/(6.02 \times 10^{23} \text{ mol}^{-1}) e^{5/2}] \)

\[ S = 123 \text{ J K}^{-1}. \]
4. A microwave spectrum of LiH shows a series of lines separated by $4.511 \times 10^{11} \text{ s}^{-1}$. The first line at $4.511 \times 10^{11} \text{ s}^{-1}$ corresponds to the $J = 0$ to $J = 1$ transition. Calculate the length (in Å) of the bond between Li and H.

$$\Delta \nu = 4.511 \times 10^{11} \text{ s}^{-1} = \frac{\Delta E_{\text{rot}}}{h} = 1(1 + 1)\frac{\hbar}{8\pi^2 I}$$

$$I = \frac{\hbar}{4\pi^2(4.511 \times 10^{11} \text{ s}^{-1})} = \frac{(6.63 \times 10^{-34} \text{ Js})}{4\pi^2(4.511 \times 10^{11} \text{ s}^{-1})} = 3.72 \times 10^{-47} \text{ kg m}^2$$

$$\mu = [(6.941)(1.008)/(6.941 + 1.008) \text{ amu}] (1.661 \times 10^{-27} \text{ kg/amu}) = 1.46 \times 10^{-27} \text{ kg}$$

$$r_0^2 = I/\mu = 3.72 \times 10^{-47} \text{ kg m}^2/1.14 \times 10^{-26} \text{ kg} = 2.55 \times 10^{-20} \text{ m}.$$  

$$r_0 = 1.60 \times 10^{-10} \text{ m} = 1.60 \text{ Å}$$

5. Consider a particle in a 2-dimensional square box. What is the lowest energy of the particle? What is the energy of the first excited state? What is the degeneracy of the first excited state?

Ground state energy: $$E = 2\frac{\hbar^2}{8m_e a^2} = \frac{\hbar^2}{4m_e a^2}$$

First excited state energy: $$E = \frac{\hbar^2}{8m_e a^2} + 4\frac{\hbar^2}{8m_e a^2} = 5\frac{\hbar^2}{8m_e a^2}.$$ 

The first excited state is doubly degenerate.

6. An IR spectrum for carbon monoxide (CO) shows a line at 2143.3 cm$^{-1}$. Calculate the force constant, $k$, for the carbon-oxygen bond.

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

$$\nu = \frac{(1/2\pi)(k/\mu)^{1/2}}{\mu} = 4\pi^2\nu^2 \mu$$

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

$$k = 1.86 \times 10^3 \text{ N m}^{-1}$$
7. An IR spectrum for carbon monoxide (CO) shows a line at 2143.3 cm\(^{-1}\). 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 25 °C.

\[
\frac{n_1}{n_0} = \exp\left(-\frac{(6.63 \times 10^{-34} \text{ J s})(6.43 \times 10^{13} \text{ Hz})}{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}\right)
\]

\[
\frac{n_1}{n_0} = 3.15 \times 10^5
\]

8. Calculate the frequency of the radiofrequency field in resonance with \(^1\text{H}\) when the magnetic field strength is \(B_0 = 5.50 \text{ T}\).

The condition for resonance is \(\nu = \frac{\gamma B_0}{2\pi}\).

For \(^1\text{H}\), \(\gamma = 26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}\). Then

\[
\nu = \frac{26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}}{2\pi} (5.50 \text{ T}) = 2.34 \times 10^8 \text{ s}^{-1}
\]

9. You have a system with 3 states. The energies \(\varepsilon_2\) and \(\varepsilon_3\) of states 2 and 3 relative to the ground state (\(\varepsilon_1 = 0\)) are \(9.53 \times 10^{-21} \text{ J}\) and \(1.86 \times 10^{-20} \text{ J}\), respectively. Find the probabilities \(p_1\), \(p_2\) and \(p_3\) at \(T = 300 \text{ K}\).

\[
q = 1 + \exp\left(-\frac{\varepsilon_2}{k_B T}\right) + \exp\left(-\frac{\varepsilon_3}{k_B T}\right) = 1.11
\]

\[
p_1 = \frac{\varepsilon_1}{q} = \frac{1}{q} = 0.9
\]

\[
p_2 = \exp\left(-\frac{\varepsilon_2}{k_B T}\right) / q = 0.9 \exp\left(-\frac{\varepsilon_2}{k_B T}\right) = 0.09
\]

\[
p_3 = \exp\left(-\frac{\varepsilon_3}{k_B T}\right) / q = 0.9 \exp\left(-\frac{\varepsilon_3}{k_B T}\right) = 0.01
\]

Therefore \(p_1 = 0.9\), \(p_2 = 0.09\) and \(p_3 = 0.01\) at \(T = 300 \text{ K}\).
10. For Ar at 273 K and 1 atm, the thermal conductivity is 0.0177 J K\(^{-1}\) m\(^{-1}\) s\(^{-1}\). Determine the collisional cross section of Ar.

We can determine this ratio in terms of the ratio of the thermal conductivity:

\[
\sigma = \frac{1}{3} \frac{C_{V,m} \nu_{ave}}{\sqrt{2 \kappa}} = \frac{1}{3} \left( \frac{3R}{2N_A} \right) \sqrt{\frac{8RT}{\pi M \sqrt{2 \kappa}}} \frac{1}{\sqrt{2 \kappa}}
\]

\[
= \left( \frac{8.314 \text{ J mol}^{-1} \text{K}^{-1}}{2(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{K}^{-1})(273\text{K})}{\pi(0.040 \text{ kg mol}^{-1})}} \frac{1}{\sqrt{2(0.00177 \text{ J K}^{-1} \text{m}^{-1}\text{s}^{-1})}}.
\]

Therefore, \(\sigma = 1.1 \times 10^{-19} \text{ m}^2\)

11. The diffusion coefficient of sucrose in water at 298 K is 0.522 x 10\(^{-9}\) m\(^2\) s\(^{-1}\). Determine the time it will take a sucrose molecule on average to diffuse an rms distance of 1 cm.

\(r_{rms} = (6Dt)^{1/2}\), so \(t = r_{rms}^2 / 6D = 1 \text{ cm}^2 (1 \text{ m} / 100 \text{ cm})^2 / 6(0.522 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})\).

\(r_{rms} = 3.19 \times 10^4 \text{ s}\).

12. β-Carotene has 22 \(\pi\) electrons and it absorbs light with \(\lambda = 481\) nm. (1 nm = 10\(^{-9}\) m). Estimate the length (in Å) of β-carotene by assuming that the energy levels of each of its \(\pi\) electrons can be calculated as a particle in a box.

\[
\Delta E = \frac{hc}{\lambda} = \frac{(N+1)\hbar^2}{8m_ea^2}
\]

\[
a = \left[23(4.80 \times 10^{-7} \text{ m})(6.63 \times 10^{-34} \text{ Js})/8(3.00 \times 10^8 \text{ ms}^{-1})(9.11 \times 10^{-31} \text{ kg})\right]^{1/2}
\]

\(a = 1.83 \times 10^{-9} \text{ m} = 18.3 \text{ Å}\)
13. It takes 334 J to melt 1 g of ice at 0 °C. How many photons at 660 nm must be absorbed to melt 5.0 x 10² g of ice? (1nm = 10⁻⁹ m).

Need energy: 334 J/g ice (500 g ice) = 1.67 x 10⁵ J

From 1 photon: \[ E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m s}^{-1})}{(6.60 \times 10^{-7} \text{ m})} = 3.01 \times 10^{-19} \text{ J} \]

Number of photons needed = \[ \frac{(1.67 \times 10^5 \text{ J})}{(3.01 \times 10^{-19} \text{ J})} = 5.55 \times 10^{23} \text{ (roughly 1 mole)} \]

14. A π electron is somewhere along a linear polyene of length 16.2 Å, but within this length we are uncertain where. What is the minimum uncertainty in its velocity? (1Å = 1 x 10⁻¹⁰ m.)

The uncertainty in momentum is
\[ \Delta p = \frac{h}{4\pi\Delta x} = \frac{6.63 \times 10^{-34} \text{ J s}}{4\pi(16.2 \times 10^{-10} \text{ m})} = 3.26 \times 10^{-26} \text{ kg m s}^{-1} \]

The uncertainty in velocity is just the uncertainty of the electron’s momentum over its mass,
\[ \Delta v = \frac{\Delta p}{m} = \frac{3.26 \times 10^{-26} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 3.57 \times 10^4 \text{ m s}^{-1} \]

I________________    II_______________  III______________      Total____________