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 at the end.

Some useful constants and equations:

\( R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} \) \hspace{1cm} \( R_H = 109,737 \text{ cm}^{-1} \) (Ryderberg constant)

\( m_e = 9.11 \times 10^{-31} \text{ kg} \) \hspace{1cm} \( h = 6.63 \times 10^{-34} \text{ J s} \)

\( c = 3.00 \times 10^8 \text{ m s}^{-1} \) \hspace{1cm} \( e = 1.60 \times 10^{-19} \text{ C} \) (charge on electron)

\( \varepsilon_s = 8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \) \hspace{1cm} \( c = \lambda \nu \) \hspace{1cm} \( \lambda = h/mv \)

\( \ln \left( \frac{[A]}{[A]_0} \right) = -kt \) (first order) \hspace{1cm} \( 1/[A] = 1/[A]_0 + kt \) (second order)

\( t_{1/2} \propto [A]_0^{1-n} \), \( n = \) reaction order \hspace{1cm} (half-life)

\( ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2) \) \hspace{1cm} \( \ln k = \ln A - E_a/RT \)

\( \Delta E = h c R_H (1/n_i^2 - 1/n_f^2) \) (hydrogen atom)

\( \Delta E = (N+1)h^2/8m_eL^2 \) \hspace{1cm} \( \lambda = 8m_eL^2c/(N+1)h \) (linear polyene)

\( \Delta x \Delta p \geq h/4\pi \)

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

B 1. Increasing the value of which of the following raises the reaction rate for the reaction A $\rightarrow$ products?
   (A) Activation energy  (B) temperature  (C) concentration of products

B 2. If the reaction NO$_2$(g) + CO(g) $\rightarrow$ NO(g) + CO$_2$(g) is known to follow second order kinetics, give an expression for the rate, $-\frac{d[NO_2]}{dt} =$
   (A) $k[NO_2]$  (B) $k[NO_2][CO]$  (C) $k[NO]^2$  (D) $k[CO_2]^2$

A 3. Which of the following diatomic molecules has the shortest bond?
   (A) H$_2$  (B) H$_2^-$  (C) He$_2^+$

D 4. The wave function for the particle in the box is 0 everywhere outside the box. This means that
   (A) the particle is neither inside nor outside the box.
   (B) the particle is as likely to be found outside the box as inside the box.
   (C) the particle cannot be found in the middle of the box.
   (D) the particle cannot be found outside the box.

C 5. In a temperature jump experiment we measure the
   (A) half-life of the reactant  (B) half-life of the product
   (C) relaxation time of reaction to equilibrium

A 6. An electron of the hydrogen atom has angular momentum quantum number, $l = 1$. Which of the following is not a possible value of the principal quantum number, $n$?
   (A) 1  (B) 2  (C) 3  (D) 4

D 7. Which of the following is a diamagnetic compound? ($\Delta =$ crystal field splitting.)
   (A) octahedral complex with metal ion in d$^8$ configuration and small $\Delta$.
   (B) octahedral complex with metal ion in d$^8$ configuration and large $\Delta$.
   (C) octahedral complex with metal ion in d$^6$ configuration and small $\Delta$.
   (D) octahedral complex with metal ion in d$^6$ configuration and large $\Delta$.

B 8. Fill in the blank: The wavelength of light needed to ionize the hydrogen atom from the $n=1$ level ________ the wavelength of light needed to excite the hydrogen atom from the $n=1$ level to the $n=2$ level.
   (A) is longer than  (B) is shorter than  (C) is the same as

C 9. The electronic configuration of which homonuclear diatomic is
   \[ (\sigma_1s)^2(\sigma_1s^*)^2(\sigma_2s)^2(\sigma_2s^*)^2(\pi_x)^2(\pi_x^*)^2(\pi_y)^2(\pi_y^*)^1 \]?
   (A) He$_2$  (B) N$_2$  (C) O$_2$  (D) F$_2$

D 10. The carbon orbitals of C$_2$H$_2$ are hybridized as (A) sp$^4$  (B) sp$^3$  (C) sp$^2$  (D) sp
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. Consider the reaction $A \rightarrow \text{products}$, which is known to follow second order kinetics. The initial concentration is $[A]_0 = 2.1 \, \text{M}$. If the half-life of the reaction is 0.79 s, what is the rate constant? (Please remember to include units.)

At $t = t_{1/2}$, $[A] = [A]_0/2$, so that $k = 1/[A]_0 t_{1/2} = 1/((2.1 \, \text{M})(0.79 \, \text{s}))$

$$k = 0.60 \, \text{M}^{-1} \text{s}^{-1}$$

2. A $\pi$ 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? (1 Å = 1 x 10^{-10} m.)

The uncertainty in momentum is

$$\Delta p = \frac{h}{4\pi \Delta x} = 6.63 \times 10^{-34} \, \text{J} \text{s} / 4\pi (16.2 \times 10^{-10} \, \text{m}) = 3.26 \times 10^{-26} \, \text{kg} \, \text{m} \, \text{s}^{-1}$$

The uncertainty in velocity is just the uncertainty of the electron’s momentum over its mass,

$$\Delta v = \frac{\Delta p}{m} = \frac{3.26 \times 10^{-26} \, \text{kg} \, \text{m} \, \text{s}^{-1}}{9.11 \times 10^{-31} \, \text{kg}} = 3.57 \times 10^4 \, \text{m} \, \text{s}^{-1}$$

3. The hydrolysis of urea to ammonia and carbon dioxide in the presence of the enzyme urease at 21 °C, which has an activation energy of 44 kJ mol^{-1}, has a rate constant of $1.53 \times 10^3 \, \text{s}^{-1}$. Calculate the rate constant for hydrolysis at 37 °C.

$$\ln(\frac{k_2}{k_1}) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

$$\ln(\frac{k_2}{1.53 \times 10^3 \, \text{s}^{-1}}) = (44,000 \, \text{J} \, \text{mol}^{-1}/8.314 \, \text{J} \, \text{mol}^{-1} \, \text{K})(\frac{1}{294 \, \text{K}} - \frac{1}{310 \, \text{K}})$$

$$k_2 = 3.87 \times 10^3 \, \text{s}^{-1}$$
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. A certain protein molecule P dimerizes to P₂ when it is allowed to stand in solution at 45 °C. A plausible mechanism is that the protein molecule is first denatured, P*, before it dimerizes:

Step 1: \(2P \rightarrow 2P^*\) rate constant, \(k_1\) (slow step; unimolecular)

Step 2: \(2P^* \rightarrow P_2\) rate constant, \(k_2\) (fast step; bimolecular)

(a) What is the overall reaction? (Note that P* is an intermediate.) (5 points)

\[2P \rightarrow P_2\]

(b) Write the rate law for the rate of disappearance of \([P]\). (5 points)

\[-\frac{d[P]}{dt} = k_1[P]\]

(c) If \(k_1 = 1.3 \times 10^{-1}\) s⁻¹ and the initial concentration of P is \([P]_0 = 1.6 \times 10^{-1}\) M, at what time, \(t_{1/2}\), is one half of \([P]_0\) remaining? (7 points)

Step 1 is the slow step and it is first order in [P]. Then \(\ln([P]/[P]_0) = -k_1t\)

When \([P] = [P]_0/2\), \(\ln(([P]_0/2)/[P]_0) = -k_1t_{1/2}\)

Then \(t_{1/2} = \ln(2)/k_1 = \ln(2)/1.3 \times 10^{-1}\) s⁻¹ = 5.33 s
2. Consider a linear polyene with 12 \( \pi \) electrons that absorbs light with frequency \( \nu = 3.94 \times 10^{14} \text{ s}^{-1} \).

(a) Estimate the length of this polyene (in Å) by assuming that the energy levels of each of its \( \pi \) electrons can be calculated as a particle in a box. (14 points)

\[
\Delta E = \hbar \nu = (N+1)\frac{\hbar^2}{8m_e L^2}
\]

\[
L = \left[ \frac{13(6.64 \times 10^{-34} \text{ Js})}{8(9.11 \times 10^{-31} \text{ kg})} \left( 3.94 \times 10^{14} \text{ s}^{-1} \right) \right]^{1/2}
\]

\[
L = 1.73 \times 10^{-9} \text{ m} = 17.3 \text{ Å}
\]

(b) What is the energy of a mole of photons (in kJ/mol) of frequency \( \nu = 3.94 \times 10^{14} \text{ s}^{-1} \)? (3 points)

\[
\text{Photon energy} = \hbar \nu = (6.64 \times 10^{-34} \text{ Js})(3.94 \times 10^{14} \text{ s}^{-1})(1 \text{ kJ/1000 J})(6.02 \times 10^{23} \text{ mol}^{-1})
\]

\[
\text{Photon energy} = 157 \text{ kJ mol}^{-1}
\]