R = 0.08206 L atm/mol K = 8.314 J/mol K

\[ k = \Lambda e^{-E_a/R} \]

1. State the four factors that affect the rate of chemical reactivity. (8 pt)
   a. Temp.
   b. Conc.
   c. Catalyst
   d. State of Subdivision

2. Nitric oxide gas reacts with chlorine gas according to the equation

\[ 2 \text{H}_2(g) + 2 \text{NO}(g) \rightarrow 2 \text{H}_2\text{O}(g) + \text{N}_2(g) \]

The following initial rates of reaction have been observed for certain reactant concentrations:

<table>
<thead>
<tr>
<th>[H₂], mol L⁻¹</th>
<th>[NO], mol L⁻¹</th>
<th>Rate, mol L⁻¹ h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.025</td>
<td>2.4 x 10⁻⁶</td>
</tr>
<tr>
<td>0.0050</td>
<td>0.025</td>
<td>1.2 x 10⁻⁶</td>
</tr>
<tr>
<td>0.010</td>
<td>0.0125</td>
<td>6.0 x 10⁻⁶</td>
</tr>
</tbody>
</table>

What is the rate equation for the describing the rate dependence on the concentration of NO and H₂? (5 pt) \[ \text{rate} = k [\text{H}_2]^2 [\text{NO}]^2 \]

What is the value of the rate constant? (4 pt)

\[ k = \frac{\text{rate}}{[\text{H}_2][\text{NO}]^2} = \frac{2.4 \times 10^{-6} \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}}{[0.010][0.025]^2} = 3.84 \times 10^{-5} \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{h}^{-1} \]

What is the order of the reaction in each reactant and the overall order of the reaction? (5 pt)

[H₂] 1st order [NO] 2nd Order Overall - 3rd Order
3. The thermal decomposition of phosphine ($\text{PH}_3$) into phosphorus and molecular hydrogen is a first order reaction:

$$4 \text{ PH}_3 (g) \rightarrow \text{ P}_4(g) + 6 \text{ H}_2(g)$$

The half-life of the reaction is 35.0 s at 680°C.

a. Calculate the first-order rate constant for the reaction. (5 pt)

$$\ln \frac{[\text{PH}_3]}{[\text{PH}_3]_0} = -kt$$

$$\ln \frac{0.093}{0.693} = 1.98 \times 10^{-2} \text{ s}^{-1}$$

$$t = \frac{3.00}{1.98 \times 10^{-2} \text{ s}^{-1}} = 151 \text{ sec}$$

b. How long does it take for 95 percent of the phosphine to decompose? (5 pt)

$$\ln \frac{1.0}{0.05} = (1.98 \times 10^{-2} \text{ s}^{-1})t$$

$$t = \frac{3.00}{1.98 \times 10^{-2} \text{ s}^{-1}} = 151 \text{ sec}$$

4. Based on the proposed mechanism for the reaction of NO with $\text{Cl}_2$

Step1: $\text{NO} (g) + \text{Cl}_2(g) \rightarrow \text{NOCl}_2(g)$ (slow)

Step2: $\text{NOCl}_2(g) + \text{NO}(g) \rightarrow 2 \text{ NOCl}(g)$ (fast)

a. What is the overall reaction? (4 pt)

$$2 \text{ NO} + \text{Cl}_2 \rightarrow 2 \text{ NOCl}$$

b. What is the molecularity of each step? (4 pt)

Step 1 - Bimolecular  
Step 2 - Bimolecular

c. Which is the rate determining step? (2 pt)

Step 1

d. Write the rate equation for the overall reaction. (2 pt)

$$\text{rate} = -\frac{d[\text{NO}]}{dt} = k[\text{NO}][\text{Cl}_2]$$

e. List any intermediates in the reaction. (2 pt)

$\text{NOCl}_2$
5. The rate constant for a particular reaction is $1.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 150°C, and $1.1 \times 10^{-3}$ \text{ M}^{-1} \text{ s}^{-1}$ at 200°C. What is the energy of activation? (5 pt)

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

$$\ln \left( \frac{1.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}}{1.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}} \right) = -\frac{E_a}{8.314 \frac{\text{ J}}{\text{ mol} \cdot \text{ K}}} \left( \frac{1}{473} - \frac{1}{423} \right)$$

$$E_a = 71.0 \text{ kJ}$$

6. At equilibrium, the pressure of the reacting mixture.

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

is 0.105 atm at 350°C. Calculate $K_p$ and $K_c$ for this reaction. (4 pt)

$$K_p = P_{\text{CO}_2} = 0.105$$

$$K_p = K_c \left( RT \right)^{\alpha}$$

$$K_c = K_p \left( \frac{RT}{\alpha} \right)^{\alpha} = \frac{0.105}{\left( 0.08206 \frac{\text{ atm} \cdot \text{ L}}{\text{ mol} \cdot \text{ K}} \right) \left( 25 \text{ K} \right)} = 0.0020$$

7. The value of $K_c$ for the following reaction is $2.0 \times 10^{-10}$ at 100°C:

$$\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$$

What is the value of $K_c$ for the reaction below at 100°C? (4 pt):

$$\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$$

$$K_c = 5.0 \times 10^{10}$$
8. For the following reaction between gases at equilibrium, determine the effect on the equilibrium concentrations of the products (circle one of the following: shift left, no change, shift right when the following changes take place. (10 pt)

\[ \text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \quad \Delta H = +92.5 \text{ kJ} \]

a. Increase the temperature  
   shift left  
   no change  
   shift right

b. More chlorine gas is added to the reaction  
   shift left  
   no change  
   shift right

c. Some PCl₃ is removed from the reaction  
   shift left  
   no change  
   shift right

d. Pressure on the gases is increased  
   shift left  
   no change  
   shift right

e. Catalyst is added to the reaction mixture  
   shift left  
   no change  
   shift right

9. Predict which acid in each of the following pairs is stronger. (6 pt)

a. HNO₂ and \( \text{HNO}_3 \)

b. \( \text{NH}_3 \) and \( \text{H}_2\text{O} \)

d. \( \text{HOAc} \quad (K_a = 1.8 \times 10^{-5}) \) and \( \text{HCHO}_2 \quad (K_a = 1.8 \times 10^{-4}) \)

10. Rank the compounds in each of the following groups in order of increasing acidity. (6 pt)

a. HI, HCl, HF  
   \( \text{HF} < \text{HCl} < \text{HI} \)

b. HBrO₄, HBrO₂, HBrO, HBrO₃  
   \( \text{HBrO} < \text{HBrO}_2 < \text{HBrO}_3 < \text{HBrO}_4 \)

c. \( \text{H}_2\text{CO}_3 \), \( \text{HClO}_4 \), \( \text{NaOH} \)  
   \( \text{NaOH} < \text{H}_2\text{CO}_3 < \text{HClO}_4 \)

11. In the following reaction, identify the acid (A), conjugate acid (CA), base (B), and conjugate base (CB). (8 pt)

\[ \text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightarrow + \text{CH}_3\text{NH}_3^+ + \text{OH}^- \]
12. Identify the **Lewis acid** and **Lewis base** in the reactions below. (4 pt)

\[ \text{LA} \quad \text{LB} \]
\[ \text{SO}_3 + \text{CaO} \rightarrow \text{CaSO}_4 \]

\[ \text{LB} \quad \text{LA} \]
\[ \text{NH}_3 + \text{BF}_3 \rightarrow \text{NH}_3\text{BH}_3 \]

13. Hydrosulfuric acid, \( \text{H}_2\text{S} \), is a diprotic acid with \( K_{a1} = 9.5 \times 10^{-8} \) and \( K_{a2} = 1.0 \times 10^{-19} \). For a 0.10 M solution of \( \text{H}_2\text{S} \), what is

a. the pH? (4 pt)
b. the concentration of \( \text{S}^{2-} \)? (3 pt)

\[
\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^- \\
K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \\
[\text{H}^+] = \frac{K_{a1} [\text{H}_2\text{S}]}{[\text{HS}^-]} \\
[\text{H}^+] = \sqrt{K_{a1}[\text{H}_2\text{S}]} = \left[ (9.5 \times 10^{-8})(0.10) \right]^{1/2} = 9.75 \times 10^{-5} \\
\text{pH} = -\log([\text{H}^+]) = -\log(9.75 \times 10^{-5}) = 4.01
\]

\( b \) \[ [\text{S}^{2-}] \approx K_{a2} = 1.0 \times 10^{-19} \]