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TR 5:00-6:15 pm, 206 BrL
Quiz #1

Problem 1 (5 points). ***Derive*** the general expression for the most probable speed in ideal gas based on Maxwell-Boltzman three-dimensional speed distribution function.

$$F(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)v^2dv \quad \text{(section 8, page 8-1)}$$

v_p means that the first derivative of the probability distribution function should be 0

$$\frac{dF(v)}{dv} = 0 = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \times \left(\left(-\frac{2mv}{2kT}\right)\exp\left(-\frac{mv^2}{2kT}\right)v^2 - 2v\exp\left(-\frac{mv^2}{2kT}\right)\right) \quad \text{or}$$

$$-\frac{2mv_p^3}{2kT} = 2v_p \text{ or } \quad v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$, which is the first formula on page 8-2.

Problem 2 (5 points). Estimate the mean distance travelled by a neon molecule (3 D) in 1 minute at room temperature and 1 bar.

$$root-mean-square\ (rms)\ DISTANCE: \delta x \equiv \sqrt{\langle x^2\rangle} = \sqrt{6Dt} = \sqrt{6\times\frac{1}{2}\langle v\rangle\lambda t} = \sqrt{3\sqrt{\frac{8RT}{\pi M}}\times\frac{t}{\sqrt{2}\sigma_{AA}n_A^*}} =$$

$$= \sqrt{3\sqrt{\frac{8RT}{\pi M}}\times\frac{t}{\sqrt{2}\sigma_{AA}n_A^*}} = \sqrt{\frac{3RT}{PN_A}\sqrt{\frac{8RT}{\pi M}}\times\frac{t}{\sqrt{2}\times\pi\left(0.2328\times10^{-9}\,m\right)^2}} =$$

$$= \sqrt{\frac{3\times 8.3144\frac{J}{mol\times K}298.15K}{100000Pa\times6.022\times10^{23}mol^{-1}}\sqrt{\frac{8\times8.3144\frac{J}{mol\times K}298.15K}{\pi 0.020\frac{kg}{mol}}}\times\frac{60\text{ sec}}{\sqrt{2}\times\pi\left(0.2328\times10^{-9}\,m\right)^2}} = 0.132\ m = 13.2\ cm$$

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Quiz #2

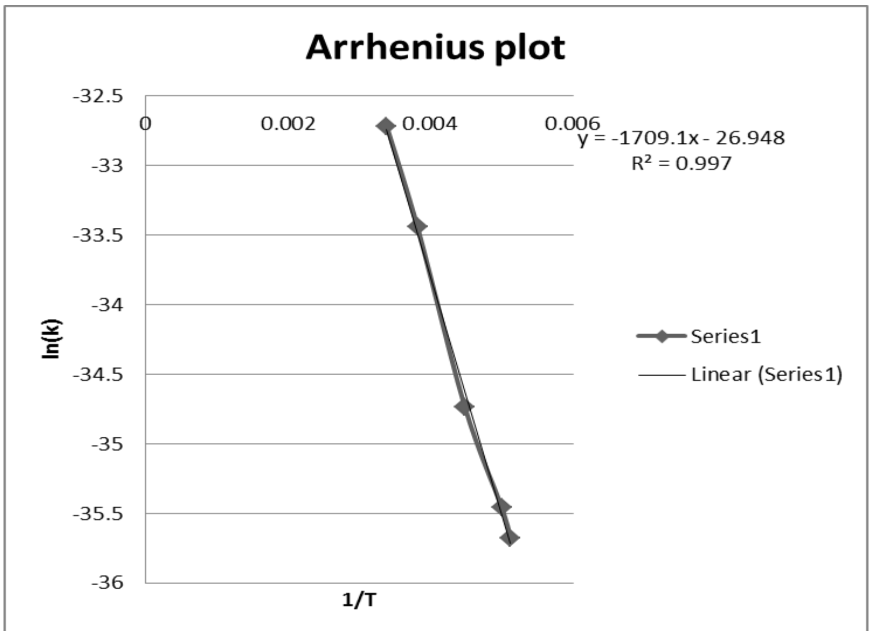
Problem 1 (8 points). For the reaction of the second order that we considered in class:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

We used a similar set of data to calculate the activated-complex theory parameters:

T/K	195	200	223	262	295
$k/10^{-15}$ cm^3/molecule-sec	0.32	0.40	0.82	3.00	6.15

Use the same data to calculate the Arrhenius parameters for this reaction. Show all your work clearly. You can use calculators to calculate these parameters but you must use the attached chart to show what you are plotting and how you obtain the results.



As per the Arrhenius equation, the slope of this line is $-E_a/R$, so $E_a = 1709.1K^{-1}$ x 8.3144 J/mol/K or E_a = 14210 J/mol or 14.21 kJ/mol, which is rather small.
The pre-exponential factor is A = exp(-26.948) = 2 x 10^{-12} cm^3/molecule-sec (same units as the rate constant). The obtained Arrhenius activation energy is somewhat outside the normal values but it is an unusual reaction. The pre-exponential factor is actually very reasonable, considering that its units are per molecule. Multiplying by the Avogadro's number will yield an appropriate value per mole.

Problem 2 (2 points). Describe in a couple of sentences uses and limitations of the steady-state approximation.
Steady state approximation describes the behavior of very reactive species, whose concentrations are rather small during the entire course of the reaction and the time-derivatives of their concentrations can be set to be equal to zero. This helps to solve the set of differential equations describing complex reaction mechanisms. One has to be certain that the species in question are actually very reactive (most of the time, radicals, ions, occasionally reactive oxides, etc.) in order for this approach to be applicable. Also, it does not describe the initial stages of the reaction (often referred to as **induction period**).

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Quiz #3

Problem 1 (6 points). Derive the rate law for the product formation of the Michaelis-Menten Mechanism (Page 10-3). The final expression can contain any combination of rate constants, concentration of the substrate and the total concentration of the enzyme but not the concentration of free enzyme or the substrate-bound enzyme, which are often difficult to determine experimentally.

On page 10-3 of the Handbook, you are given the Michaelis-Menten mechanism. This answer will use the same constants as shown there:

$$E + S \xrightarrow{k_1} E \sim S$$
$$E \sim S \xrightarrow{k_{-1}} E + S$$
$$E \sim S \xrightarrow{k_2} P + E$$

The rate of product formation is $v = k_2[E \sim S]$

Applying the steady-state approximation to the [E~S] yields:

$$0 \approx \frac{d[E \sim S]}{dt} = k_1[E][S] - k_{-1}[E \sim S] - k_2[E \sim S]. \text{ Thus, } [E \sim S] = \frac{k_1[E][S]}{k_{-1} + k_2} = \frac{[E][S]}{K_m}$$

On the other hand, $[E_0] = [E] + [E \sim S] = [E] + \frac{[E][S]}{K_m}$ or $[E] = \frac{[E_0]}{1 + \frac{[S]}{K_m}} = \frac{K_m[E_0]}{K_m + [S]}$

Thus, $Rate = k_2[E \sim S] = \frac{k_2[E][S]}{K_m} = \frac{k_2}{K_m}\frac{K_m[E_0]}{K_m + [S]}[S] = \frac{k_2[S][E_0]}{K_m + [S]}$

.

Problem 2 (4 points). If the adsorption of a gas is described by the Langmuir isotherm with Langmuir constant b = 0.7 kPa^{-1} at 100°C. Calculate the pressure at which the fractional coverage is 0.3.

$\Theta = b\mathrm{P}/(1+b\mathrm{P})$
$\mathrm{P} = \Theta/(\mathrm{b}*(1-\Theta))$
$\mathrm{P} = 0.3/(0.7\ \mathrm{kPa}^{-1}*(1-0.3)) = 0.61\ \mathrm{kPa}$

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Quiz #4

Problem 1 (3 points). Find the following commutator: $\left[\frac{d}{dx}, x^2\right]$

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

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

Problem 2 (3 points). Explore if the function F = $\exp(-ix)$ is the eigenfunction of operator $\frac{d^2}{dx^2}$?
Prove your statement explicitly.

$$\frac{d^2}{dx^2}\exp(-ix) = \frac{d}{dx}\left(\frac{d}{dx}\exp(-ix)\right) = \frac{d}{dx}\left(-i\exp(-ix)\right) = -\exp(-ix) = Const \times F$$

Thus, F is an eigenfunction of this operator

Problem 3 (4 points). Normalize the following function (find the normalization constant A) on an interval $0 \le x \le b$:

$\Psi = A \times \sin(3\pi x)$
Assume that the function only exists within this interval

Normalization means that $\int\limits_{all\ space} A^2 \sin^2(3\pi x)dx = 1$ or $\int_0^b A^2 \sin^2(3\pi x)dx = 1$

$$A^2\int_0^b \sin^2(3\pi x)dx = 1 = A^2\left(\frac{x}{2} - \frac{1}{12\pi}\sin(6\pi x)\right)\Big|_0^b = A^2\left(\frac{b}{2} - \frac{1}{12\pi}\sin(6\pi b)\right)$$ or

$$A = \frac{1}{\sqrt{\frac{b}{2} - \frac{1}{12\pi}\sin(6\pi b)}}$$

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Quiz #5

Problem 1 (6 points). Normalize the wavefunction of the quantum mechanical harmonic oscillator corresponding to the lowest possible energy state.

$\Psi_n(x) = A_n H_n\left(\frac{x}{\alpha}\right)\exp\left(-\frac{x^2}{2\alpha^2}\right)$; $\Psi_0(x) = A_0 \exp\left(-\frac{x^2}{2\alpha^2}\right)$ is the function corresponding to n = 0.

$$\int_{-\infty}^{\infty} A_0^2 \exp\left(-\frac{x^2}{\alpha^2}\right)dx = 1 = A_0^2 \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{\alpha^2}\right)dx = A_0^2 \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{\alpha^2}\right)dx = 2A_0^2 \int_{0}^{\infty} \exp\left(-\frac{x^2}{\alpha^2}\right)dx = 2A_0^2 \frac{1}{2}\sqrt{\pi\alpha^2}$$

or $A_0 = \frac{1}{\sqrt{\alpha\sqrt{\pi}}}$. Here $\alpha = \left(\frac{\hbar^2}{km}\right)^{1/4}$, which is different from the text.

Problem 2 (2 points). Write down a Hamiltonian that describes quantum mechanical harmonic oscillator.

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2}$$

Problem 3 (2 points). Fill in the blanks.

a) Two quantum particles whose properties are coupled in such a way that their properties are no longer independent of one another no matter how far apart they may be are called _______entangled_____

b) Name at least two differences between classical and quantum mechanical oscillator models:

1) In quantum mechanical model every energy level has oscillatory functions describing probability, while classical mechanics predicts relatively flat probability distribution functions;
2) Quantum mechanical model suggests finite probability for a particle described to be inside the wall of the limiting potential;
3) For the lowest energy state, quantum mechanical model yields the highest probability being in the middle of the well, when classical mechanics suggests this to be the place with lowest probability of finding the particle.

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Quiz #6

Problem 1 (6 points). Find the average distance between an electron in 1s orbital of hydrogen atom and the nucleus.

$$\psi_n = R_{nl}(r)Y_{lm}(\Theta,\varphi)$$

$$R_{nl}(\frac{r}{a_0}) = A_{nl}\left(\frac{Zr}{a_0}\right)^l L_{nl}\left(\frac{r}{a_0}\right)\exp\left(-\frac{Zr}{na_0}\right);\ R_{10}(\frac{r}{a_0}) = A_{10}\left(\frac{r}{a_0}\right)^0 \exp\left(-\frac{r}{a_0}\right)$$

Since the corresponding spherical harmonic is already normalized and does not depend on the two angles of the spherical coordinates, we only need to include the radial component:

$$\langle r\rangle = \int_0^\infty R_{10}^2 r^2 r dr = \frac{a_0^4\int_0^\infty A_{10}^2\left(\frac{r}{a_0}\right)^3 \exp\left(-\frac{2r}{a_0}\right)d\left(\frac{r}{a_0}\right)}{a_0^3\int_0^\infty A_{10}^2\left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{2r}{a_0}\right)d\left(\frac{r}{a_0}\right)} = a_0\frac{\frac{3!}{2^{3+1}}}{\frac{2!}{2^{2+1}}} = 1.5a_0$$

, where a_0 is Bohr radius

Problem 2 (2 points). What is the wavelength of the light with 3 eV energy?

$E = h\nu = h\frac{c}{\lambda}$; Thus,

$$\lambda = \frac{hc}{E} = \frac{6.626\times10^{-34}\,J\times s\times 2.998\times10^{8}\,m/s}{3\,eV\times 96.4853\frac{kJ}{mol}\times 1000\frac{J}{kJ}\times\frac{1}{6.022\times10^{23}\frac{molecules}{mol}}} = 4.12\times10^{-7}m = 412\ nm$$

Problem 3 (2 points).). From the possible statements in column B, select the best match for each phrase in column A and put its number in the adjacent blank. There is only one best match for each phrase.

Column A	Column B
1. For the rigid rotor description corresponding to l=3, the following set of quantum numbers m is appropriate: ____d_____ 2. The degeneracy of the solution for the rigid rotor state with l=5 is ____e_____	a) m= -2, -1, 0, 1, 2 b) 5 c) 10 d) m= -3, -2, -1, 0, 1, 2, 3 e) 11 f) 9 g) m= -2.5, -1.5, -0.5, 0.5, 1.5, 2.5

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Quiz #7

Problem 1 (5 points). Be^{2+} is an example of 2-electron system. Calculate the 3rd ionization potential of Be (that is the energy required to remove one electron from Be^{2+}) using variation principle applied to the ground state of 2-electron systems.

$$Be^{2+}(1s^2) \to Be^{3+}(1s^1) + e$$

$$\text{IP=E(Be}^{3+}\text{) - E(Be}^{2+}\text{)}$$

$$= -\frac{Z^2 E_h}{2n^2} - \left(-\left(Z - \frac{5}{16} \right)^2 E_h \right) = -\frac{4^2}{2} E_h - \left(-\left(4 - \frac{5}{16} \right)^2 E_h \right) = -8E_h + \left(\frac{59}{16} \right)^2 E_h = 5.598 E_h = 152.32\ eV$$

The actual number is 153.893, eV, which is pretty close to our approximation.

Problem 2 (3 points). Write down all the possible the terms for the following atomic systems that we have covered:

$1s^2$	^1S
$1s^1 2s^1$	^1S and ^3S
$1s^1 2p^1$	^1P and ^3P

Problem 3 (2 points). For the following atomic systems, indicate all possible values of the total orbital angular momenta (L) and total spin angular momenta (S):

Configuration	L	S
$1s^2 2s^1$	0	1/2
$1s^2 2s^2 2p^1$	1	1/2

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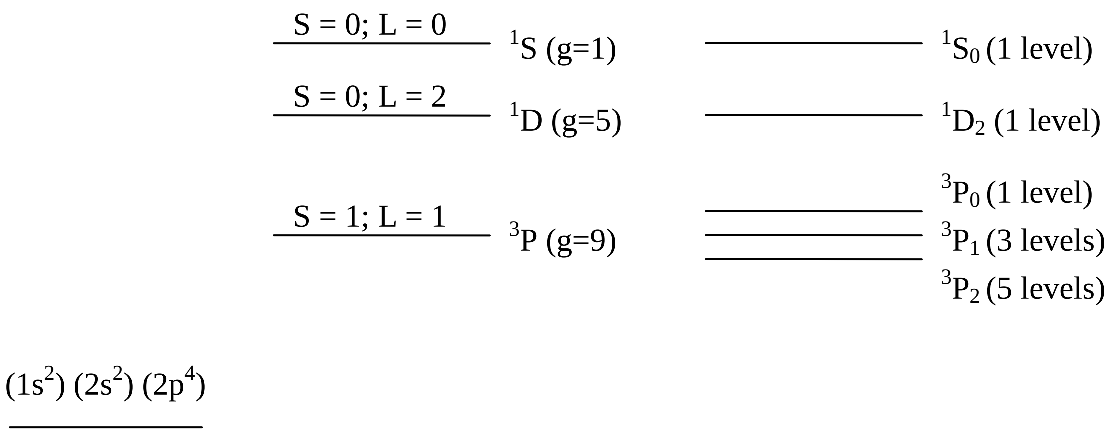
Quiz #8

Problem 1 (5 points). Sketch a complete Grotrian diagram of all the terms arising from the ground state configuration of an oxygen atom. **Take the spin-orbit coupling into account and indicate the degeneracy (g) of each manifold produced**. Remember that Hund's rules apply strictly only to the ground state but are often used to produce the order of other states.



Problem 2 (2 points). Circle all that apply:

The $^3P_1$ to $^1D_2$ transition for a d^6 configuration will violate the following selection rules for atomic spectroscopy:

$\Delta S = 0$ $\quad$ $\Delta L = \pm 1$ $\quad$ $\Delta J = 0, \pm 1$ $\quad$ Laporte's rule

Problem 3 (3 points). Explain in three sentences or less the differences between Auger electron spectroscopy and X-ray photoelectron spectroscopy.

Both spectroscopies follow the ejection of electron following primary excitation and therefore both require vacuum but AES uses electron beam as a primary excitation source, while XPS uses X-rays. This also causes different sensitivities of these two techniques with respect to the surface layers of the samples. XPS measures kinetic energy of an ejected electron to ultimately yield the binding energy of an electron on a specific energy level, while AES follows the number of electrons corresponding to a *difference* between the electron energy levels. Other differences may include different spacial resolution (better for AES because of the ways to focus primary electron beam) and chemical environment sensitivity (better for XPS).

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Quiz #9

Problem 1 (5 points). Use data in Table 12.1 to calculate the frequency (you can leave the answer in terms of commonly used cm^{-1} units) of the n=0, J=1 to n=1, J'=2 transition for $^{19}F^{35}Cl$ in cm^{-1} as accurately as you can. You can disregard the centrifugal distortion term.

$$E_{nJ} = -D_e + \left(n+\frac{1}{2}\right)\hbar\varpi_e - \left(n+\frac{1}{2}\right)^2 \hbar x_e\varpi_e + hB_n J(J+1) - hD_c J^2(J+1)^2$$

$$\Delta E_{nJ} = \hbar\varpi_e - \left(\frac{9}{4}-\frac{1}{4}\right)\hbar x_e\varpi_e + h\Delta\left(\left(B_e - \left(n+\frac{1}{2}\right)\alpha_e\right)J(J+1)\right) =$$

$$\hbar\varpi_e - 2\hbar x_e\varpi_e + h(4B_e - 8\alpha_e)$$

$$\Delta E_{nJ} = 793.2\ cm^{-1} - 2\times 9.9\ cm^{-1} + \left(4\times 0.516\ cm^{-1} - 8\times 0.004358\ cm^{-1}\right) = 775.429\ cm^{-1}$$

Problem 2 (5 points). Rotational constant B_e for a diatomic $^{23}Na^{19}F$ molecule in a gas phase has been measured to be 0.43506 cm^{-1}. Find the equilibrium bond length for this molecule.

$B_e = \dfrac{h}{8\pi^2 I}$, where $I = \mu R_e^2$ and the units of B_e can be converted to inverse centimeters by dividing by *c*:

$$B_e = \frac{h}{8\pi^2 c\mu R_e^2} \text{ or } R_e = \sqrt{\frac{h}{8B_e\pi^2 c\mu}}$$

Since $\mu = \dfrac{22.9898\times 18.9984}{22.9898+18.9984} g/mol = 10.4022 g/mol$,

$$R_e = \sqrt{\frac{6.6260755\times 10^{-34}\ J\times s\times 6.022\times 10^{23}\ \frac{1}{mol}}{8\pi^2\times 2.997925\times 10^8\ m/s\times 10.4022 g/mol\times 10^{-3}\frac{kg}{g}\times 0.43506\ cm^{-1}\times 100\frac{cm}{m}}} = 0.193\times 10^{-9}\ m = 1.93\text{A}$$

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Quiz #10

Problem 1 (9 points). Determine ground state (unless indicated otherwise) configurations, bond order, total orbital angular momentum, total spin angular momentum, and all the terms arising from these configurations (indicate the symmetry under inversion (g vs. u) **only for the ground state species** and symmetry under reflection through the mirror plane σ (+ vs -) **only for $^1\Sigma$ terms of the ground state species**) for the following diatomic homonuclear molecules and ions:

Molecule	Configuration	BO =	Λ =	S =	Term
H_2 in its **first excited state**	2e: $(\sigma_g 1s)^1$, $(\sigma_u{*}1s)^1$,	½*(1-1) = 0	0	0 or 1	$^1\Sigma$ and $^3\Sigma$
He_2	4e: $(\sigma_g 1s)^2$, $(\sigma_u{*}1s)^2$	½*(2-2) = 0	0	0	$^1\Sigma_g^+$
O_2^+	15 e: $(\sigma_g 1s)^2$, $(\sigma_u{*}1s)^2$, $(\sigma_g 2s)^2(\sigma_u{*}2s)^2(\sigma_g 2s)^2(\pi_u)^4(\pi_g^{*})^1$	½*(10-5) = 2.5	1	½	$^2\Pi_g$

Problem 2 (1 point). State Born-Oppenheimer approximation (use no more than 2-3 sentences).

Since the electron is lighter than proton by a factor of nearly 2000, the timescales for nuclear and electron motion are very different. Thus, these two motions can be decoupled, we can solve the Schrödinger equation for a fixed nuclear separation, and calculate the energy for a molecule for that distance. If this procedure is repeated for many values of the internuclear separation, we can determine energy as a function of the internuclear distance.