I. Introduction to Reactions

1. Explain why the following fits the definition of a chemical reaction.

\[ \text{CH}_3\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaBr} \]

2. Using the chemical reaction above, give all compounds which match the description.
   a) reactant(s):
   b) product(s):
   c) starting material(s):
   d) reagent(s):

3. Redraw the reaction above in the form more commonly used in organic chemistry.

4. On the axes below, draw an energy diagram for an exothermic reaction.
   a) Label what the x and y axis are.
   b) Label the energy of the reactants and products.
   c) Label the transition state.
   d) Label the activation energy.
   e) Label the enthalpy of the reaction.
   f) Will the enthalpy be positive or negative?
5. Give a brief definition of the following terms:

a) activation energy

b) endothermic reaction

c) $\Delta H$

d) exothermic reaction

e) transition state

6. Explain what causes a reaction to be endothermic or exothermic.

7. Why is the activation energy always positive? (yes, you have enough information to answer this; think about it for a minute)

II. Kinetics of Reactions

8. Explain why we need to know the kinetics of both desirable and undesirable reactions.

9. Why won't a reaction occur under the following conditions?

a) the molecules do not collide
b) molecules collide with the wrong orientation

c) their energy is lower than the activation energy

10. Explain why each of the following would slow down a reaction:

   a) cooling down the temperature (2 reasons)

   b) adding solvent to dilute the reactants

11. Explain why one reaction would be slower than the other in each of the following situations.

   a) one reaction has a higher activation energy than the other

   b) the probability factor for one reaction is smaller than the other

12. Write the general form for a rate law, including the rate constant, concentration of two reagents, and their exponents. Briefly explain what each of these are.

13. The reaction below is a one step reaction. Write its rate law, explain the exponents that you chose, and give the overall order of the reaction.

    \[ \text{CH}_3\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaBr} \]
14. The reaction below has three steps, but only the first reactant is involved in the rate limiting step. Write the rate law for this reaction, give the order of each reactant, and the overall order of the reaction.

\[
(CH_3)_3CBr + 2 H_2O \rightarrow (CH_3)_3COH + H_3O^+ Br^- 
\]

15. Why are \((CH_3)_3COH\) and \(H_3O^+ Br^-\) not found in the rate law for this reaction?

III. Thermodynamics of Reactions

16. Consider the following equation: \(CH_3Br + NaOH \rightarrow CH_3OH + NaBr\)

a) This reaction is reversible; how do we show this?

b) Write the equation for the equilibrium constant of the reaction.

c) Both the forward and backward reactions are one-step collisions. Write the rate law for both reactions.

d) When this reaction has reached equilibrium, what has happened to these two rates?

e) At equilibrium, the concentration of products is much greater than the concentration of reactants. What does this tell us about the equilibrium constant?

f) Which (collectively) have a higher free energy, the products or the reactants?

g) What is the sign of \(\Delta G\)?
17. What does thermodynamics tell us about a reaction, and how does it differ from what kinetics can tell us?

18. Explain why each of the following is true.

   a) If a reaction has a small $K_{eq}$ it will have more reactants than products at equilibrium.

   b) If a reaction has a large $K_{eq}$, then the free energy change will be negative.

   c) If the forward reaction has a higher activation energy than the backward reaction, then there will be more reactants than products at equilibrium.

19. Explain what would happen in each of the following situations if the reaction was at equilibrium, then each of the following occurred.

\[
\text{CH}_3\text{Br} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{OH} + \text{NaBr}
\]

   a) NaOH is added

   b) NaBr is removed

   c) CH$_3$OH is added

   d) a large amount of CH$_3$Br is added
20. Match the following definitions with the words they define.

   _____ acid                          A. electron pair acceptor (gets attacked)
   _____ base                          B. proton acceptor (takes a H)
   _____ electrophile                  C. electron pair donor (attacker)
   _____ nucleophile                   D. proton donor (gives up a H)

21. Draw arrows in each of the following reactions to indicate the flow of electrons. Then indicate whether the reaction is an association, dissociation, or displacement.

   a) \[
   \begin{array}{c}
   \text{+} \\
   \text{-O-} \\
   \text{H-O-H} \\
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{+} \\
   \text{O-} \\
   \text{H} \\
   \end{array}
   \]
   b) \[
   \begin{array}{c}
   \text{+} \\
   \text{CH}_3 \text{CH}_2 \text{Br} \\
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{+} \\
   \text{CH}_3 \text{CH}_2 \text{Br} \\
   \end{array}
   \]
   c) \[
   \begin{array}{c}
   \text{CH}_2 \text{C} \text{O} \text{H} \\
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{CH}_3 \text{CH}_2 \text{NH}_2 \\
   \end{array}
   \]
   d) \[
   \begin{array}{c}
   \text{CH}_3 \text{OH} \\
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{CH}_3 \text{OH} \\
   \end{array}
   \]
   e) \[
   \begin{array}{c}
   \text{CH}_2 \text{C} \text{Br} \text{H} \\
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{+} \\
   \text{CH}_3 \text{CO} \text{H} \\
   \text{Br} \\
   \text{+} \\
   \text{H}_3 \text{C} \text{O} \text{H} \\
   \end{array}
   \]
   f) \[
   \begin{array}{c}
   \text{O} \\
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{O} \\
   \end{array}
   \]
22. Give the products of the following reactions. Make sure to include any formal charges present in the products. Then write "Nu," "E," "acid," or "base" by each reagent to indicate whether it is acting as a nucleophile, electrophile, acid, or base, unless there is only one starting material in the reaction.

a) \( \text{+} + \text{H}^+ \text{O}^- \text{H} \rightarrow \)

b) \( \text{H}^+ \text{O}^- \text{H} + \text{H}^- \rightarrow \)

c) \( \text{Br}^- + \text{H}^+ \rightarrow \)

d) \( \text{H}^+ \text{O}^- \text{H} + \text{H}^+ \rightarrow \)

e) \( \text{H}^+ \text{O}^- \text{H} \rightarrow \)
23. Use curved arrow notation to indicate how the resonance structures in the following resonance structures can be interconverted.

a) 
\[
\begin{bmatrix}
\text{O}^+ & \text{O}^+ \\
\text{O}^- & \text{O}^-
\end{bmatrix}
\]

b) 
\[
\begin{bmatrix}
\text{O}^+ & \text{O}^+ \\
\text{O}^+ & \text{O}^+
\end{bmatrix}
\]

c) 
\[
\begin{bmatrix}
\text{O}^+ & \text{O}^- \\
\text{O}^- & \text{O}^+ \\
\text{O}^- & \text{O}^+
\end{bmatrix}
\]
24. Circle the compound in each pair which will be the stronger nucleophile, and briefly explain why.

a) \( \text{OH} \) \( \text{NH}_2 \)

b) \( \text{NH}_2^- \) \( \text{OH}^- \)

c) \( \text{Br}^- \) \( \text{Cl}^- \)

d) \( \text{O}^- \) \( \text{OH} \)

25. Circle the compound in each pair which will be the stronger electrophile, and briefly explain why.

a) \( \text{O}^- \) \( \text{O} \)

b) \( \text{Br}^- \) \( \text{Br} \)
26. What is the difference between

a) a nucleophile and a base?

b) an electrophile and an acid?

27. Draw the arrows to show how the electrons flow each of the following reactions. Then label the reactants as acids, bases, nucleophiles, or electrophiles.

a) \[
\begin{align*}
\text{Intermediate} + \text{Nu}^- & \rightarrow \text{Nu}^- + \text{Intermediate} \\
\end{align*}
\]

b) \[
\begin{align*}
\text{Intermediate} + \text{Nu}^- & \rightarrow \text{Nu}^- + \text{Intermediate} \\
\end{align*}
\]
28. Draw the arrows to show how the electrons flow each of the following reactions. Then label the acid, base, conjugate acid, and conjugate base.

\[
\text{H}^+ + \text{CH}_3\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3^+ \\
\]

29. Write a reaction in which:

a) an alcohol reacts as an acid with sodium hydride (NaH)

\[\text{CH}_3\text{OH} + \text{NaH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{Na} \]

b) an alcohol reacts as a base with nitric acid (HNO₃)

\[\text{CH}_3\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{ONNO}_3 \]

30. The pKa of sodium bicarbonate (NaHCO₃) is 10.25. Explain where this number comes from and what it means.

31. Using your pKₐ chart, give the pKₐ of each acid. Then circle the stronger acid.

a) HCl HBr

b) \[\text{-CH}_2\text{OH} \quad \text{-CH}_2\text{SH}\]

c) \[\text{H}_2\text{O}^+ \quad \text{H}_2\text{O}_2\]

d) HF HCN

e) NH₃ H₂O
32. Compare the strength of the following bases by drawing the structure (or giving the formula) of the conjugate acid and giving its pK_a. Then circle the stronger base.

a) Cl^-  Br^-  

b) bicarbonate (HCO_3^-)  hydroxide (OH^-) 

c) 

d) 

e) NaOH  NaHN_2 

33. Using your pK_a chart, put the following in order of most basic (1) to least basic (6).

III) Give the pK_a of the two acids, and indicate which side of the reaction will be favored.

34. I) Label the acid, base, conjugate acid, and conjugate base in each of the following reactions. 
II) Draw arrows to indicate the movement of electrons. 
III) Give the pK_a of the two acids, and indicate which side of the reaction will be favored.

a) 

b) 

c) 

H--C≡N:+  +  H_2S:  \rightarrow  \cdot C≡N:  +  H_2S:
35. Which of the following compounds can be deprotonated using NaOH? (Hint: we did this in page 21 of the LG)

a) \( \text{O}^{\cdot}\)  

b) \( \text{C}_3\text{H}_7^{\cdot}\)

c) \( \text{C}_6\text{H}_4\text{O}^{\cdot}\)

d) \( \text{C}_3\text{H}_7\text{S}^{\cdot}\)

e) \( \text{H}^-\text{C}≡\text{N}^{\cdot}\)

f) \( \text{H}≡\text{C}≡\text{H} \)

g) \( \text{C}_2\text{H}_5\text{O}^{\cdot}\)

h) \( \text{C}_2\text{H}_3\text{O}^{\cdot}\)
36. Circle the stronger acid of each pair, then explain your choice. Use the acid characteristics, not your pKa chart!

a) \( \text{NH}_4^+ \quad \text{H}_3\text{O}^+ \)

b) 
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

c) 
\[
\begin{align*}
\text{NH}_3^+ & \quad \text{NH}_2^+ \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

d) 
\[
\begin{align*}
\text{PhOH} & \quad \text{PhOH} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

e) 
\[
\begin{align*}
\text{C}_5\text{H}_{11}\text{CO}^- & \quad \text{C}_5\text{H}_{11}\text{OH}^- \\
\text{H} & \quad \text{H}
\end{align*}
\]

f) 
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{NH}_3^- & \quad \text{CH}_3\text{CH}_2\text{H}^- \\
\text{H} & \quad \text{H}
\end{align*}
\]

37. Circle the stronger base of each pair, then explain your choice. Check your answers using your pKa chart.

a) 
\[
\begin{align*}
\text{NH}_3^- & \quad \text{NH}_2^- \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

b) 
\[
\begin{align*}
\text{H}_2\text{O}^- & \quad \text{H}^- \\
\text{H} & \quad \text{H}
\end{align*}
\]

c) 
\[
\begin{align*}
\text{CH}_3\text{C} & \quad \text{N} \equiv \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\]