Directions: (1) Put your name on PART 1 and your name and signature on PART 2 of the exam where indicated.
   (2) Sign the Aggie Code on PART 2 of this exam.
   (3) Each multiple choice question is actually 2 questions on your scanning sheet. If you are sure of an answer, put the same answer down for both questions for 5 pts. If you cannot decide between two answers, put your best answer down for the first (odd) question and the other answer down for the second (even) question. If you get the first one correct you'll get 3 pts; if you get the second one correct you'll get 2 pts. If there is an ambiguous multiple choice question, use the last page to explain your answer.
   (4) Do NOT write on the envelope.
   (5) When finished, put everything in the envelope and wait to be excused. At the table, take everything out of the envelope. You can pick up the multiple choice part with the answers outside my office after 3pm.
   (6) There are a total of 35 questions (19 actual questions).

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**PART 1**

1&2. Which is the correct $K_c$ expression for the equilibrium: $\text{Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)}$?

- (a) $K_c = \frac{[\text{Ni(CO)}_4]}{[\text{Ni}][\text{CO}]}$
- (b) $K_c = \frac{[\text{Ni}][\text{CO}]}{[\text{Ni(CO)}_4]}$
- (c) $K_c = \frac{[\text{Ni(CO)}_4]}{[\text{CO}]}$
- (d) $K_c = \frac{[\text{Ni(CO)}_4]}{4[\text{CO}]}$
- (e) $K_c = \frac{[\text{Ni}][\text{CO}]}{[\text{Ni(CO)}_4]}$

3&4. The units of the specific rate constant for a reaction that is third order overall is __________.

- (a) $\text{s}^{-1}$
- (b) $\text{M}^{-2}\text{s}^{-1}$
- (c) $\text{M}^{-1}\text{s}^{-1}$
- (d) $\text{M}^{-3}\text{s}^{-1}$
- (e) $\text{M}\text{s}^{-1}$

5&6. The **principal** reason for the increase in reaction rate with increasing temperature is:

- (a) molecules increase in size at high temperatures.
- (b) the pressure exerted by reactant molecules increases with increasing temperature.
- (c) the activation energy increases with increasing temperature.
- (d) the fraction of high energy molecules increases with increasing temperature.
- (e) the activation energy decreases with increasing temperature.

7&8. Which statement or statements is/are TRUE about the purpose of a catalyst?

1. Catalysts increase the number of collisions between the reactants in the overall reaction.
2. A catalyst cannot appear as a reactant in a rate law expression.
3. A catalyst lowers the activation energy of both the forward and reverse reaction.

- (a) 1 & 2
- (b) 2 & 3
- (c) 1 & 3
- (d) only 1
- (e) only 3
9&10. Determine the activation energy for the reverse reaction if the $\Delta H = \Delta E$ for the reaction is $-30 \text{ kJ}$ and the activation energy for the forward reaction is $70 \text{ kJ}$. (It may be useful to draw the potential energy diagram.)

(a) $+100 \text{ kJ}$  (b) $-100 \text{ kJ}$  (c) $+40 \text{ kJ}$  (d) $-40 \text{ kJ}$  (e) $+30 \text{ kJ}$

11&12. The rate law for the chemical reaction, $2\text{ClO}_2(\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{ClO}_3^- (\text{aq}) + \text{ClO}_2 (\text{aq}) + \text{H}_2\text{O}(\ell)$ has been determined experimentally to be:

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

The reaction order with respect to the hydroxide ions is:

(a) 3  (b) 2  (c) 1  (d) $k[\text{OH}^-]^2$  (e) $k[\text{ClO}_2]^2[\text{OH}^-]$  

13&14. The dilution of concentrated sulfuric acid can be dangerous because the temperature of the solution can increase so rapidly that the solution can boil. What are the signs of $\Delta H$, $\Delta S$ and $\Delta G$ for this process?

(a) $\Delta H<0$, $\Delta S<0$ and $\Delta G<0$
(b) $\Delta H<0$, $\Delta S>0$ and $\Delta G<0$
(c) $\Delta H<0$, $\Delta S>0$ and $\Delta G>0$
(d) $\Delta H>0$, $\Delta S>0$ and $\Delta G<0$
(e) $\Delta H>0$, $\Delta S<0$ and $\Delta G>0$

15&16. Consider the equilibrium, $\text{B}_2 \rightleftharpoons 2\text{B}$ with $K_c >> 1$. Which picture represents this system?

(a)  (b)  (c)  (d)  (e)
17&18. Consider the reaction: \( X + Y \rightarrow Z \). When the concentration of \( X \) is halved and the concentration of \( Y \) is tripled, the rate increases by a factor of \( 9/4 \). The appropriate rate law expression is:

(a) \( \text{Rate} = k[X]^2 \)  
(b) \( \text{Rate} = k[X]^2[Y]^2 \)  
(c) \( \text{Rate} = k[X]^2[Y]^3 \)  
(d) \( \text{Rate} = k[X]^2[Y] \)  
(e) \( \text{Rate} = k[X][Y] \)

19&20. At what temperatures will a reaction be spontaneous if \( \Delta H^\circ = -12.7 \text{ kJ/mol rxn} \) and \( \Delta S^\circ = -135 \text{ J/mol rxn K} \).

(a) The reaction will be spontaneous at any temperature.
(b) The reaction will never be spontaneous.
(c) All temperatures below 94.1 K
(d) All temperatures above 94.1 K
(e) Temperatures between 12.7 K and 135 K
21&22. Rate data were collected for the following reaction at a particular temperature. What is the correct rate
law expression?

\[ 2A + B + 3C \rightarrow \text{products} \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A]_{initial}</th>
<th>[B]_{initial}</th>
<th>[C]_{initial}</th>
<th>Initial Rate of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 M</td>
<td>0.30 M</td>
<td>0.20 M</td>
<td>6.4 x 10^{-3} M/s</td>
</tr>
<tr>
<td>2</td>
<td>0.30 M</td>
<td>0.30 M</td>
<td>0.20 M</td>
<td>5.76 x 10^{-2} M/s</td>
</tr>
<tr>
<td>3</td>
<td>0.10 M</td>
<td>0.60 M</td>
<td>0.40 M</td>
<td>1.28 x 10^{-2} M/s</td>
</tr>
<tr>
<td>4</td>
<td>0.60 M</td>
<td>0.90 M</td>
<td>0.20 M</td>
<td>2.3 x 10^{-1} M/s</td>
</tr>
<tr>
<td>5</td>
<td>0.10 M</td>
<td>0.80 M</td>
<td>0.40 M</td>
<td>1.28 x 10^{-2} M/s</td>
</tr>
</tbody>
</table>

(a) Rate = k[A][B][C]  
(b) Rate = k[B]^2[C]  
(c) Rate = k[A][C]^2  
(d) Rate = k[A]^2[C]  
(e) Rate = k[A]^2

23&24. Consider the gas-phase equilibrium at a certain temperature:  

\[ 2X \rightleftharpoons Y \]

A reaction begins with 2.0 moles of Y in a 1.0 L container. When the system reaches equilibrium, there is
1.0 mole of Y present. What is the value of the equilibrium constant, K_c?

(a) 1  
(b) 2  
(c) 4  
(d) 1/2  
(e) 1/4
**25&26.** Consider the following equilibrium in which the $K_c = 36$: $2 \text{HBr}(g) \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g)$

Initially in the container there is 0.30 M of HBr. At equilibrium, what is the concentration of HBr?

(a) 0.15 M  (b) 0.089 M  (c) 0.018 M  (d) 0.023 M  (e) 0.14 M

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**27&28.** Calculate the $\Delta G$ for the reaction at 25°C: $\text{N}_2\text{O}_4(g) \rightarrow \text{N}_2(g) + 2 \text{O}_2(g)$

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^\circ_{298}$ (kJ/mol)</th>
<th>$S^\circ$ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2\text{O}_4(g)$</td>
<td>9.16</td>
<td>304.2</td>
</tr>
<tr>
<td>$\text{N}_2(g)$</td>
<td>0</td>
<td>191.5</td>
</tr>
<tr>
<td>$\text{O}_2(g)$</td>
<td>0</td>
<td>205.1</td>
</tr>
</tbody>
</table>

(a) +827 kJ  (b) −77.5 kJ  (c) +691 kJ  (d) −114 kJ  (e) −97.8 kJ
29&30. The activation energy for a reaction was determined to be 215 kJ/mol rxn. If the rate constant is 1.0 x 10^{-2} \text{ min}^{-1} at 0^\circ\text{C}, what would the rate constant be at when the temperature was raised to 25^\circ\text{C}?

\[
\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{T_2}{T_1} - 1\right) \quad \text{or} \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]

\[R = 8.314 \text{ J/mol} \cdot \text{K}\]

(a) 28 min^{-1} \quad (b) 0.032 min^{-1} \quad (c) 71 min^{-1} \quad (d) 0.25 min^{-1} \quad (e) 1.01 min^{-1}

31&32. The decomposition of formic acid follows first-order kinetics:

\[
\text{HCOOH}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g)
\]

At 550^\circ\text{C}, the half-life for the reaction is 24.0 s. How much time (in minutes) must pass for 8.0% of a formic acid sample to remain unreacted?

(a) 2.9 min \quad (b) 4.6 min \quad (c) 3.0 min \quad (d) 1.5 min \quad (e) 0.10 min
(4 pts) **33.** Consider the equilibrium:  \( X(g) + 2Y(g) \rightleftharpoons Z(g) \)

The reaction as written is strongly endothermic. Predict how the following changes will affect the moles of \( Y \) at equilibrium,

The possible answers are: increase (I), decrease (D), or remain unchanged (U)

<table>
<thead>
<tr>
<th>Moles of ( Y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) The concentration of ( X ) is decreased.</td>
</tr>
<tr>
<td>(b) The temperature is increased.</td>
</tr>
<tr>
<td>(c) A catalyst is introduced.</td>
</tr>
<tr>
<td>(d) The volume of the container is halved.</td>
</tr>
</tbody>
</table>

(3 pt) How does temperature affect the value of \( K_c \) for this reaction? Explain briefly.

(3 pts) **34.** Consider the equilibrium:  \( 4A(g) \rightleftharpoons 2B(g) \) with \( K_c = 64 \).

Calculate the equilibrium constant for  \( B(g) \rightleftharpoons 2A(g) \)

(3 pts) **35.** Consider the following gas phase reaction:  \( 2A + B \rightarrow C \).
The experimentally-derived rate-law expression is: $\text{Rate} = k[A][B]$. For each mechanism below, write the rate-law expression that fits it AND state whether or not that mechanism could be the correct one. **Show your work for Part (c)** - I want to know that you understand how the equilibrium constant works into the problem.

(2 pts) (a) Step 1 $B + B \rightarrow B_2$ slow  
Step 2 $B_2 + A \rightarrow X + B$ fast  
Step 2 $X + A \rightarrow C$ fast  
Overall $2A + B \rightarrow C$

(2 pts) (b) Step 1 $A + B \rightarrow X$ slow  
Step 2 $X + A \rightarrow D$ fast  
Step 3 $D \rightarrow C$ fast  
Overall $2A + B \rightarrow C$

(4 pts) (c) Step 1 $A + X \Leftrightarrow E$ fast equilibrium  
Step 2 $E + A \rightarrow F$ slow  
Step 3 $F + B \rightarrow C + X$ fast  
Overall $2A + B \rightarrow C$

(1 pt) (d) In mechanism (c), what is/are the intermediate(s) (if any): _____________________

(1 pt) In mechanism (c), what is the catalyst (if any): _____________________