PART I:  True-false statements  (3 points each)

1. A positive sign for $\Delta S_{\text{rxn}}$ indicates that the reaction is spontaneous.  F

2. A negative sign for $\Delta G$ indicates that the reaction is exothermic.  F

3. $\Delta G^\circ_f$ of an element in its standard state is zero.  T

4. For a second-order reaction, the rate of reaction decreases as reactant is consumed.  T

PART II:  Multiple Choice  (3 points each)

5. Which one of the sets below has the species listed in order of increasing standard entropy, $S^\circ$?

   [a] NaHCO$_3$(s) < C$_2$H$_5$OH(l) < Cr(s) < N$_2$(g)
   [b] N$_2$(g) < C$_2$H$_5$OH(l) < NaHCO$_3$(s) < Cr(s)
   [c] Cr(s) < C$_2$H$_5$OH(l) < NaHCO$_3$(s) < N$_2$(g)
   [d] Cr(s) < NaHCO$_3$(s) < C$_2$H$_5$OH(l) < N$_2$(g)
   [e] N$_2$(g) < NaHCO$_3$(s) < Cr(s) < C$_2$H$_5$OH(l)

6. Consider the following processes:
   I. a solid melts
   II. a vapor condenses to a liquid
   III. a solid sublimes
   IV. a liquid freezes

   Which processes are characterized by a negative change in entropy?

7. Use the following data to calculate $\Delta S^\circ$ for the reaction:

$$\text{N}_2 (g) + 3 \text{H}_2 (g) \rightarrow 2 \text{NH}_3 (g)$$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S^\circ$ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ (g)</td>
<td>130.6</td>
</tr>
<tr>
<td>N$_2$ (g)</td>
<td>191.5</td>
</tr>
<tr>
<td>NH$_3$ (g)</td>
<td>192.3</td>
</tr>
</tbody>
</table>

\[ [a] \ -198.7 \ J/K \quad [b] \ -129.8 \ J/K \quad [c] \ 62.5 \ J/K \quad [d] \ 129.8 \ J/K \quad [e] \ 198.7 \ J/K \]

8. For the following reaction, $\Delta H^\circ = -20.2 \text{ kJ}$ and $\Delta S^\circ = +43.1 \text{ J/K}$. Which of the following statements about this reaction is true?

$$\text{H}_2 (g) + \text{S} (s) \rightarrow \text{H}_2\text{S} (g)$$

[a] the reaction is not spontaneous.  
[b] the reaction is always spontaneous.  
[c] the reaction will become spontaneous at higher temperatures.  
[d] the reaction will become nonspontaneous at higher temperatures.  
[e] impossible to determine from the information given.

9. The following reaction is not spontaneous at 25°C.

$$\text{Fe}_2\text{O}_3 (s) + 3 \text{H}_2 (g) \rightarrow 2 \text{Fe} (s) + 3 \text{H}_2\text{O} (g)$$

If $\Delta H = 98.8 \text{ kJ}$ and $\Delta S$ is 141.5 J/K, calculate the temperature at which the reaction becomes spontaneous.

\[ [a] \ 698 \text{ K} \quad [b] \ 1.43 \text{ K} \quad [c] \ 1432 \text{ K} \quad [d] \ 425 \text{ K} \quad [e] \ 971 \text{ K} \]

10. Given that the normal freezing point of ammonia, NH$_3$, is −78°C, predict the signs of $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ for ammonia when it freezes at −100°C at 1 atm pressure.

$$\text{NH}_3 (l) \rightarrow \text{NH}_3 (s)$$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a]</td>
<td>−</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>[b]</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>[c]</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>[d]</td>
<td>+</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>[e]</td>
<td>−</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

11. Consider the reaction:

$$\text{C}_2\text{H}_2 (g) + 2 \text{H}_2 (g) \rightarrow \text{C}_2\text{H}_6 (g)$$

If C$_2$H$_6$ is appearing at a rate of 2.0 M/s, at what rate is H$_2$ disappearing.

\[ [a] \ 0.5 \text{ M/s} \quad [b] \ 1.0 \text{ M/s} \quad [c] \ 2.0 \text{ M/s} \quad [d] \ 4.0 \text{ M/s} \quad [e] \ 8.0 \text{ M/s} \]

12. A particular reaction has the following units for the rate constant, $k$: \( \frac{1}{M^3 \cdot \text{s}} \). What is the order of the reaction?

\[ [a] \ 4^{th} \quad [b] \ 1^{st} \quad [c] \ 2^{nd} \quad [d] \ 3^{rd} \quad [e] \ not \ enough \ information \ to \ determine \]
13. Which one of the following would alter the value of the rate constant \( k \) for the reaction:

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

[a] increasing the concentration of A.
[b] increasing the concentration of B.
[c] **increasing the temperature.**
[d] measuring \( k \) again after the reaction had run for a while.
[e] all of these would alter the rate constant.

14. The rate of a **zero-order** reaction:

[a] increases as reactant is consumed.
[b] depends on the concentration of products.
[c] decreases as reactant is consumed.
[d] is independent of temperature.
[e] **is independent of the concentrations of reactants and products.**

15. A reaction has the rate law, Rate = \( k[A][B]^2 \). Which one of the following changes will cause the greatest increase in the reaction rate?

[a] decreasing the temperature without changing the concentrations
[b] doubling the concentration of \([B]\)
[c] doubling the concentration of \([A]\)
[d] increasing the concentration of \([A]\) by a factor of 8
[e] ** tripling the concentration of \([B]\)**

16. Consider the reaction, \( \text{A} \rightarrow \text{products} \). A plot of \( \ln[A] \) versus time produces a straight line. Which of the following statements is **true**?

[a] the rate constant for the reaction can be obtained from the value of the intercept on the y-axis.
[b] **the rate constant is equal to the negative of the slope.**
[c] the rate of the reaction does **not** depend on the concentration of A.
[d] the reaction is second order.
[e] the initial concentration of A can be calculated from the intercept on the x-axis.

17. For the reaction, \( X + Y \rightarrow Z \), the reaction rate is found to depend only upon the concentration of X. A plot of \( 1/[X] \) versus time gives a straight line. What is the rate law for this reaction?

[a] rate = \( k[X] \)
[b] **rate = \( k[X]^2 \)**
[c] rate = \( k[X][Y] \)
[d] rate = \( k[X]^2[Y] \)
[e] rate = \( k[Y] \)

18. Consider the following **second-order** reaction at 35°C.

\[
\text{NOCl (g)} \rightarrow \text{NO (g)} + \frac{1}{2} \text{Cl}_2 (g)
\]

With an initial concentration of \([\text{NOCl}]_0 = 4.46 \, M\), the concentration of NOCl drops to 3.74 \( M \) after 60.0 minutes. Calculate the **half-life** for this reaction.

[a] 7.19 \( \times 10^4 \) min
[b] 312 min
[c] 0.0866 min
[d] 186 min
[e] 268 min
19. Below is a plot of $\ln k$ versus $1/T$ for the reaction

$2 \text{N}_2\text{O}_5 (g) \rightarrow 2 \text{N}_2\text{O}_4 (g) + \text{O}_2 (g)$

![Graph of ln k vs 1/T](image)

Based on this information, the activation energy, $E_a$, for this reaction is:

[a] $9.50 \times 10^3$ J/mol  
[b] $1143$ kJ/mol  
[c] $1143$ J/mol  
[d] $79.0$ kJ/mol  
[e] $79.0$ J/mol

20. Which of the following “setups” would allow the calculation of the activation energy, $E_a$, of a reaction which has $k = 4.0 \times 10^{-3} /s$ at $20^\circ C$ and $k = 7.5 \times 10^{-3} /s$ at $26^\circ C$?

[a] $\ln \left( \frac{4.0 \times 10^{-3}}{7.5 \times 10^{-3}} \right) = \frac{E_a}{8.314} \left( \frac{1}{26} - \frac{1}{20} \right)$  
[b] $\ln \left( \frac{4.0 \times 10^{-3}}{7.5 \times 10^{-3}} \right) = \frac{E_a}{8.314} \left( \frac{1}{20} - \frac{1}{26} \right)$  
[c] $\ln \left( \frac{4.0 \times 10^{-3}}{7.5 \times 10^{-3}} \right) = \frac{E_a}{8.314} \left( \frac{1}{293} - \frac{1}{299} \right)$  
[d] $\ln \left( \frac{7.5 \times 10^{-3}}{4.0 \times 10^{-3}} \right) = \frac{E_a}{8.314} \left( \frac{1}{293} - \frac{1}{299} \right)$  
[e] none of these

21. According to collision theory, all collisions do not lead to product formation. Which choice gives the reasons why all collisions between reactant molecules do not lead to product formation?

I. The total energy of the colliding molecules is less than some minimum amount of energy.
II. Molecules cannot react with each other unless a catalyst is present.
III. Molecules can only collide if they are in the same phase.
IV. Molecules that are improperly oriented during collision may not react.

[a] I and II  
[b] II and III  
[c] I and IV  
[d] I and III  
[e] III and IV

22. For the reaction, $A + B \rightarrow \text{products}$, the experimentally determined rate law is: Rate $= k[B]^2$.
If $I$ indicates an intermediate and $P$ indicates a product, which of the following is the most likely reaction mechanism?

[a] $B + B \rightarrow I$ (slow)  
$A + I \rightarrow P + B$ (fast)  
[b] $A + B \rightarrow I$ (fast)  
$I + B \rightarrow P$ (slow)  
[c] $A + B \rightarrow C$ (slow)  
$C \rightarrow P$ (fast)

[d] $B + B \rightarrow I$ (slow)  
$A + I \rightarrow P$ (fast)  
[e] $A + B \rightarrow P$ (one step)  
$A + I \rightarrow P$ (fast)
PART III: Problems

23. Consider a reaction at 25°C for which $\Delta H_{\text{sys}} = -32 \text{ kJ/mol}$ and $\Delta S_{\text{sys}} = -98 \text{ J/K/mol}$.

   [a] Calculate $\Delta S_{\text{univ}}$. [4 pts]

   
   \[
   \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}
   \]

   \[
   \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-(-32 \times 10^3 \text{ J/mol})}{298 \text{ K}} = 107.4 \text{ J/K mol}
   \]

   \[
   \Delta S_{\text{univ}} = -98 \text{ J/K mol} + 107.4 \text{ J/K mol} = 9.4 \text{ J/K mol}
   \]

   [b] Is the reaction spontaneous at 25°C? Your response must be based on your answer to part (a). [2 pts]

   Yes, spontaneous. The 2nd Law of Thermodynamics states that the entropy of the universe increases in a spontaneous process.

24. The rate constant, $k$, for the reaction, $A \rightarrow B$, is $2.6 \times 10^{-2} \text{ s}^{-1}$.

   [a] Calculate the half-life, $t_{1/2}$, for this reaction. [2 pts]

   
   \[
   t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.6 \times 10^{-2} \text{ s}^{-1}} = 26.7 \text{ s}
   \]

   [b] If the initial concentration of $A$ is 0.55 $M$, what is the concentration of $A$ after 3.0 minutes? [4 pts]

   \[
   \ln[A]_t = -kt + \ln[A]_0
   \]

   \[
   \ln[A]_t = -(2.6 \times 10^{-2} \text{ s})(180 \text{ s}) + \ln(0.55)
   \]

   \[
   \ln[A]_t = -5.278
   \]

   \[
   e^{\ln[A]_t} = e^{-5.278}
   \]

   \[
   [A]_t = 0.0051 \text{ M}
   \]
25. Consider the following reaction

\[ 3 \text{B} + \text{C} \rightarrow \text{E} + 2 \text{F} \]

for which the following rate data were obtained.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[B] (M)</th>
<th>[C] (M)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.250</td>
<td>0.000250</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>0.250</td>
<td>0.000500</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.750</td>
<td>0.00225</td>
</tr>
</tbody>
</table>

[a] Determine the rate law for this reaction. **SHOW WORK!** [3 pts]

Exp. 1 and 2:

\[
\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{B}]_2^x}{[\text{B}]_1^x} = \frac{0.200 \text{ M}^x}{0.100 \text{ M}^x}
\]

\[
\frac{0.000500 \text{ M/s}}{0.000250 \text{ M/s}} = 2^x
\]

\[
x = 1
\]

Exp. 1 and 3:

\[
\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{[\text{C}]_3^y}{[\text{C}]_1^y} = \frac{0.750 \text{ M}^y}{0.250 \text{ M}^y}
\]

\[
\frac{0.00225 \text{ M/s}}{0.000250 \text{ M/s}} = 3^y
\]

\[
y = 2
\]

\[\text{Rate} = k[\text{B}][\text{C}]^2\]

[b] Calculate the rate constant, \( k \), for this reaction. [2 pts]

\[\text{Rate} = k[\text{B}][\text{C}]^2\]

\[0.000250 \text{ M/s} = k(0.100 \text{ M})(0.250 \text{ M})^2\]

\[k = 0.0400 \text{ M}^{-2} \cdot \text{s}\]

[c] Calculate the rate of the reaction if \([\text{B}] = 0.0500 \text{ M}\) and \([\text{C}] = 0.100 \text{ M}\)? [2 pts]

\[\text{Rate} = k[\text{B}][\text{C}]^2\]

\[\text{Rate} = (0.0400 \text{ M}^{-2} \cdot \text{s})(0.0500 \text{ M})(0.100 \text{ M})^2\]

\[\text{Rate} = 2.00 \times 10^{-5} \text{ M/s}\]
**Potentially Useful Information**

\[ \Delta G_{\text{rxn}} = \Sigma n \Delta G_f^o (\text{products}) - \Sigma n \Delta G_f^o (\text{reactants}) \]

\[ \Delta H_{\text{rxn}} = \Sigma n \Delta H_f^o (\text{products}) - \Sigma n \Delta H_f^o (\text{reactants}) \]

\[ \Delta S_{\text{rxn}} = \Sigma n S^o (\text{products}) - \Sigma n S^o (\text{reactants}) \]

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]

\[ K = ^\circ C + 273 \]

\[ \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \]

\[ \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \]

\[ M = \frac{\text{mol solute}}{\text{L soln}} \]

\[ \ln k = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T} \right) + \ln A \]

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

\[ \text{Rate} = \frac{\Delta[\text{conc}]}{\Delta t} \]

\[ \text{Rate} = k[A]^x[B]^y \]

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

\[ \ln[A]_t = -kt + \ln[A]_0 \]

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

\[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]

\[ t_\frac{1}{2} = \frac{0.693}{k} \]

\[ t_\frac{1}{2} = \frac{1}{k[A]_0} \]

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