## CH302 Worksheet 4: Chemical Equilibria

## Part 1: Some general equilibrium problems usually found on exams.

1. LeChatelier and pressure: If the pressure is decreased in a vessel containing the following equilibrium mixtures, which way will the reaction shift?
(a) $\mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \leftrightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$
(b) $\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2(\mathrm{~g})} \leftrightarrow 2 \mathrm{NO}_{(\mathrm{g})}$
2. LeChatelier and temperature: How would increasing the temperature affect the following equilibria?
(a) $2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \leftrightarrow 2 \mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})}$
$\Delta \mathrm{H}=484 \mathrm{~kJ}$
(b) $\mathrm{C}_{3} \mathrm{H}_{8(\mathrm{~g})}+5 \mathrm{O}_{2(\mathrm{~g})} \leftrightarrow 3 \mathrm{CO}_{2(\mathrm{~g})}+4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$
$\Delta \mathrm{H}=-2043 \mathrm{~kJ}$
(c) $\mathrm{CH}_{4(\mathrm{~g})}+2 \mathrm{O}_{2(\mathrm{~g})} \leftrightarrow \mathrm{CO}_{2(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$
$\Delta \mathrm{H}=-890.4 \mathrm{~kJ}$

## 3. LeChatelier and concentration:

(a) What happens to $\mathrm{C}_{2} \mathrm{H}_{6}$ when HCl gas is added? $\mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \leftrightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}(\mathrm{s})+\mathrm{HCl}(\mathrm{g})$
(b) What happens to $\mathrm{NH}_{3}$ when $\mathrm{H}_{2}$ gas is added? $\quad \mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \leftrightarrow 2 \mathrm{NH}_{3(\mathrm{~g})}$
4. Relating Chapter 7 to Chapter 9: What is $\mathrm{K}_{\mathrm{c}}$ at room temperature for the reaction:

$$
\mathrm{K}_{(\mathrm{aq})}^{+}+\mathrm{OH}_{(\mathrm{aq})}^{-} \leftrightarrow \mathrm{KOH}_{(\mathrm{aq})} \quad \Delta \mathrm{G}_{f}^{\circ}=-439.6 \mathrm{~kJ} / \mathrm{mol}
$$

## Part 2: General Approach to Solving Chemical Equilibria Problems

The general form of a chemical reaction is $\mathrm{aA}+\mathrm{bB}=\mathrm{cC}+\mathrm{dD}$
Where A and B are reactants in the forward direction and C and D are products in the forward direction. The lower case letters are the stoichiometric coefficients for the balanced equation. The general form of the equilibrium constant equation is then

$$
\mathrm{K}_{\mathrm{eq}}=[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}} /[\mathrm{A}]^{\mathrm{a}}[\mathrm{~B}]^{\mathrm{b}}
$$

Problems involving chemical equilibria can be placed into a matrix format with two kinds of concentrations identified: the initial or non-equilibrium concentration $\mathbf{C}_{\mathbf{x}}$ and the equilibrium concentration $[\mathbf{X}]$. (Note the bracket versus the Capital C. It is the equilibrium concentrations, $[\mathrm{X}]$, that are used to calculate $\mathrm{K}_{\text {eq }}$.

| reaction | A | B | C | D |
| :--- | :---: | :---: | :---: | :---: |
| initial | $\mathrm{C}_{\mathrm{A}}$ | $\mathrm{C}_{\mathrm{B}}$ | $\mathrm{C}_{\mathrm{C}}$ | $\mathrm{C}_{\mathrm{D}}$ |
| change | $\mathrm{C}_{\mathrm{A}}-[\mathrm{A}]$ | $\mathrm{C}_{\mathrm{B}}-[\mathrm{B}]$ | $[\mathrm{C}]-\mathrm{C}_{\mathrm{C}}$ | $[\mathrm{D}]-\mathrm{C}_{\mathrm{D}}$ |
| equilibrium | $[\mathrm{A}]$ | $[\mathrm{B}]$ | $[\mathrm{C}]$ | $[\mathrm{D}]$ |

There are a variety of equilibrium problems that can be solved using the construction above. In some cases the problems are solved directly, with one unknown per equation. Others problems require significant algebraic manipulation. All of them are easy if you can identify the type of information used and place it in the matrix. The four three most common problem types are below:

## Model chemical equilibrium for the following four calculations: $\quad 2 \mathbf{N H}_{3} \rightarrow 3 \mathbf{H}_{2}+\mathbf{N}_{2} \mathbf{K}_{\text {eq }}=\mathbf{3 . 8}$

## Eqilibrium Problem Type 1. Calculating $\mathrm{K}_{\mathrm{eq}}$ from equilibrium concentrations.

In these problems it is necessary to determine all the bottom row equilibrium concentrations (the ones in $[\mathrm{X}]$ ) and with the stoichiometric coefficients, $\mathrm{K}_{\mathrm{eq}}$ is determined.

Calculation 1. For the ammonia equilibrium above, equilibrium concentrations are $\left[\mathrm{N}_{2}\right]=.10 \mathrm{M},\left[\mathrm{H}_{2}\right]=.50 \mathrm{M},\left[\mathrm{NH}_{3}\right]=.057 \mathrm{M}$. What is $\mathrm{K}_{\mathrm{eq}}$ ? This is the easiest of problems because you are told what all the bottom row equilibria are.

|  | $\mathrm{NH}_{3}$ | $\mathrm{H}_{2}$ | $\mathrm{~N}_{2}$ |
| :--- | :--- | :--- | :--- |
| initial |  |  |  |
| change |  |  |  |
| equilibrium | .057 | .50 | .10 |

Solve: $\mathbf{K}_{\text {eq }}=$

Eqilibrium Problem Type 2. Using stoichiometry to complete the array.
A complex problem provides some of the initial and some of the equilibria concentrations and you are asked to solve for the rest of the concentrations in the array.

These problems are accomplished using stoichiometry and simple substitutions for unknowns.
Calculation 2. Given $\mathrm{K}_{\mathrm{eq}}=3.8,\left[\mathrm{~N}_{2}\right]=0.3 \mathrm{M},\left[\mathrm{H}_{2}\right]=0.2 \mathrm{M}$ and $\mathrm{C}_{\mathrm{NH} 3}=0.04 \mathrm{M}$. What is the initial concentration of $\mathrm{C}_{\mathrm{N} 2}$ ?
Fill in all empty boxes below.

|  | 2 NH 3 | 3 H 2 | N 2 |
| :--- | :--- | :--- | :--- |
| initial | .04 |  | $?$ |
| change |  |  |  |
| final |  | .2 | .3 |

Solve: $\mathrm{C}_{\mathrm{N} 2}=$

## Eqilibrium Problem Type 3. Problem solving using $\mathrm{K}_{\mathrm{eq}}$ and initial concentrations.

The most realistic kind of equilibrium problem, the one you will use most often in Chapter 18 through 20, involves knowing the initial concentration of materials in the reaction, and the $\mathrm{K}_{\mathrm{eq}}$, obtained from a table. The equilibrium concentrations are then found through a series of algebraic substitutions. Note this problem represents what happens in real life. We can measure what we add to a reaction container, and we know $\mathrm{K}_{\mathrm{eq}}$

|  | A | B | C | D |
| :--- | :--- | :--- | :--- | :--- |
| initial | known | known | known | known |
| change |  |  |  |  |
| final | unknown | unknown | unknown | unknown |

This problem type is about the only kind you will work after Chapter 17. it is the most challenging and often requires solution of higher order polynomial equations.

## Calculation 3. A quartic (which you would never be asked to solve on a test.)

Your initial concentration of $\mathrm{C}_{\mathrm{NH} 3}$ is 0.1 M . What is the equilibrium concentration of $\left[\mathrm{N}_{2}\right]$ ? (Remember that $\left.\mathrm{K}_{\mathrm{eq}}=3.8\right)$.

|  | $2 \mathrm{NH}_{3}$ | $3 \mathrm{H}_{2}$ | $\mathrm{~N}_{2}$ |
| :--- | :--- | :--- | :--- |
| initial | .1 | 0 | 0 |
| change |  |  |  |
| final |  |  | $x$ |

To solve this problem you need to generate an algebraic solution for the equilibrium values all in terms of a single variable. So let $\mathrm{x}=$ the amount of $\left[\mathrm{N}_{2}\right]$ at equilibrium. Then solve for the other unknowns using the stoichiometric relationship between the concentrations. Don't bother solving the equation unless you have a calculator that does it. Simply set up the expression for [N2]

Solve: $\left[\mathbf{N}_{2}\right]=$

Calculation 4. A quadratic (which you will need to be able to solve on an exam.)
$[H+]$ of a weak monoprotic acid. What is the $\left[\mathrm{H}^{+}\right]$concentration for a 0.3 M solution of acetic acid $\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}\right)$.

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}
$$

|  | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $\mathrm{H}^{+}$ | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$ |
| :--- | :--- | :--- | :--- |
| initial | $\mathbf{. 3}$ | $\mathbf{0}$ | $\mathbf{0}$ |
| change |  |  |  |
| final |  | $\mathbf{x}$ |  |

Solve this problem the same way as Calculation 3. But the solution is easier and as a quadratic can be solved using the quadratic equation solution.

Solve: $\left[\mathbf{H}^{+}\right]=$

