CHM 3400 – Fundamentals of Physical Chemistry
Third Hour Exam

There are five problems on the exam. Do all of the problems. Show your work

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R = 0.08206 L•atm/mole•K	N_A = 6.022 x 10^{23}
R = 0.08314 L•bar/mole•K	1 L•atm = 101.3 J
R = 8.314 J/mole•K	1 atm = 1.013 bar = 1.013 x 10^5 N/m^2
F = 96485. C/mol	1 atm = 760 torr
h = 6.626 x 10-34 J•s	(1 volt)•(1 Coulomb) = 1 Joule
c = 2.998 x 108 m/s	1 amu = 1.661 x 10^{-27} kg
R_∞ = 109737 cm^{-1}	1 cm^{-1} = 1.986 x 10^{-23} J
R_H = 109678. cm^{-1}	1 eV = 1.902 x 10^{-19} J

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1. (16 points) Consider the following two mechanisms for the formation of $COCl_2$ from CO and Cl_2 in a gas mixture of CO/Cl_2/air. Note that M = air, and [M] >> [CO], [Cl_2]

stoic. $CO + Cl_2 \rightarrow COCl_2$ (1.1)

mechanism 1

step 1 $Cl_2 + M \rightarrow Cl + Cl + M$ slow

step 2 $CO + Cl + M \rightarrow COCl + M$ fast

step 3 $COCl + Cl + M \rightarrow COCl_2 + M$ fast

mechanism 2

step 1 $Cl_2 + M \leftrightarrows Cl + Cl + M$ fast, reversible

step 2 $CO + Cl + M \leftrightarrows COCl + M$ fast, reversible

step 3 $COCl + Cl_2 \rightarrow COCl_2 + Cl$ slow

Find the rate law predicted for each of the above three mechanisms. Indicate the order of reaction for each substance appearing in your rate law. Show your work.

2. (20 points) An argon ion laser provides monochromatic light at a wavelength λ = 488.0 nm.

a) How many photons are produced by the above laser when it emits a pulse of monochromatic light with total energy E = 4.45 x 10^{-3} J?

b) A low energy pulse of light from the above laser is used to illuminate a metal surface in a photoelectric effect experiment. The work function for the metal is Φ = 3.18 eV. Will electrons be produced? Justify your answer. If your answer is yes, also give the maximum kinetic energy and speed of electrons that are produced.

3. (14 points) Neutron diffraction is a common method for studying crystal structures in solids. The mass of a neutron is m_N = 1.675 x 10^{-27} kg. Based on this, find the value for the speed of a neutron with a de Broglie wavelength λ_{dB} = 0.200 nm.

4. (25 points) The rotational and vibrational constants for the molecule $^{12}C^{16}O$ are B = 1.9313 cm^{-1} and ω = 2170.2 cm^{-1}. Based on this information, find the following:

a) r_e, the equilibrium bod length for $^{12}C^{16}O$. Give your final answer in units of nm

b) k, the force constant for $^{12}C^{16}O$. Give your final answer in units of N/m(newtons/meter).

c) B, the rotational constant for $^{14}C^{16}O$.

Note the following:	$m(^{12}C) = 12.0000$ amu	$m(^{16}O) = 15.9949$ amu
	$m(^{14}C) = 14.0032$ amu	

5. (25 points) The lowest few electronic energy levels of a boron atom are given below

state	$\tilde{E}$ (cm^{-1})
^2P	0.
^4P	28650.
^2S	40040.
^2D	47860.
$^2P'$	48610.

a) What are the values for L and S for the ^2D electronic state?

b) What are the possible values for J for the ^4P electronic state?

c) List all of the allowed transitions between the above electronic states of a boron atom. Give both the energy (in cm^{-1}) and wavelength (in nm) where each allowed transition is predicted to occur.

Solutions.

1) a) The overall rate is the rate of the slow step, and so

$$\text{rate} = k_1 [Cl_2] [M]$$

So the rate law predicted from this mechanism is 1st order in Cl_2 and 1st order in M.

b) rate = $k_3 [COCl][Cl_2]$ This is in terms of a reaction intermediate, which must be eliminated.

The second step is fast and reversible, and so

$$k_2 [CO][Cl][M] = k_{-2} [COCl] [M] \qquad [COCl] = \frac{k_2 [CO][Cl][M]}{k_{-2} [M]} = \frac{k_2 [CO][Cl]}{k_{-2}}$$

The first step is also fast and reversible, and so

$$k_1 [Cl_2][M] = k_{-1} [Cl]^2[M] \qquad [Cl]^2 = \frac{k_1 [Cl_2][M]}{k_{-1} [M]} = \frac{k_1 [Cl_2]}{k_{-1}}$$

and so $[Cl] = (k_1/k_{-1})^{1/2} [Cl_2]^{1/2}$

Substituting for [Cl] in the expression for [COCl] gives

$$[COCl] = \frac{k_2 [CO]}{k_{-2}} (k_1/k_{-1})^{1/2} [Cl_2]^{1/2} = (k_1/k_{-1})^{1/2}(k_2/k_{-2}) [CO][Cl_2]^{1/2}$$

Substituting into our expression for the rate of reaction we get our final result

$$\text{rate} = k_3 [Cl_2] \{(k_1/k_{-1})^{1/2}(k_2/k_{-2}) [CO][Cl_2]^{1/2}\} = (k_1/k_{-1})^{1/2}(k_2/k_{-2})k_3 [CO][Cl_2]^{3/2} = k [CO][Cl_2]^{3/2}$$

where $k = (k_1/k_{-1})^{1/2}(k_2/k_{-2})k_3$

So the rate law predicted from this mechanism is 1st order in CO and $^3/_2$ order in Cl_2.

2) a) The energy of one photon from the laser is

$$E_\gamma = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J•s})(2.998 \times 10^8 \text{ m/s})}{(488.0 \times 10^{-9} \text{ m})} = 4.071 \times 10^{-19} \text{ J}$$

Since the energy of the laser pulse is 4.45×10^{-3} J, the number of photons produced is

$$\text{\# photons} = \frac{4.45 \times 10^{-3} \text{ J}}{4.071 \times 10^{-19} \text{ J/photon}} = 1.09 \times 10^{16} \text{ photons}$$

b) For the photoelectric effect

$$E_\gamma = E_{K,max} + \Phi$$

or $E_{K,max} = E_\gamma - \Phi$

where a negative value for E_K means no electrons are produced.

The work function for the metal is $\Phi = 3.18$ eV $(1.602 \times 10^{-19}$ J/eV$) = 5.094 \times 10^{-19}$ J

The energy of one photon of light is $E_\gamma = 4.071 \times 10^{-19}$ J

If we insert these values into the equation for $E_{K,max}$, we get a negative number, which is not physically possible. What this means is that electrons will not be produced by light at this wavelength.

3) The de Broglie wavelength for a particle is

$$\lambda_{dB} = \frac{h}{mv}$$

And so $v = \frac{h}{m\,\lambda_{dB}} = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})}{(1.675 \times 10^{-27}\ \text{kg})\,(0.200 \times 10^{-9}\ \text{m})} = 1978.\ \text{m/s}$

4) For this problem we will need the reduced masses for $^{12}C^{16}O$ and $^{14}C^{16}O$. Note $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

$$\mu(^{12}C^{16}O) = \frac{(12.0000)\,(15.9949)}{(12.0000 + 15.9949)} = 6.856\ \text{amu}\ \frac{1.661 \times 10^{-27}\ \text{kg}}{\text{amu}} = 1.139 \times 10^{-26}\ \text{kg}$$

$$\mu(^{14}C^{16}O) = \frac{(14.0032)\,(15.9949)}{(14.0032 + 15.9949)} = 7.466\ \text{amu}\ \frac{1.661 \times 10^{-27}\ \text{kg}}{\text{amu}} = 1.240 \times 10^{-26}\ \text{kg}$$

a) $B = \frac{h}{8\pi^2 c\mu r_e^2}$ So $r_e = (h/8\pi^2 c\mu B)^{1/2}$

$B = (1.9313\ \text{cm}^{-1})\ (100\ \text{cm/m}) = 193.13\ \text{m}^{-1}$

So $r_e = [\ (6.626 \times 10^{-34}\ \text{J}\cdot\text{s})/8\pi^2(2.998 \times 10^8\ \text{m/s})(1.139 \times 10^{-26}\ \text{kg})(193.13\ \text{m}^{-1})\ ]^{1/2}$

$= 1.128\ \text{m} = 0.1128\ \text{nm}$

b) $\omega = \frac{1}{2\pi c}\ (k/\mu)^{1/2}$ So $k = 4\pi^2 c^2 \omega^2 \mu$

$\omega = 2170.2\ \text{cm}^{-1}\ (100\ \text{cm/m}) = 2.1702 \times 10^5\ \text{m}^{-1}$

So $k = 4\pi^2(2.998 \times 10^8\ \text{m/s})^2(2.1702 \times 10^5\ \text{m}^{-1})^2(1.139 \times 10^{-26}\ \text{kg})$

$= 1903.7\ \text{N/m}$

c) $B \sim \frac{1}{\mu}$ So $\frac{B(^{14}C^{16}O)}{B(^{12}C^{16}O)} = \frac{\mu(^{12}C^{16}O)}{\mu(^{14}C^{16}O)}$

or $B(^{14}C^{16}O) = B(^{12}C^{16}O)\ \frac{\mu(^{12}C^{16}O)}{\mu(^{14}C^{16}O)} = (1.9313\ \text{cm}^{-1})\ \frac{1.139}{1.240} = 1.7740\ \text{cm}^{-1}$

5) a) For a ^2D state $L = 2$ $S = ½$

b) For a ^4P state $L = 1$ $s = {}^3/_2$ $J = |\ L + S\ |\ \ldots\ |\ L - S\ | = {}^5/_2 \ldots {}^1/_2 = {}^5/_2, {}^3/_2, ½$

c) Selection rules are $\Delta S = 0$, $\Delta L = 0, \pm 1$, so the allowed transitions are

transition	Energy (cm^{-1})	wavelength (nm)
(^2P,^2S)	40040.	249.8
(^2P,^2D)	47860.	208.9
(^2P,$^2P'$)	48610.	205.7
(^2S,$^2P'$)	8570.	1167.
(^2D,$^2P'$)	750.	13333.