**Instructions:**

*Do not open the main portion of the test until you are told to do so.* The first three pages consist of equations and tables for your use. You may carefully remove them now. Finally, write your name on what is now the front cover of this test and wait until you are told to open the exam.

When you are told to proceed, first scan over *all* the questions and make sure that you have 16 questions written on the 7 pages following the page you wrote your name on.

Please make sure there are no books, notes or bags around you. Place all items, except for your calculator and writing implements, off to the side of the room. If you have a programmable calculator, please delete all programs in memory now.

*Hint:* Do the problems you feel most comfortable with first. Show all calculations clearly, and write down units everywhere to receive full credit. Partial credit will be given if you set the problems up correctly.

**Equations and Constants:**

STP is defined as 298.15K and 1.00 atm

\[ 1 \text{ J} = 1 \text{ kg m}^2/\text{sec}^2 \quad N_A = 6.022 \times 10^{23} \text{ 1/mol} \quad 1 \text{ atm} = 760 \text{ torr} = 101325 \text{ Pa} \]

\[ 1 \text{ Pa} = 1 \text{ N/m}^2 = 1\text{kg/sec}^2 \quad 1 \text{ L-atm} = 101.3 \text{ J} \]

\[ R = 8.314 \text{ J/ mol K} = 0.08206 \text{ L} \cdot \text{ atm/mol K} \quad 4.184 \text{ J} = 1 \text{ calorie} \]

\[ p_A = \chi_A P_{TOT} \quad H = E + PV \quad \ln(vp) = -\frac{\Delta H_{exp}}{RT} + \frac{\Delta S_{exp}}{R} \]

\[ \Delta E = q + w \quad q = nC_p \Delta T \quad w_{exp} = -P \Delta V \]

\[ \Delta G_{rxn} = \Delta H_{rxn} - T \Delta S_{rxn} \quad \Delta G = \Delta G^\circ + RT \ln Q \]

\[ S = S^\circ - R \ln c \quad S = S^\circ - R \ln Q \quad S = k \ln W \quad \Delta S = \frac{q}{T} \]

\[
\text{Rate} = \left( -\frac{1}{a} \right) \left( \frac{\Delta[A]}{\Delta t} \right) = \left( \frac{1}{a} \right) \left( \frac{\Delta[D]}{\Delta t} \right)
\]

\[
\ln \left( \frac{[A]_0}{[A]} \right) = kt \quad \text{or} \quad \ln [A] = \ln [A]_0 - kt
\]

\[
\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad \text{or} \quad \frac{1}{[A]} = \frac{1}{[A]_0} + kt
\]

\[
[A] = [A]_0 - kt
\]

\[
k = A e^{-\frac{E_a}{RT}} \quad \ln \left( \frac{[A]}{[A]_0} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

Periodic table and molecular structures are provided on the next two pages.

Thermodynamic values are provided throughout the exam.
Purines

- Guanine, G (found in RNA and DNA)
- Adenine, A (found in RNA and DNA)
- Uracil, U (found in RNA)
- Thymine, T (found in DNA)
- Cytosine, C (found in RNA and DNA)

Pyrimidines

- Phosphoric acid (phosphate group)
- Adenosine
- Adenosine monophosphate (nucleotide)

Polar side chains:

- Serine Ser
- Threonine Thr
- Aspartic acid Asp
- Glutamic acid Glu
- Asparagine Asn
- Glutamine Gln
- Cysteine Cys
- Lysine Lys
- Arginine Arg
- Histidine His
- Tyrosine Tyr

Nonpolar side chains:

- Glycine Gly
- Alanine Ala
- Valine Val
- Isoleucine Ile
- Leucine Leu
- Methionine Met
- Phenylalanine Phe
- Tryptophan Trp
- Proline Pro
Remember:

This is only a test.

Check your units.

Show your work.
For questions 1-4 use the following expression: \( \text{Rate} = k[A]^m[B]^n \)

1. (2 pts) \( k \) is called the
   a) rate factor
   b) reaction quotient
   c) rate constant
   d) reaction constant

2. (2 pts) \( m \) is called the
   a) power
   b) order
   c) overall order
   d) constant

Still using the expression from above, now further use the following information, \( k = 2.2 \times 10^6 \text{ M}^{-2} \text{ s}^{-1} \), \( [A] = 0.31 \text{ M} \), \( [B] = 0.068 \text{ M} \), \( m = 1 \), and \( n = 2 \).

3. (2 pts) The overall order of this reaction is
   a) zero
   b) first
   c) second
   d) third

4. (3 pts) Solve for the rate at the above conditions:

5. (8 pts) Name the monomers that make up this small polymer.

\[ \text{NH}_2 \quad \text{SH} \quad \text{NH} \quad \text{O} \quad \text{O} \quad \text{N} \quad \text{N} \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{SH} \]
6. (10 pts, 2 pts for each pair) For each pair of materials, circle the item with the higher entropy

a) 1 mole H\textsubscript{2} at STP
    1 mole Ne at STP

b) 1 mole H\textsubscript{2}O\textsubscript{(s)} at 273K
    1 mole H\textsubscript{2}O\textsubscript{(l)} at 273K

c) 1 mole C\textsubscript{6}H\textsubscript{6}\textsubscript{(l)}
    1 mole C\textsubscript{6}H\textsubscript{14}\textsubscript{(l)}

d) 1 mole H\textsubscript{2}O\textsubscript{(s)} at 180 K
    1 mole H\textsubscript{2}O\textsubscript{(s)} at 150 K

e) 

7. (4 pts) When substance A and substance B are combined in a beaker, they are completely miscible and the beaker becomes cold to the touch. What can you say about the value of $\Delta S$ for the mixing process?

a) $\Delta S < 0$

b) $\Delta S > 0$

c) $\Delta S = 0$

d) nothing

For questions 8-10 use the condensation reaction of ethanol with acetic acid carried out at the given concentrations

$$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$$

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\Delta G^\circ_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>$-174.8$ kJ/mol</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>$-389.9$ kJ/mol</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>$-332.7$ kJ/mol</td>
</tr>
<tr>
<td>Water</td>
<td>$-237.1$ kJ/mol</td>
</tr>
</tbody>
</table>
8. (10 pts) At 375 K and the given concentrations, does this reaction spontaneously make more ethanol or more ethyl acetate? **Be sure to show your work for full credit!**

9. (4 pts) Given the above thermodynamic information, what can you say about the rate of this reaction at 375K?

10. (5 pts) At what temperature do the above concentrations represent an equilibrium between products and reactants?
11. (10 pts) The concentrations of ozone as a function of time are plotted below for the reaction

$$2 \text{O}_3(\text{g}) + \text{CS}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{SO}_2(\text{g})$$

Each graph contains a line fit through the ozone data. The equation for the line is given on the graph.

For the initial partial pressures $P_{\text{CS}_2} = 15 \text{ atm}$ $P_{\text{O}_3} = 1.76 \text{ atm}$

![Graph 1](image1)

![Graph 2](image2)

For the initial partial pressures $P_{\text{CS}_2} = 20 \text{ atm}$ $P_{\text{O}_3} = 1.76 \text{ atm}$

![Graph 3](image3)

![Graph 4](image4)

Give the rate law for the overall reaction.
13. Consider the overall reaction  \( \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \) as well as the following 2-step mechanism

1. \( \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \) rate \( k_1 \)
2. \( \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \) rate \( k_2 \)

a) (6 pts) Identify the role played by each compound in the overall mechanism: reactant, product, catalyst, or intermediate.

- \( \text{CO}_2 \) ______________________________
- \( \text{CO} \) ______________________________
- \( \text{NO} \) ______________________________
- \( \text{NO}_2 \) ______________________________
- \( \text{NO}_3 \) ______________________________

b) (5 pts) Predict the observed overall rate law if \( k_1 \) is much slower than \( k_2 \).
c) (8 pts) Predict the observed overall rate law if \( k_2 \) is much slower than \( k_1 \). (Also assume that the first step is reversible with a backward rate of \( k_{-1} \).)

d) (4 pts) Briefly describe what experiment(s) you could perform to identify which rate law is incorrect.
14. (6 pts) The rate of the reaction $\text{HO}_2 (g) + \text{OH} (g) \rightarrow \text{H}_2\text{O} (g) + \text{O}_2 (g)$ is measured at two temperatures to give the following data:

\[
\begin{align*}
    k_1 &= 5.94 \times 10^{11} \text{ (atm·s)$^{-1}$} & T_1 &= 300 \text{ K} \\
    k_2 &= 9.73 \times 10^{11} \text{ (atm·s)$^{-1}$} & T_2 &= 400 \text{ K}
\end{align*}
\]

Determine the Arrenhius prefactor and the activation energy for this reaction.

15. (8 pts) Sketch the energy profile for the situation in #14. Label the profile as completely as possible. (Please make it large and easy to read.)

16. (3 pts) If a catalyst is added to the reaction, the profile you sketched in #15 would change. Add to your profile in #15 to indicate the change induced by a catalyst.