1. The equilibrium expression for the reaction: \( \text{Ni(CO)}_4(\ell) \rightleftharpoons \text{Ni(s)} + 4 \text{CO(g)} \) is:

a) \( K_{eq} = \frac{[\text{Ni(CO)}_4]}{[\text{Ni}][\text{CO}]^4} \)

b) \( K_{eq} = \frac{1}{[\text{Ni(CO)}_4]} \)

c) \( K_{eq} = \frac{[\text{Ni}][\text{CO}]^4}{[\text{Ni(CO)}_4]} \)

d) \( K_{eq} = [\text{CO}]^4 \)  

Problem 15.7c

e) \( K_{eq} = \frac{[\text{Ni}(\ell)]}{[\text{Ni(CO)}_4]} \)

2. For the equilibrium \( \text{H}_2(\ell) + \text{I}_2(\ell) \rightleftharpoons 2 \text{HI(g)} \) which of the following would result in a shift of the equilibrium to the right?

a) Increasing pressure  
b) Adding a catalyst  
c) Adding HI  
d) Decreasing pressure  
e) Adding NaOH

3. At equilibrium, which is/are true?

a) All chemical processes have stopped.

b) The rate of the forward reaction equals that of the reverse.

c) The rate constant for the forward reaction equals that of the reverse.

d) The sum of the concentrations of the reactants equals that of the products.

e) None of the above.

4. The reaction \( \text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \) (all gases) has an equilibrium constant equal to what value, if at equilibrium in a 2.00 L vessel, there are 0.302 atm \( \text{H}_2 \), 0.170 atm \( \text{CO} \), and 0.0406 atm \( \text{CH}_3\text{OH} \) present.

a) 0.0955  
b) 1.58  
c) 2.61  
d) 10.5  
e) 26.2

5. A Brønsted-Lowery acid is:

a) a proton acceptor.  
b) an electron pair acceptor.  
c) a proton donor.  
d) a substance that ionizes to produce protons.  
e) an electron pair donor.

6. Which of the following is a weak base?

a) KOH  
b) Sr(OH)_2  
c) NH_2OH  
d) NaNH_2  
e) Mg(OH)_2

7. In which of the following would HCl be the strongest acid?

a) pyridine(\ell)  
b) HOAc(\ell)  
c) H_2O(\ell)  
d) NH_3(\ell)  
e) 1.0 M NaOH(aq)

8. What is the \([\text{H}^+]\) of a HCl solution that has a pH = 3.21?

a) \( 6.2 \times 10^{-4} \text{ M} \)  
b) \( 4.0 \times 10^{-2} \text{ M} \)  
c) \( 3.2 \text{ M} \)  
d) \( 25 \text{ M} \)  
e) \( 1600 \text{ M} \)

Discussion questions
1. Define the following: (20 points)

- **Lewis acid** – an electron pair acceptor
- **amphoteric** – molecules that can act both as an acid and base
- **homogeneous equilibrium** – an equilibrium in which all components are in the same phase
- **reaction order** – the sum of the exponents \((x + y)\) in a rate law

2. At 373 K, \(K_{eq} = 0.416\) for the equilibrium \(2 \text{NOBr} \rightleftharpoons 2 \text{NO} + \text{Br}_2\) (all gases). If the pressures of NOBr and NO are equal, what is the equilibrium pressure of Br\(_2\)? \(6\) points

Let \(P_{\text{NOBr}} = P_{\text{NO}} = x\), then \(P_{\text{Br}_2} = \frac{1}{2}x\)

\[
0.416 = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2} = \frac{(x)^2 \left(\frac{1}{2}x\right)}{(x)^2} = \frac{1}{2}x
\]

\(x = 0.832\) atm

\(\Rightarrow P_{\text{Br}_2} = \frac{1}{2}(0.832\ \text{atm}) = 0.416\ \text{atm}\) (Problem 15.37)

3. Consider an equilibrium whose forward reaction is exothermic. Which way will the equilibrium shift if the reaction is heated? Provide a physical explanation for your prediction. \(6\) points

In exothermic reactions, heat is released. Le Châtelier’s principle tells us that if heat is added, the reaction will shift to consume some of this heat, so the reaction will shift in the reverse direction. The energy diagram below shows equilibrium of an exothermic reaction:

![Energy Diagram](image)

In an exothermic reaction a higher percentage of reactions in the forward direction have sufficient energy to cross the barrier than do reactions moving in the reverse direction. The physical rationale for the prediction is that when heat is added it will affect more reactions going in the reverse direction than the forward reaction because more of them are lacking the necessary energy to go to completion. There will be **more reactions in both directions**, but there will be a relative increase in the reverse direction.

4. Explain why HNO\(_3\) is a stronger acid than HNO\(_2\). \(6\) points

Nitric acid is a stronger acid than nitrous acid because the nitrogen in the former is in the +5 oxidation state as opposed to +3 for nitrous acid. The higher oxidation state on nitrogen in HNO\(_3\) polarizes the N-O bond (and hence the O-H bond) more. This makes it easier for an H\(^+\) ion to separate from the molecule. (Problem 16.81)
5. What is the pH of (12 points)
   a) 0.32 M HNO₂ (K_a = 4.5 x 10⁻⁴)
   \[ \text{HNO}_2 \leftrightharpoons \text{H}^+ + \text{NO}_2^- \quad K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} \]
   init 0.32 M 0 M 0 M
   equil 0.32 - x x x
   \[ 4.5 \times 10^{-4} = \frac{(x)(x)}{0.32 - x} \]
   Since [HNO₂]_i > 100K_a, assume x is negligible in the denominator
   \[ 4.5 \times 10^{-4} = \frac{x(x)}{0.32} \]
   \[ x = [\text{H}^+] = 1.2 \times 10^{-2} \text{ M} \quad (0.32 - 0.012 = 0.321 \cong 0.32, \text{ so the assumption was OK}) \]
   pH = -\log(0.012) = 1.92

   b) 0.121 M H₂S (K_b(HS⁻) = 5.56 x 10⁻⁸)
   \[ \text{H}_2\text{S} \leftrightharpoons \text{HS}^- + \text{H}^+ \quad K_a = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \]
   init 0.121 M 0 M 0 M
   equil 0.121 - x x x
   \[ K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.56 \times 10^{-8}} = 1.8 \times 10^{-7} \]
   \[ 1.8 \times 10^{-7} = \frac{(x)(x)}{0.121 - x} \]
   Since [H₂S]_i >> 100K_a, assume x is negligible in the denominator
   \[ 1.8 \times 10^{-7} = \frac{x(x)}{0.121} \]
   \[ x = [\text{H}^+] = 1.5 \times 10^{-4} \text{ M} \quad (0.121 - 0.00015 \cong 0.121, \text{ so the assumption was OK}) \]
   pH = -\log(1.5 \times 10^{-4}) = 3.83

6. Consider the hypothetical reaction where A converts to a product (A → B). Given the following data, determine the rate law for the reaction and the rate constant. What is the half life of this reaction? (You must use a half-life equation to answer this part.) (15 points)

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[A] (M)</th>
<th>ln[A]</th>
<th>1/[A] (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4562</td>
<td>-0.7848</td>
<td>2.192</td>
</tr>
<tr>
<td>4</td>
<td>0.2041</td>
<td>-1.589</td>
<td>4.900</td>
</tr>
<tr>
<td>11</td>
<td>0.1020</td>
<td>-2.283</td>
<td>9.804</td>
</tr>
<tr>
<td>15</td>
<td>0.0794</td>
<td>-2.533</td>
<td>12.59</td>
</tr>
</tbody>
</table>
This is a second-order reaction, so rate = \( k[A]^2 \).

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

substituting the final data set in yields

\[
\frac{1}{0.0794 \text{ M}} = k(15 \text{ min}) + \frac{1}{0.4562 \text{ M}}
\]

\( k = 0.694 \text{ s}^{-1}\text{M}^{-1} \)

\( t_{1/2} = \frac{1}{k[A]} - \frac{1}{(0.6935 \text{ min}^{-1}\text{M}^{-1})(0.4562 \text{ M})} = 3.16 \text{ sec} \)