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.

\[
r_{\text{rms}} = \sqrt{4Dt}
\]

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

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.

<table>
<thead>
<tr>
<th>Column A</th>
<th>Column B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. By definition, \textit{intrinsic viscosity} is ___ D ___</td>
<td>A) pressure.</td>
</tr>
<tr>
<td>2. From the \textit{Kinetic Theory of Gases}, it follows that the viscosity of a gas increases as a square root of ___ J ___</td>
<td>B) ( \eta_{sp} = \eta - \eta_0 / \eta_0 )</td>
</tr>
<tr>
<td>3. G. G. Stokes showed that the friction constant ( f = 6\pi\eta r ) for particles of ___ K ___ shape.</td>
<td>C) solutions of ethylene in bromoethylene</td>
</tr>
<tr>
<td>4. \textit{Fick’s first law of diffusion} ___ H ___</td>
<td>D) ( [\eta] = \lim_{c_n \to 0} \left( \frac{\eta_{sp}}{c_n} \right) ).</td>
</tr>
<tr>
<td>5. Mark-Houwink equation is applicable to ___ N ___</td>
<td>E) is given by equation 9.29 in you Handbook.</td>
</tr>
<tr>
<td></td>
<td>F) elliptical</td>
</tr>
<tr>
<td></td>
<td>G) ( [\eta] = K \frac{R_G^3}{M} )</td>
</tr>
<tr>
<td></td>
<td>H) is given by equation 9.27 in you Handbook.</td>
</tr>
<tr>
<td></td>
<td>I) gives the shape of van der Waals potential.</td>
</tr>
<tr>
<td></td>
<td>J) temperature</td>
</tr>
<tr>
<td></td>
<td>K) spherical</td>
</tr>
<tr>
<td></td>
<td>L) mixtures of solid grains</td>
</tr>
<tr>
<td></td>
<td>M) any</td>
</tr>
<tr>
<td></td>
<td>N) solutions of random-coil polymers</td>
</tr>
</tbody>
</table>
Problem 1 (8 points). Hydrogen iodide can be synthesized from the elements in a gas-phase reaction. One proposed mechanism for the process is

\[ I_2 \rightarrow 2I, v_1 = k_1[I_2] \]
\[ 2I \rightarrow I_2, v_2 = k_2[I]^2 \]
\[ H_2 + 2I \rightarrow 2HI, v_3 = k_3[H_2][I]^2 \]

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 ____________________________
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 $\alpha$. 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

$$\int_{-\infty}^{\infty} \Psi_0^2 dx = 1$$

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.

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.

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

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.

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

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

$$Z = 4; \text{E}_h = 27.212 \text{ eV}$$

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

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

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

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”.

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

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

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

$$\Psi_3 = \frac{1}{\sqrt{2}} \Psi_{1s}(1)\Psi_{1s}(2)\{\alpha(1)\alpha(2) - \alpha(1)\alpha(2)\}$$
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 $^1\text{H}^7\text{Br}$, in cm$^{-1}$, as accurately as possible (Do not 
disregard the centrifugal distortion!)

Table 13.1 gives for $^1\text{H}^7\text{Br}$: $\sigma_e = 2649.67$ cm$^{-1}$; $x_0 \sigma_e = 45.21$ cm$^{-1}$; $B_e = 8.473$ cm$^{-1}$; $\alpha_e = 0.226$ cm$^{-1}$

From these data: $D_e = 4 \frac{B_e^3}{\sigma_e^2} = 3.46568 \times 10^{-4}$ cm$^{-1}$ (using formula 13.23)

$$E(n,J) = \left( n + \frac{1}{2} \right) \sigma_e - \left( n + \frac{1}{2} \right)^2 \sigma_e x_0 + \left( B_e - \alpha_e \left( n + \frac{1}{2} \right) \right) J(J+1) - D_e J^2 \{J+1\}^2$$

$$\Delta E = E(1,1) - E(0,0) = \left( 1 + \frac{1}{2} - \frac{1}{2} \right) \sigma_e - \left( \left( 1 + \frac{1}{2} \right)^2 - \left( \frac{1}{2} \right)^2 \right) \sigma_e x_0 + \left( B_e - \alpha_e \left( 1 + \frac{1}{2} \right) \right) (1+1) - 0 - D_e \{1+1\}^2 + 0$$

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

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.
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):

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Configuration</th>
<th>Term</th>
<th>Bond Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$</td>
<td>$(\sigma^g_1s)^2(\sigma^u_1s)^2(\sigma^g_2s)^2$</td>
<td>$^1\Sigma^+_g$</td>
<td>1</td>
</tr>
<tr>
<td>F$_2^-$</td>
<td>$(\sigma^g_1s)^2(\sigma^u_1s)^2(\sigma^g_2s)^2(\sigma^u_2s)^2(\sigma^g_2p)^2(\pi^u_2p)^4(\pi^g_2p)^4(\sigma^u_2p)^1$</td>
<td>$^2\Sigma_u$</td>
<td>1/2</td>
</tr>
<tr>
<td>B$_2^+$</td>
<td>$(\sigma^g_1s)^2(\sigma^u_1s)^2(\sigma^g_2s)^2(\sigma^u_2s)^2(\pi^u_2p)^1$</td>
<td>$^2\Pi_u$</td>
<td>1/2</td>
</tr>
</tbody>
</table>

Problem 2 (2 points). The $(\pi^u_2p)^3(\pi^g_2p)^3$ configuration of O$_2$ has the following terms:

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

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.

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

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

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

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