## Worksheet 4 answer key: General Approach to Solving Chemical Equilibria Problems

The general form of a chemical reaction is:

$$
\mathrm{aA}+\mathrm{bB} \Leftrightarrow \mathrm{cC}+\mathrm{dD}
$$

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 $\mathbf{C}$. It is the equilibrium concentrations, $[\mathbf{X}]$, that are used to calculate $\mathrm{K}_{\text {eq }}$.

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

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.

## Examples:

Model Equilibrium System As the chemical system for all the problems on this work sheet, we will use

$$
2 \mathrm{NH}_{3} \Leftrightarrow 3 \mathrm{H}_{2}+\mathrm{N}_{2} \quad \mathrm{~K}_{\mathrm{eq}}=3.8=\left[\mathrm{H}_{2}\right]^{3}\left[\mathrm{~N}_{2}\right] /\left[\mathrm{NH}_{3}\right]^{2}
$$

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

In these problems it is necessary to identify all the bottom row equilibrium concentrations (the ones in [X]) so that $\mathrm{K}_{\mathrm{eq}}$ is determined directly. 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 $\mathrm{K}_{\text {eq }}$ ? This is the easiest of problems because you are told what all the bottom row equilibria are.

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

$$
\mathrm{K}_{\mathrm{eq}}=[.10]^{1}[.50]^{3} /[.057]^{2}=3.8
$$

Note that for constant temperaure, this value for K never changes. You will see it used in every example in the handout.

## Problem 2. Using stoichiometry to complete the array.

A more complex type of 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.

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 $\mathrm{C}_{\mathrm{N} 2}$ ?

|  | $2 \mathrm{NH}_{3}$ | $3 \mathrm{H}_{2}$ | $\mathrm{~N}_{2}$ |
| :--- | :--- | :--- | :--- |
| initial | .04 |  | $?$ |
| change |  |  |  |
| final |  | .2 | .3 |

First find $\left[\mathrm{NH}_{3}\right]$ at equilibrium from the $\mathrm{K}_{\mathrm{eq}}$ expression: $3.8=\left((.2)^{3}(.3) /\left[\mathrm{NH}_{3}\right]^{2}\right.$ and $\left[\mathrm{NH}_{3}\right]=.025 \mathrm{M}$.
Then use the stoichimetric relationships to back substitute throughout the matrix. Follow the steps shown.

|  | $2 \mathrm{NH}_{3}$ | $3 \mathrm{H}_{2}$ | $\mathrm{~N}_{2}$ |
| :--- | :--- | :--- | :--- |
| initial | $\mathbf{. 0 3 5}$ | .185 step 3 | .295 step 3 |


| change | -.01 step 1 | +.015 step 2 | +.005 step 2 |
| :--- | :--- | :--- | :--- |
| final | .025 | $\mathbf{. 2}$ | $\mathbf{. 3}$ |

## Problem 3. Problem solving using $K_{\mathrm{eq}}$ and initial concentrations.

The most realistic kind of equilibrium problem, the one you will use most often in Chapter 10 through 11, 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.

## Example. A quartic.

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

|  | $2 \mathrm{NH}_{3}$ | $3 \mathrm{H}_{2}$ | $\mathrm{~N}_{2}$ |
| :--- | :--- | :--- | :--- |
| 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.

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

So the equilibrium equation in terms of the single variable $x$ (which happens to be [N2] that we want to know) is

$$
3.8=(3 x)^{3}(x) /(.1-2 x)^{2}=27 x^{4} /\left(.01-4 x+4 x^{2}\right)
$$

Yikes, a quartic. I will leave it to one of you to solve with your fancy calculators. This is why I don't write test questions. Don't worry, you'll never get one like this on a quiz or exam. Instead I will start giving you easier algebraic problems that are still solved the same way. Like this one from Chapter 10 on acids and bases.

Problem 4. $[\mathrm{H}+]$ in a weak monoprotic acid. What is the $\left[\mathrm{H}^{+}\right]$concentration for a 0.3 M solution of acetic acid $\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}\right)$.

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \Leftrightarrow \mathrm{H}^{+}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-} \quad \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}=\left[\mathrm{H}^{+}\right]\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right] /\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]
$$

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

Solve in the same way, finding a single variable to substitute for equilibrium unknowns

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

So $\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}=(\mathrm{x})(\mathrm{x}) /(.3-\mathrm{x})=\mathrm{x}^{2} /(.3-\mathrm{x})$. A quadratic. Well I do know how to solve those using the quadratic formula.
$\mathrm{x}=\left[\mathrm{H}^{+}\right]=2.31 \times 10^{-4}$. The answer says that there is not much $\left[\mathrm{H}^{+}\right]$in solution, which we would have guessed, because acetic acid is a weak acid.

Note that the way you solve an equilibrium for a weak acid in CH 10 is exactly the same procedure you learned in Chapter 9. Don't lose sight of that fact as we start to get more and more complicated about things in later chapters. You can always set up an array and do the necessary substitutions for x , and solve for an unknown.

