22th National and the 10th International Chemistry Olympiad
Summer 2017
Iran

Physical Chemistry I · II
and Introduction to Quantum Chemistry

Time: 90 minutes

<table>
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<tr>
<th>Question No.</th>
<th>Points for each question</th>
<th>Signature</th>
<th>total score (out of 100)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>20</td>
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<td>10</td>
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Important Note:
Please write your personal information only in the appropriate boxes provided on this page. Do not write on any other pages.
1- Consider two equal masses of a perfect gas, one maintained at $T_{1i}$ and the other at $T_{2i}$. Suppose that the containers have rigid walls. When the two containers are brought into thermal contact, they achieve the equilibrium temperature $T_e$.

(a) what is the equilibrium temperature ($T_e$)?  
(b) Find the total entropy change.  
(c) Prove that $T_e^2 \geq T_{1i} \cdot T_{2i}$.  

2- The molar Gibbs free energy of some gas is

\[ G_m(T, P) = a + bT + cT \ln T + RT \ln P - \left( \frac{d}{T^3} \right) P \]

Where \(a, b, c\) and \(d\) are constants. Find the equation of state of this gas.
3- With a brief explanation, indicate which of the following sets of diagrams belong to "Meta stable equilibrium", "Stable equilibrium" and "Unstable equilibrium".

a) 
\begin{align*}
\text{variation of parameter of added constraint} \\
\end{align*}

b) 
\begin{align*}
\text{variation of parameter of added constraint} \\
\end{align*}

c) 
\begin{align*}
\text{variation of parameter of added constraint} \\
\end{align*}
4- What is the rate law for the following mechanism?

\[
[\text{Cr(H}_2\text{O)}_6]^{3+} \xrightleftharpoons[k_{-1}]{k_1} [\text{Cr(H}_2\text{O)}_3]^{3+} + \text{H}_2\text{O}
\]

\[
[\text{Cr(H}_2\text{O)}_3]^{3+} + \text{NCS}^- \xrightarrow{k_1} [\text{Cr(H}_2\text{O)}_3\text{NCS}]^{2+}
\]

What are the apparent orders of reaction for [NCS\textsuperscript{-}] very small and for [NCS\textsuperscript{-}] very large?
5- Bromotrifluoride acts as a catalyst for the equilibrium between acetaldehyde (CH$_3$CHO) and paraldehyde (a trimer of acetaldehyde). The partial pressures of the components on the trimerization reaction are too low to accurately determine the equilibrium constant by direct measurement, but this problem can be overcome by ensuring that the liquid forms of the two substances are always present. Assuming that the gases are perfect, derive an expression for the equilibrium constant of the trimerization reaction in terms of $P_A^*$ (the vapor pressure of pure acetaldehyde), $P_P^*$ (that of pure paraldehyde) and $P$ (total pressure).
6- Calculate $\Delta \hat{L}_2$ for the $2p_z$ stationary state of hydrogen atom.