*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

1. (10 points) From the phrases in column B, select the best match for each statement in column A and put its letter in the adjacent blank. There is only one best match for each phrase.

Column A	Column B
1. __i__ The evolution of a system in response to the nonequilibrium distribution of a property.	a)　　catalyst
2. __b__ The process by which particle density evolves in response to a spatial gradient in concentration.	b)　　diffusion
3. __g__ The process in which energy migrates in response to a gradient in temperature.	c)　　Michaelis-Menten mechanism
4. __j__ The property that characterizes resistance to flow	d)　　molecularity
5. __f__ The process of settling under an external force that is overcoming a buoyant force.	e)　　rate law
6. __e__ The empirical relationship between concentrations and rate of a chemical reaction.	f)　　sedimentation
7. __d__ The stoichiometric quantity of reactants involved in a single elementary step.	g)　　thermal conduction
8. __h__ The maximum in energy along the path between reactants and products.	h)　　transition state
9. __a__ A substance that participate in a chemical reaction by increasing the reaction rate, but remains intact after reaction is complete.	i)　　transport phenomenon
10. __c__ A description of the reactivity of an enzyme.	j)　　viscosity

2. (10 points) Engel and Reid report the viscosity of argon at 300 K to be 227 micropoise. Determine the collision cross-section of argon at 300 K.

Using kinetic theory, the relationship between the viscosity and the collision cross-section is:

$$\eta = \sqrt{\frac{mkT}{\pi \sigma_{AA}^2}}$$

Rearranging this equation, one gets

$$\sigma_{AA} = \sqrt{\frac{mkT}{\pi \eta^2}}$$

Let's first convert everything to SI units:

$$\eta = 227 \times 10^{-6} \, poise = 0.1 \frac{kg \, m^{-1} s^{-1}}{poise} (227 \times 10^{-6} \, poise) = 2.27 \times 10^{-5} \, kg \, m^{-1} s^{-1}$$

$$m = \frac{0.039948 \, kg/mol}{6.02211415 \times 10^{23} molecule/mol} = 6.6336 \times 10^{-26} kg$$

Putting this into the equation one has

$$\sigma_{AA} = \sqrt{\frac{(6.6336 \times 10^{-26} kg)(1.3806505 \times 10^{-23} J/K)(300K)}{\pi(2.27 \times 10^{-5} kg \, m^{-1} s^{-1})^2}} = 4.12 \times 10^{-19} \, m^2 = 41.2 \, Å^2$$

Score for Page

3. (15 points) Leu and DeMore studied the reaction of chlorine monoxide with nitric oxide (*J. Phys. Chem.* 1978, *82*, **2049 – 2052.) These two materials, extremely important in atmospheric chemistry, have been of concern in ozone-depleting scenarios, but the authors analyzed their reaction with each other by the following reaction:**

$$ClO \ (g) \ + \ NO \ (g) \quad \rightarrow \quad Cl \ (g) \ + \ NO_2 \ (g)$$
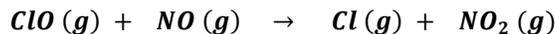
liberating a Cl radical. They propose the following simple mechanism for this reaction based on their results:

$$ClO \ + \ NO \quad \overset{k_1}{\rightarrow} \quad [ClO \cdot NO]$$

$$[ClO \cdot NO] \quad \overset{k_2}{\rightarrow} \quad ClO \ + \ NO$$

$$[ClO \cdot NO] \quad \overset{k_3}{\rightarrow} \quad Cl \ + \ NO_2$$
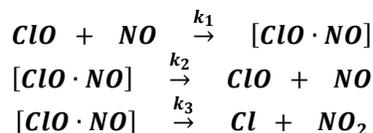
(a) Derive the steady-state rate law for this mechanism. (b) What is the expected order with respect to chlorine monoxide? (c) In terms of the elementary rate constants, give an expression for the steady-state rate constant for formation of the chlorine radical.

(a) Use the steady-state approximation on the intermediate complex:

$$\frac{d[ClO \cdot NO]}{dt} \ = \ v_1 \ - \ v_2 \ - \ v_3 \ = \ 0$$

This equation leads to the following relation:

$$k_1[ClO][NO] \ = \ k_2[ClO \cdot NO]_{ss} \ + \ k_3[ClO \cdot NO]_{ss}$$

Rearranging this equation, one finds:

$$[ClO \cdot NO]_{ss} \ = \ \frac{k_1}{k_2 \ + \ k_3}[ClO][NO]$$

The formation of chlorine radical occurs only in the third step, so the rate of the reaction is given by:

$$\frac{d[Cl]}{dt}_{ss} \ = \ v_3 \ = \ k_3[ClO \cdot NO]_{ss} \ = \ \frac{k_1 k_3}{k_2 \ + \ k_3}[ClO][NO]$$

(b) As one can see from this equation, the order with respect to ClO is expected to be 1.

(c) From the final equation the steady-state <u>rate constant</u> is of the form:

$$k_{ss} \ = \ \frac{k_1 k_3}{k_2 \ + \ k_3}$$

Score for Page

4. (10 points) The third-order reaction between nitric oxide and chlorine to produce nitrosyl chloride

$$2\,NO\,(g)\; +\;\; Cl_2\,(g)\;\;\;\rightarrow\;\;\; 2\,NOCl\,(g)$$
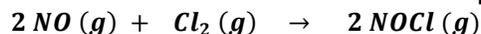
has been studied by Welinsky and Taylor (*J. Chem. Phys.* **1938**, *6*, 466 – 472.) **The temperature-dependent rate constants they reported are given in the table. From these, determine the _enthalpy of activation_ for this reaction. You must provide an appropriate graph, with appropriate axis labels, to receive full credit.**

T (°C)	k_3 ($cm^2\ mol^{-2}s^{-1}$)
-25.0	4.04×10^6
-10.0	6.32×10^6
0.0	8.97×10^6
22.0	1.60×10^7
27.5	1.70×10^7
60.0	3.55×10^7
100.0	8.35×10^7
146.0	1.84×10^8
196.0	4.58×10^8
203.0	4.53×10^8

One finds the enthalpy of activation by plotting the logarithm of $\ln(k_3/T)$ versus $1/T$. The slope of that plot is $-\Delta H^{\ddagger}/R$. The plot is shown below.
To obtain the enthalpy of activation, we use the slope

$$\Delta H^{\ddagger}\;\;=\;\;-R(slope)\;\;=\;\;2132.2\,K(8.3144349\,J\,K^{-1}\,mol^{-1})\;\;=\;\;17.728\,kJ\,mol^{-1}$$

In the plot: $\ln(k_3/T) = -2132.2/T + 18.151$, $R^2 = 0.9935$. Y-axis: $\ln(k_3/T)$. X-axis: $1/T\ (1/K)$.

Score for Page
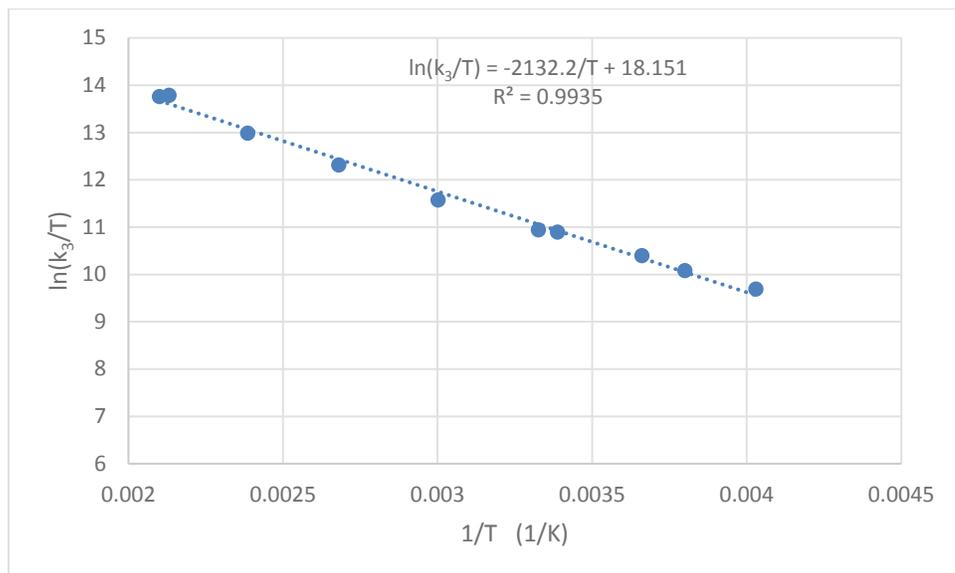
5. (10 points) Determine the <u>simplest form</u> of each of the following commutators, assuming that the various co-ordinates are independent. (Put answer in the space provided; show work below the equation.)

(a) $sin\varphi$ **and** $cos\varphi \frac{d}{d\varphi}$ _____

This is given by the following exercise: $\left[sin\varphi, cos\varphi \frac{d}{d\varphi}\right] F = sin\varphi \, cos\varphi \frac{dF}{d\varphi} - cos\varphi \frac{d}{d\varphi}(sin\varphi \, F)$

$$\left[sin\varphi, cos\varphi \frac{d}{d\varphi}\right] F = sin\varphi \, cos\varphi \frac{dF}{d\varphi} - cos^2\varphi \, F - cos\varphi \, sin\varphi \frac{dF}{d\varphi} = -cos^2\varphi \, F$$

Thus, one sees that the equivalent operation to the commutator is just multiplication by $sin\theta$.
$$\left[sin\varphi, cos\varphi \frac{d}{d\varphi}\right] = -cos^2\varphi$$

b) $\frac{d^2}{dx^2}$ **and** x^2 _____

$$\left[\frac{d^2}{dx^2}, x^2\right] f(x) = \frac{d^2}{dx^2}(x^2 f(x)) - x^2 \frac{d^2 f(x)}{dx^2} = \frac{d}{dx}\left(2xf(x) + x^2 \frac{df(x)}{dx}\right) - x^2 \frac{d^2 f(x)}{dx^2}$$
$$= 2f(x) + 2x\frac{df(x)}{dx} + 2x\frac{df(x)}{dx} + x^2 \frac{d^2 f(x)}{dx^2} - x^2 \frac{d^2 f(x)}{dx^2} = 2f(x) + 4x\frac{df(x)}{dx}$$

$$\left[\frac{d^2}{dx^2}, x^2\right] = 2 + 4x\frac{d}{dx}$$

Score for Page

6. (10 points) Fill in the blanks with the appropriate phrase or word from the list below.

a. The observation that light and small particles such as atoms behave as both particles and waves is the concept of <u>wave-particle duality</u>.

b. The <u>deBroglie</u> relation states that, for a particle, its momentum as a particle and its wavelength as a wave are related.

c. In a <u>bounded</u> system, only certain energies are allowed.

d. A quantum mechanical system is described mathematically by the solution of the <u>Schroedinger</u> equation.

e. The eigenfunctions of a quantum mechanical system are <u>orthogonal</u>.

f. The operators corresponding to measurable quantities of a quantum system are <u>Hermitian</u>.

g. A free particle has a <u>continuous</u> energy spectrum.

h. A state of a quantum system that is not an eigenstate can always be expressed as a <u>superposition</u> of the eigenstates of an operator that describes the system.

i. The fact that a system is quantized is a result of the imposition of <u>boundary conditions</u>.

j. The specification of operators for a quantum system is generally done by the <u>correspondence principle</u>.

Select from the following words or phrases:

blackbody radiation, Bohr, boundary conditions, bounded, commutator, complete set, complex conjugate, continuous, correspondence principle, deBroglie, degeneracy, deterministic, entanglement, Heisenberg, Hermitian, interference, operator, orthogonal, Planck, quantization, Schroedinger, superposition, tunneling, unbounded, valence, wave function, wave-particle duality, work function

Score for Page

7. (10 points) Consider the following approximate orbital for the radial part of the ground state of the hydrogen-atom:

$$R(r) \;=\; A\,exp\!\left(-cr^2/a_0^2\right)$$

where A and c are constants and a_0 is the Bohr radius. Normalize this wave function properly over the range of r.

The normalization requires the following integral to be 1.

$$\int_0^\infty R^2 r^2 dr \;=\; 1 \;=\; A^2 \int_0^\infty r^2\, exp(-2cr^2/a_0^2)dr$$

One may evaluate the integral from the integral table in the handbook, which gives

$$A^2 \left(\frac{a_0^2}{8c}\right)\sqrt{\frac{\pi a_0^2}{2c}} \;=\; 1$$

Solution of this equation gives

$$A \;=\; \frac{1}{\sqrt{a_0^3}}\sqrt[4]{\frac{128c^3}{\pi}}$$

Score for Page

8. (15 points)

a) **(10 points) Fill in the table below. All atoms are in their ground state configurations. In the term symbols, you do not have to provide an indication of the total angular momentum (J).**

Atom	Configuration	S	L	List all term symbols. Circle the lowest energy term for multiple terms.
He	$1s^2$	0	0	^1S
C	$1s^2 2s^2 2p^2$	0 or 1	0, 1, or 2	^1S, $\boxed{^3P}$, ^1D
O	$1s^2 2s^2 2p^4$	0 or 1	0, 1, or 2	^1S, $\boxed{^3P}$, ^1D
N	$1s^2 2s^2 2p^3$	3/2 or 1/2	0, 1, or 2	$\boxed{^4S}$, ^2P, ^2D
F	$1s^2 2s^2 2p^5$	1/2	1	^2P

b) **(5 points) For the terms corresponding to the lowest energy state of every atom in the table, indicate the TOTAL angular momentum corresponding to the lowest possible energy state according to the Hund's rules (HINT: Remember how spin-orbit coupling constant depends on whether the shell is less than half-filled or more than half-filled).**

Helium $^1S_0$

Carbon $^3P_0$

Oxygen $^3P_2$

Nitrogen $^4S_{3/2}$

Fluorine $^2P_{3/2}$

Score for Page

9. (10 points) Use data in Table 12.1 of your Handbook to calculate the frequency (in cm⁻¹) of the transition n=1, J=2 to n=2, J'=1 transition for ¹²⁷I³⁵Cl _as accurately as you can_. (a so-called "hot band" because it appears when the sample is heated) [HINT: Neglect centrifugal distortion effects.]

The general formula for the energy of a state is

$$E_{n,J} = -D_e + \left(n + \frac{1}{2}\right)\hbar\omega_e - \left(n + \frac{1}{2}\right)^2 \hbar x_e\omega_e + hB_nJ(J + 1) - hD_cJ^2(J + 1)^2$$

By taking the difference of the energies of the beginning and ending states, one has, neglecting the centrifugal distortion term,

$$\Delta E = E_{2,1} - E_{1,2} = \hbar\omega_e - \left(\frac{25}{4} - \frac{9}{4}\right)\hbar x_e\omega_e + h\left(\left(B_e - \left(2 + \frac{1}{2}\right)\alpha_e\right)1(1 + 1) - \left(B_e - \left(1 + \frac{1}{2}\right)\alpha_e\right)2(2 + 1)\right)$$

$$\Delta E = \hbar\omega_e - 4\hbar x_e\omega_e + h\left(\left(-4B_e - \left(\frac{5}{2}\right)2\alpha_e + \left(\frac{3}{2}\right)6\right)\alpha_e\right)$$

Substitution of the appropriate constants of ¹²⁷I³⁵Cl gives the explicit value for this molecule

$$\Delta E = 384.18 cm^{-1} - 4 \times 1.465 cm^{-1} - 4 \times 0.114162 cm^{-1} + 4 \times 0.000536 cm^{-1}$$

$$\Delta E = 377.87 \ cm^{-1}$$

10. (10 points) The work function of palladium is 5.22 eV. What is the minimum frequency of light required to observe the photoelectric effect in palladium?

The photoelectric effect will just barely be observed when the energy of the incident light is equal to the work function. First, let's convert this energy to joules using Table 3.5 of the Handbook.

$$E_{mol} \quad = \quad 5.22\ eV\ (96.4853\ J\ mol^{-1}) \quad = \quad 503.7\ kJ\ mol^{-1}$$

But we need the energy per atom, so we divide this by Avogadro's number.

$$E_{molecule} \quad = \quad \frac{503.7\ kJ\ mol^{-1}}{6.02211415 \times 10^{23} molecule\ mol^{-1}} \quad = \quad 8.364 \times 10^{-19}\ J\ molecule^{-1}$$

This is the minimum energy of a photon to remove the electron, but we know a formula that relates this energy to frequency, Planck's formula, and so:

$$\nu \quad = \quad \frac{E}{h} \quad = \quad \frac{8.364 \times 10^{-19}\ J}{6.6260693 \times 10^{-34}\ J\ s} \quad = \quad 1.262 \times 10^{15}\ Hz$$

One may also determine the wavelength (not asked for in this question) of this light:

$$\lambda \quad = \quad \frac{c}{\nu} \quad = \quad \frac{2.99792458 \times 10^{8}\ m\ s^{-1}}{1.262 \times 10^{15}\ Hz} \quad = \quad 2.376 \times 10^{-7}\ m \quad = \quad 237.6\ nm$$

This light falls in the ultraviolet region of the spectrum, as one might expect.

Score for Page

11. (15 Points) Fill in the table below. All molecules and ions are in their ground state configurations. In the term symbols, you must indicate the symmetry under reflection in the σ plane only for $^1\Sigma$ terms and symmetry under inversion for ALL terms. If more than one term corresponds to the same configuration, indicate the lowest-energy term according to the Hund's rules by circling this term.

Molecule	Configuration	S	Λ	List all term symbols. Circle the lowest energy term for multiple terms.
H_2	$1\sigma_g^2$	0	0	$^1\Sigma_g^+$
Be_2^+	$1\sigma_g^2 1\sigma_u*^2 2\sigma_g^2 2\sigma_u*^1$	1/2	0	$^2\Sigma_u$
He_2^+	$1\sigma_g^2 1\sigma_u*^1$	1/2	0	$^2\Sigma_u$
N_2^+	$1\sigma_g^2 1\sigma_u*^2 2\sigma_g^2 2\sigma_u*^2 1\pi_u^4 3\sigma_g^1$	1/2	0	$^2\Sigma_g$
O_2	$1\sigma_g^2 1\sigma_u*^2 2\sigma_g^2 2\sigma_u*^2 1\pi_u^4 3\sigma_g*^2 1\pi_g*^2$	0 or 1	0 or 2	$^1\Sigma_g^+$, $\boxed{^3\Sigma_g^-}$, $^1\Delta_g$

12. (10 Points). **For each molecule below, give the point group in the box to its right.**

Molecule	Point group
D$_2$O (deuterated water)	C$_{2v}$
1,4-dichlorobenzene	D$_{2h}$
Buckminsterfullerene, C$_{60}$	I$_h$
NO	C$_{\infty v}$
Dichloromethane	C$_{2v}$

Score for Page

13. (10 points, extra credit) For the ionic association in water at a pH of 7.00 and room temperature by

$$H^+ \; + \; OH^- \; = \; H_2O$$

The relaxation time is reported to be 36 microseconds. Calculate the rate constants, k_f and k_r for the forward and reverse reactions respectively, including the proper units, for these reactions.

First, find the concentrations of the two ions. A pH of 7.00 indicates that the concentration of hydrogen ions is 1.00×10^{-7} mol dm^{-3}. Since this is a neutral solution, the concentration of hydroxyl ions is equal to the concentration of hydrogen ions, so its concentration is also 1.00×10^{-7} mol dm^{-3}.

A relaxation experiment is carried out by disturbing the concentrations away from the equilibrium concentrations and watching the return to equilibrium. The rate of formation of H$_2$O is given by

$$\frac{d\left([H_2O]_{eq} + x\right)}{dt} \; = \; k_f[H^+][OH^-] \; - \; k_r[H_2O] \; = \; k_f\left([H^+]_{eq} - x\right)\left([OH^-]_{eq} - x\right) \; - \; k_r\left([H_2O]_{eq} + x\right)$$

where x is the deviation from equilibrium. This can be rewritten as

$$\frac{dx}{dt} \; = \; k_f\left([H^+]_{eq} - x\right)\left([OH^-]_{eq} - x\right) \; - \; k_r\left([H_2O]_{eq} + x\right)$$

By multiplying this out, one has the following equation:

$$\frac{dx}{dt} \; = \; k_f[H^+]_{eq}[OH^-]_{eq} \; - \; k_r[H_2O]_{eq} \; - \; \left\{k_f\left([H^+]_{eq} + [OH^-]_{eq}\right) + k_r\right\}x \; + k_f x^2$$

The first two terms cancel each other and the last term can be neglected because the deviation from equilibrium is generally small, to give

$$\frac{dx}{dt} \; = \; -\left\{k_f\left([H^+]_{eq} + [OH^-]_{eq}\right) + k_r\right\}x \; = \; -\frac{1}{\tau}x$$

where

$$\frac{1}{\tau} \; = \; \left\{k_f\left([H^+]_{eq} + [OH^-]_{eq}\right) + k_r\right\}$$

Using the data on equilibrium concentrations of the ions, one has

$$\frac{1}{36 \times 10^{-6} \; s} \; = \; \left\{k_f(2.00 \times 10^{-7} \; mol \; dm^{-3}) + k_r\right\}$$

But, in addition one knows that

$$K_{eq} \; = \; \frac{[H_2O]_{eq}}{[H^+]_{eq}[OH^-]_{eq}} \; = \; \frac{k_f}{k_r} \; = \; \frac{55.5 \; mol \; dm^{-3}}{1.00 \times 10^{-14} \; mol^2 \; dm^{-6}} \; = \; 5.55 \times 10^{15} \; dm^3 \; mol^{-1}$$

These can be solved simultaneously for the two rate constants:

$$\frac{1}{36 \times 10^{-6} \; s} \; = \; \left\{5.55 \times 10^{15} dm^3 \; mol^{-1}(2.00 \times 10^{-7} \; mol \; dm^{-3})k_r + k_r\right\} \; = \; 1.11 \times 10^8 k_r$$

This gives that

$$k_r \; = \; 2.50 \times 10^{-5} \; s^{-1}$$

Substitution of this back into the equilibrium expression gives

$$k_f \; = \; 1.398 \times 10^{11} \; dm^3 \; mol^{-1} \; s^{-1}$$

Score for Page