1. Consider the following reaction for the decomposition of SO₃:

\[ 2\text{SO}_3(g) \rightleftharpoons \text{O}_2(g) + 2\text{SO}_2(g) \]

A 0.0200 mol sample of pure SO₃ is placed in an evacuated 1.52 L flask at 900 K. At equilibrium, it was found that 0.0142 mol of SO₃ was in the flask. Calculate the value of \( K_c \) at 900 K.

\[ 2 \times 0.0142 = 0.0284 \text{ mol} \]

\[ \frac{0.0284}{1.52} = 0.0187 \text{ mol L}^{-1} \]

\[ \frac{0.0142}{0.0187} = 0.763 \]

\[ 2 \times \frac{0.0187}{0.0187} = 2 \]

\[ \frac{0.0187}{0.0187} = 1 \]

\[ K_c = \frac{[\text{O}_2][\text{SO}_2]^2}{[\text{SO}_3]^2} = \frac{(0.019)(0.0038)^2}{(0.00934)^2} = 3.1 \times 10^{-4} \]

2. Given the following reactions and equilibrium constants at 1200 K:

1) \( \text{C(graphite)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2(\text{g}) \quad K = 0.46 \)

2) \( \text{C(graphite)} + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{CO(g)} \quad K = 1.0 \times 10^{18} \)

Estimate the equilibrium constant for the following reaction at 1200 K.

\( \text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O(g)} \quad K = \left(\frac{0.46}{2}\right)^2 = 0.11 \)

\( 2\text{C(graphite)} + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO(g)} \quad K = (1.0 \times 10^{18})^2 \)

\( \text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O(g)} \quad K = (4.7 \times 10^{16})^2 \)

\( K_{\text{overall}} = \frac{1}{(0.11)^2} \times (1.0 \times 10^{18})^2 = 4.7 \times 10^{16} \)
3. The equilibrium constant for the following reaction is $1.30 \times 10^{-4}$ at 1000 K.

$$\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbO(s)} + \text{H}_2$$

A mixture of 1.00 mol of H$_2$O and 1.0 x 10$^{-3}$ mol of H$_2$ is introduced into a container with a volume of 5.00 L containing molten lead and lead oxide at 1000 K. (Ignore the volume of the lead and lead oxide.)

(a) To which side will the equilibrium shift?

$$[\text{H}_2\text{O}] = \frac{1.00 \text{ mol}}{5.00 \text{ L}} = 0.200 \text{ M}$$

$$[\text{H}_2] = \frac{1.0 \times 10^{-3} \text{ mol}}{5.00 \text{ L}} = 2.00 \times 10^{-4}$$

(b) What are the concentrations of the gaseous substances at equilibrium?

$$Q = \frac{[\text{H}_2]}{[\text{H}_2\text{O}]} = \frac{2.00 \times 10^{-4}}{0.200} = 1.00 \times 10^{-3}$$

$$Q > K \quad \Rightarrow \text{shift to reactants}$$

$$K = \frac{[\text{H}_2]}{[\text{H}_2\text{O}]} \Rightarrow 1.30 \times 10^{-4} = \frac{2.00 \times 10^{-4} - x}{0.200 + x}$$

$$1.30 \times 10^{-4} (0.200 + x) = 2.00 \times 10^{-4} - x$$

$$2.60 \times 10^{-5} + 1.30 \times 10^{-4} x = 2.00 \times 10^{-4} - x$$

$$-1.74 \times 10^{-4} = -1.00 x$$

$$x = 1.74 \times 10^{-4}$$

$$[\text{H}_2] = 2.00 \times 10^{-4} - x = 2.00 \times 10^{-4} - 1.74 \times 10^{-4} = 2.6 \times 10^{-5}$$

$$[\text{H}_2\text{O}] = 0.200 + x = 0.200 + 1.74 \times 10^{-4} = 0.200$$

Check $K = \frac{[\text{H}_2]}{[\text{H}_2\text{O}]} \Rightarrow \frac{2.6 \times 10^{-5}}{0.200} = 1.3 \times 10^{-4}$
4. Consider the following gas phase reaction that has enthalpy $\Delta H = +16.6 \text{ kJ/mol}$:

$$16 \text{kJ} + 2 \text{NOBr} \rightleftharpoons 2 \text{NO} + \text{Br}_2$$

Predict the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made.

(a) Adding $\text{Br}_2(g)$  
(b) Removing $\text{NOBr}(g)$  
(c) Removing $\text{NO}(g)$  
(d) Decreasing the temperature  
(e) Increasing the container volume

5. Propionic acid is a weak acid ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$, the acidic proton is in bold) with a $K_a = 1.3 \times 10^{-5}$. Calculate the pH of a solution that is 0.45 M in propionic acid.

Start: 

$$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CO}_2\text{O}^-(aq) + \text{H}_3\text{O}^+(aq)$$

Change: $-\chi$  

Equilibrium: $\chi$  

$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{CO}_2\text{O}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}]} \Rightarrow 1.3 \times 10^{-5} = \frac{\chi^2}{0.45 - \chi}$$

Check $\frac{2.5 \times 10^{-3}}{0.45} \times 100 = 5.56\%$ too big, but close to 5.5%  

6. Hydroxylamine ($\text{HONH}_2$, $K_b = 9.1 \times 10^{-9}$) is a weak base. Calculate the pH of a solution that is 0.020 M hydroxylamine.

$$\text{HONH}_2(aq) + \text{H}_2\text{O}(liq) \rightleftharpoons \text{HONH}_3^+(aq) + \text{OH}^-(aq)$$

$$K_b = \frac{[\text{HONH}_3^+] [\text{OH}^-]}{[\text{HONH}_2]} \Rightarrow 9.1 \times 10^{-9} = \frac{\chi^2}{0.020 - \chi}$$

Assume $\chi = 0.020 - \chi$  

$9.1 \times 10^{-9} = \frac{\chi^2}{0.020} \Rightarrow 1.8 \times 10^{-10} = \chi^2 \Rightarrow 1.3 \times 10^{-5} = \chi$

Check $\frac{1.3 \times 10^{-5}}{0.020} \times 100 = 0.65\%$  

$\text{pH} = -\log[\text{OH}^-] = -\log(1.3 \times 10^{-5})$
These equilibrium constants are used in problems 7 and 8

\[ \text{C}_6\text{H}_5\text{OH} \quad \text{Ka} = 6.3 \times 10^{-5} \]
\[ \text{C}_6\text{H}_4\text{NH}_2 \quad \text{ Kb} = 7.4 \times 10^{-10} \]
\[ \text{H}_2\text{S} \quad \text{ Ka1} = 1.0 \times 10^{-7}, \text{ Ka2} = 1.0 \times 10^{-19} \]

\[ \text{HNO}_2 \quad \text{ Ka} = 7.2 \times 10^{-4} \]
\[ \text{C}_6\text{H}_5\text{N} \quad \text{ Ka} = 1.5 \times 10^{-9} \]

7. Predict whether 1.0 M solutions of the following substances will be acidic, basic, or neutral.

(a) KOH

\[ \text{strong base (B)} \]

(b) C₆H₅OH

\[ \text{weak acid (A)} \]

(c) K₂S

\[ \text{s²⁻ salt of weak acid (B)} \]

(d) C₆H₅NH₂

\[ \text{C₆H₅NH₃⁺ salt of weak base (A)} \]

(e) NaNO₃

\[ \text{acid/base (N)} \]

(f) NaNO₂

\[ \text{NO₂⁻ salt of weak acid (B)} \]

(g) C₆H₅NH₂

\[ \text{weak base (B)} \]

(h) HCl

\[ \text{strong acid (A)} \]

8. Give a short answer to the following questions:

(a) Write the \( \text{Ka1} \) and \( \text{Ka2} \) chemical equations for \( \text{H}_2\text{S} \).

\[
\begin{align*}
\text{Ka1} & \quad \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{HS}^- + \text{H}_3\text{O}^+ \\
\text{Ka2} & \quad \text{HS}^- + \text{H}_2\text{O} \rightarrow \text{S}^{2⁻} + \text{H}_3\text{O}^+
\end{align*}
\]

(b) Which side of this equilibrium is favored?

\[ \text{Strongest base} \quad \text{Strongest acid} \]

\[ \text{C}_6\text{H}_5\text{NH}_2 \text{ (aq)} + \text{HNO}_2 \text{ (aq)} \rightarrow \]

\[ \text{C}_6\text{H}_5\text{NH}_3^+ \text{ (aq)} + \text{NO}_2^- \text{ (aq)} \]

\[ \text{K}_b = 7.4 \times 10^{-4} \]

\[ \text{K}_a = \text{Kw}/\text{K}_b = 1.0 \times 10^{-4} \]

\[ \text{K}_a = \text{Kw}/\text{K}_b = 1.0 \times 10^{-4} \]

\[ \text{K}_b = \text{Kw}/\text{K}_a = 1.4 \times 10^{-11} \]

(c) What is the \( \text{Kb} \) of \( \text{C}_6\text{H}_5\text{O}^- \) ?

\[ \text{K}_b = \text{Kw}/\text{K}_a = 1.0 \times 10^{-4} \]

\[ \text{K}_a = \text{Kw}/\text{K}_b = 1.4 \times 10^{-11} \]

(d) What is the conjugate acid of \( \text{OH}^- \) ?

\[ \text{H}_2\text{O} \]

(e) What is the conjugate base of \( \text{HCO}_3^- \) ?

\[ \text{CO}_3^{2⁻} \]

(f) Why are NaCl solutions neutral?

\[ \text{Na}^+, \text{Cl}^- \text{ ion are salts of strong acids, no interaction} \]

(g) Why are solutions of Al³⁺ salts acidic?

\[ \text{Al}^3⁺ + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \text{ with water} \]

(h) What is the pH of 0.134 M HCl?

\[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \text{ 100%} \]

\[ \text{pH} = -\log [\text{HCl}] \]

\[ = -\log (0.134) = -0.873 \]