

Problem 1 (5 points). Use a 2-D diffusion model to estimate the diffusion coefficient of a pentacene molecule ($C_{22}H_{14}$) on a single crystalline surface of gold from the following experimental data:
 at $T=100$ K it was observed that an average pentacene molecule moves about 50 nm every 5 seconds.

$$r_{rms} = \sqrt{4Dt}$$

$$D = \frac{r_{rms}^2}{4t} = \frac{(50 \times 10^{-9} \text{ m})^2}{4 \times 5 \text{ sec}} = 1.25 \times 10^{-16} \frac{\text{m}^2}{\text{sec}}$$

Problem 2 (5 points) From the possible statements in column B, select the best match for each phrase 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. By definition, <i>intrinsic viscosity</i> is <u> D </u>	A) pressure.
2. From the <i>Kinetic Theory of Gases</i> , it follows that the viscosity of a gas increases as a square root of <u> J </u>	B) $\eta_{sp} = \frac{\eta - \eta_0}{c_m}$
3. G. G. Stokes showed that the friction constant $f = 6\pi\eta r$ for particles of <u> K </u> shape.	C) solutions of ethylene in bromoethylene
4. <i>Fick's first law of diffusion</i> <u> H </u> .	D) $[\eta] = \lim_{c_m \rightarrow 0} \left(\frac{\eta_{sp}}{c_m} \right)$.
5. Mark-Houwink equation is applicable to <u> N </u> .	E) is given by equation 9.29 in your Handbook.
	F) elliptical
	G) $[\eta] = K' \frac{R_G^3}{M}$
	H) is given by equation 9.27 in your Handbook.
	I) gives the shape of van der Waals potential.
	J) temperature
	K) spherical
	L) mixtures of solid grains
	M) any
	N) solutions of random-coil polymers

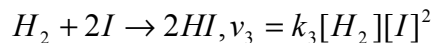
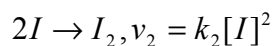
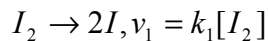
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Quiz #3

Name KEY

Problem 1 (8 points). Hydrogen iodide can be synthesized from the elements in a gas-phase reaction. One proposed mechanism for the process is



Derive a differential rate law for the rate of production of HI if:

a) I_2 and I are in a fast equilibrium throughout the reaction.

$$K_{eq} = \frac{[I]^2}{[I_2]}, \text{ therefore } [I]^2 = K_{eq}[I_2]$$

The rate of production of HI is given by:

$$\frac{d[HI]}{dt} = 2k_3[H_2][I]^2 = 2k_3K_{eq}[H_2][I_2]$$

b) steady-state approximation can be applied to the I atoms.

$$\frac{d[I]}{dt} = 0 = 2k_1[I_2] - k_2[I]^2 - 2k_3[H_2][I]^2, \text{ thus } [I]^2 = \frac{k_1[I_2]}{k_2 + k_3[H_2]}$$

Under these conditions the rate of production of HI is:

$$\frac{d[HI]}{dt} = 2k_3[H_2][I]^2 = \frac{2k_3k_1[H_2][I_2]}{k_2 + k_3[H_2]}$$

Problem 2 (2 points). If a steady state approximation is used, the period of time until the reaction reaches

a steady state is called induction period

Quiz #5

Problem 1 (4 points). Calculate the normalization constant for the harmonic oscillator function of the lowest energy level of a harmonic oscillator. Leave the final answer in terms of α . Show all work clearly.

$$\Psi_0 = A_0 H_0(y) e^{-y^2/2} = A_0 \times 1 \times e^{-y^2/2}, \text{ where } x = \alpha y \text{ and } y = \frac{x}{\alpha}$$

The normalization condition for this function is $\int_{-\infty}^{\infty} \Psi_0^2 dx = 1$

$$\text{Thus: } 1 = \int_{-\infty}^{\infty} \Psi_0^2 dx = A_0^2 \int_{-\infty}^{\infty} \exp(-y^2) dx = A_0^2 \int_{-\infty}^{\infty} \exp(-y^2) d(\alpha y) = 2\alpha A_0^2 \int_0^{\infty} \exp(-y^2) dy = 2\alpha A_0^2 \frac{1}{2} \sqrt{\pi}$$

Here, $\int_{-\infty}^{\infty} \exp(-y^2) dy = 2 \int_0^{\infty} \exp(-y^2) dy$ because $\exp(-y^2)$ is an even function.

$$\text{The final answer is } A_0 = \frac{1}{\sqrt{\alpha} \times \pi^{1/4}}$$

Problem 2 (6 points) For an electron in a three-dimensional box with dimensions $a=b=c=a_0$, where a_0 is Bohr radius, calculate the energies of the two lowest energy levels and indicate the degeneracies of these levels. Show all your work clearly.

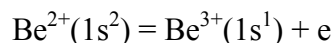
1) The lowest energy level has $n_x=n_y=n_z=1$, degeneracy 1.

$$E_1 = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8ma_0^2} = \frac{3 \times (6.6260755 \times 10^{-34} \text{ J} \times \text{s})^2}{8 \times 9.1093897 \times 10^{-31} \text{ kg} \times (5.2917725 \times 10^{-11} \text{ m})^2} = 6.4543486 \times 10^{-17} \text{ J}$$

2) The second lowest energy level has $(n_x, n_y, n_z) = (2; 1; 1)$ or $(1; 2; 1)$ or $(1; 1; 2)$, degeneracy 3.

$$E_2 = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8ma_0^2} = \frac{6 \times (6.6260755 \times 10^{-34} \text{ J} \times \text{s})^2}{8 \times 9.1093897 \times 10^{-31} \text{ kg} \times (5.2917725 \times 10^{-11} \text{ m})^2} = 12.908697 \times 10^{-17} \text{ J}$$

Problem 1 (8 points). Using the formula for estimation of the energy of a two-electron system by **variation principle** and a 0th order approximation for a one-electron system, estimate the third ionization potential of a Be atom that proceeds according to the following reaction:



$$Z = 4; E_h = 27.212 \text{ eV}$$

$$E(\text{Be}^{3+}) = -Z^2/2 \cdot E_h = -(16/2)E_h = -8 E_h$$

$$E(\text{Be}^{2+}) = -(Z-5/16)^2 E_h = -(59/16)^2 E_h$$

$$\text{IP}_{\text{second}} = E(\text{Be}^{3+}) - E(\text{Be}^{2+}) = (-8 - (-(59/16)^2)) E_h = 5.5977 E_h = 152.323 \text{ eV}$$

Problem 2 (2 points) According to Pauli's principle, which of the following functions are acceptable for representing a real state of a two-electron system (circle all that apply). This problem will be graded based on "right" – "wrong".

$$\Psi_1 = \frac{1}{\sqrt{2}} \Psi_{1s}(1)\Psi_{1s}(2)\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\}$$

$$\Psi_2 = \frac{1}{\sqrt{2}} \Psi_{1s}(1)\Psi_{1s}(2)\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$$

$$\Psi_3 = 1/2 \{\Psi_{1s}(1)\Psi_{2pz}(2)-\Psi_{1s}(1)\Psi_{2pz}(1)\} \{\alpha(1)\beta(2)+\beta(1)\alpha(2)\}$$

$$\Psi_3 = \frac{1}{\sqrt{2}} \Psi_{1s}(1)\Psi_{1s}(2)\{\alpha(1)\alpha(2)-\alpha(1)\alpha(2)\}$$

Problem 1 (9 points). Using data found in Table 13.1 calculate the frequency of the $n = 0, J = 0 \rightarrow n' = 1, J' = 1$ transition for ${}^1\text{H}^{79}\text{Br}$, in cm^{-1} , as accurately as possible (Do not disregard the centrifugal distortion!)

Table 13.1 gives for ${}^1\text{H}^{79}\text{Br}$: $\bar{\omega}_e = 2649.67 \text{ cm}^{-1}$; $x_e \bar{\omega}_e = 45.21 \text{ cm}^{-1}$; $B_e = 8.473 \text{ cm}^{-1}$; $\alpha_e = 0.226 \text{ cm}^{-1}$

From these data: $D_c = 4 \frac{B_e^3}{\bar{\omega}_e^2} = 3.46568 \times 10^{-4} \text{ cm}^{-1}$ (using formula 13.23)

$$E(n, J) = \left(n + \frac{1}{2}\right) \bar{\omega}_e - \left(n + \frac{1}{2}\right)^2 \bar{\omega}_e x_e + \left(B_e - \alpha_e \left(n + \frac{1}{2}\right)\right) J(J+1) - D_c J^2 (J+1)^2$$

$$\Delta E = E(1,1) - E(0,0) = \left(1 + \frac{1}{2} - \frac{1}{2}\right) \bar{\omega}_e - \left[\left(1 + \frac{1}{2}\right)^2 - \left(\frac{1}{2}\right)^2\right] \bar{\omega}_e x_e + \left(B_e - \alpha_e \left(1 + \frac{1}{2}\right)\right) [1(1+1) - 0] - D_c [1^2 (1+1)^2 - 0]$$

$$\Delta E = 2649.67 \text{ cm}^{-1} - 2 \times 45.21 \text{ cm}^{-1} + \left(8.473 \text{ cm}^{-1} - 0.226 \text{ cm}^{-1} \times \frac{3}{2}\right) \times 2 - 3.46568 \times 10^{-4} \text{ cm}^{-1} \times 4 = 2567.38 \text{ cm}^{-1}$$

Problem 2 (1 point). In a vibrational-rotational spectroscopic measurement of a diatomic molecule, two branches are observed in the spectrum: P-branch and R-branch. If two transitions (P and R) are initiated from the same energy level (for example ($n=0, J=2$)) the transition corresponding to which branch requires more energy?

The R-branch: $J = J' \rightarrow J = J'+1$

The P-branch: $J = J' \rightarrow J = J'-1$

The energy required for the R-branch transition to occur is larger.

Quiz #10

Problem 1 (6 points). Write down the ground state configurations, the lowest energy terms, and the bond order for the following molecules (disregard the “+” or “-” symmetry except for the $^1\Sigma_g^+$ terms):

Molecule	Configuration	Term	Bond Order
Li_2	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$	$^1\Sigma_g^+$	1
F_2^-	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4(\sigma_u^* 2p)^1$	$^2\Sigma_u$	1/2
B_2^+	$(\sigma_g 1s^2)(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^1$	$^2\Pi_u$	1/2

Problem 2 (2 points). The $(\pi_u 2p)^3, (\pi_g^* 2p)^3$ configuration of O_2 has the following terms:

$$^1\Sigma_u^-, ^3\Delta_u, ^3\Sigma_u^+, ^3\Sigma_u^-$$

Assuming that the last two terms ($^3\Sigma_u^+$ and $^3\Sigma_u^-$) correspond to the same energy, arrange all these terms in order of increasing energy: from lowest to highest.

$$^3\Delta_u < ^3\Sigma_u^+ = ^3\Sigma_u^- < ^1\Sigma_u^-$$

Problem 3 (2 points). Give the degeneracies of the following molecular states: $^1\Sigma^-$ and $^3\Delta$

$$^1\Sigma^- \quad g = (2S+1)*1 = 1*1 = 1$$

$$^3\Delta \quad g = (2S+1)*2 = 3*2 = 6$$