There are 4 Basic Types of Calculations involving Keq:

## Type 1-Calculating Keq Given Equilibrium Concentrations

It is useful to clarify the following in your mind:

## A chemical system can be thought of as being either:

## 1. At Equilibrium <br> or 2. Not At Equilibrium (Initial)

A system which is not at equilibrium will move spontaneously to a position of being at equilibrium.

In Type 1 calculations, all species in the system are at equilibrium already, so there will be no changes in concentration.

The value for Keq is calculated simply by "plugging" the values for equilibrium concentrations into the Keq expression and calculating.

Whenever a question says something like " ...the equilibrium concentrations of the following are..." or something to that effect, it is a Type 1 Calculation.

Let's do an example:
Given the equilibrium system: $\quad \mathrm{PCl}_{5(\mathrm{~g})} \rightleftarrows \mathrm{PCl}_{3(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})}$
The system is analyzed at a certain temperature and the equilibrium concentrations are as follows:

$$
\left[\mathrm{PCl}_{5}\right]=0.32 \mathrm{M},\left[\mathrm{PCl}_{3}\right]=0.40 \mathrm{M} \text { and the }\left[\mathrm{Cl}_{2}\right]=0.40 \mathrm{M} .
$$

Calculate the Keq for this reaction at the temperature this was carried out.

## SOLUTION:

Step 1 - Use the balanced equation to write the Keq expression:

$$
\begin{aligned}
& \mathrm{PCl}_{5(\mathrm{~g})} \\
& K e q=\mathrm{PCl}_{3(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})} \text { so } \\
& {\left[P C l_{3}\right]\left[\mathrm{Cl}_{2}\right] } \\
&
\end{aligned}
$$

Step 2 - "Plug in" the values for the equilibrium concentrations of the species:

$$
\begin{aligned}
& K e q=\frac{\left[\mathrm{PCl}_{3}\right]\left[\mathrm{Cl}_{2}\right]}{\left[\mathrm{PCl}_{5}\right]} \\
& K e q=\frac{[0.40][0.40]}{[0.32]}
\end{aligned}
$$

Step 3-Calculate the value of Keq :

$$
K e q=\frac{[0.40][0.40]}{[0.32]}=0.50
$$

Answer: The Keq $=0.50$ for this reaction.
Notice the answer is in 2 SD's like the lowest \# of SD's in the data.
Notice that there are no units given in the answer. Even though Keq technically has units, they are fairly meaningless and they are just dropped. So don't include any units when you state the value for Keq.
************************************************************
Try this:

1. The equilibrium equation for the formation of ammonia is:

$$
\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \longleftrightarrow 2 \mathrm{NH}_{3(\mathrm{~g})}
$$

In an equilibrium mixture at $200^{\circ} \mathrm{C}$, the concentrations were found to be as follows:
$\left[\mathrm{N}_{2}\right]=2.12 \mathrm{M}, \quad\left[\mathrm{H}_{2}\right]=1.75 \mathrm{M}$ and $\left[\mathrm{NH}_{3}\right]=84.3 \mathrm{M}$
Notice the 3 sd's in all your data.
Calculate the value of the Equilibrium Constant for this reaction at $200^{\circ} \mathrm{C}$.

Answer: $\quad$ Keq = $\qquad$

A variation of Type 1 problems is when you are given the Keq and all the equilibrium concentrations except one and you are asked to calculate that one.

The solution for this type of problem is simply writing out the Keq expression, filling in what you know and solving for the unknown.

Read through this example:
At $200^{\circ} \mathrm{C}$, the Keq for the reaction: $\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \rightleftarrows 2 \mathrm{NH}_{3(\mathrm{~g})}$ is $\underline{\mathbf{6 2 5}}$
If the $\left[\mathrm{N}_{2}\right]=0.030 \mathrm{M}$, and the $\left[\mathrm{NH}_{3}\right]=0.12 \mathrm{M}$, at equilibrium, calculate the equilibrium $\left[\mathrm{H}_{2}\right]$.

Solution: All concentrations given are at equilibrium so:

## Write out the Keq expression:

$$
K e q=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{H}_{2}\right]^{3}\left[\mathrm{~N}_{2}\right]}
$$

Plug in what is known:

$$
625=\frac{[0.12]^{2}}{\left[\mathrm{H}_{2}\right]^{3}[0.030]}
$$

## Cross-multiplying:

(625) $\left[\mathrm{H}_{2}\right]^{3}(0.030)=(0.12)^{2}$

## Solving for $\left[\mathrm{H}_{2}\right]^{3}$

$$
\left[H_{2}\right]^{3}=\frac{(0.12)^{2}}{625(0.030)}
$$

$$
\left[H_{2}\right]^{3}=\frac{0.0144}{18.75}=0.000768\left(7.68 \times 10^{-4}\right)
$$

Take the cube root of both sides:
$\left[H_{2}\right]=\sqrt[3]{7.68 \times 10^{-4}}=9.2 \times 10^{-2} \mathrm{M}=0.092 \mathrm{M}$
notice 2 sd's like data

Here's a problem for you to try:
2. At $200^{\circ} \mathrm{C}$, the Keq for the reaction: $\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \rightleftarrows 2 \mathrm{NH}_{3(\mathrm{~g})}$ is $\underline{\mathbf{6 2 5}}$

If the $\left[\mathrm{H}_{2}\right]=0.430 \mathrm{M}$, and the $\left[\mathrm{NH}_{3}\right]=0.10 \mathrm{M}$, at equilibrium, calculate the equilibrium $\left[\mathrm{N}_{2}\right]$.

Answer: Equilibrium $\left[\mathrm{N}_{2}\right]=$ $\qquad$

## Type 2 - Given Initial Concentrations of all Species and equilibrium concentration of one species and asked to calculate the equilibrium concentrations of all species or the Keq (Also called "ICE" problems) Remember:

## A chemical system can be thought of as being either:

1. At Equilibrium
or 2. Not At Equilibrium
A system which is not at equilibrium will move spontaneously to a position of being at equilibrium.

In this type of problem, we start out with "INITIAL" concentrations of all the species.
"Initial" usually means "NOT AT EQUILIBRIUM YET" or "WHAT YOU START WITH". We abbreviate Initial Concentration as [I] where "I" stands for "Initial" and not "Iodine". The [ ]'s stand for "Molar Concentration"

When the system is not at equilibrium, the "reaction will shift" left or right until it reaches equilibrium.

In this type of problem, there will be one species which we will know the concentration of initially and at equilibrium. We can find the change in the concentration (which we abbreviate as "[C]" where the "C" stands for the words "Change in" and [ ]'s stand for Concentration) of this species and by using mole ratios in the balanced equation, find the changes in concentration " $[\mathbf{C}]$ " of the other species. From this we can calculate the equilibrium concentration (which we abbreviate as " $[E]$ ") of all the species.

There is a lot to keep track of here, so this is best done using a little table (called an "ICE" table)

Remember, there are 3 stages: Initial, Change and Equilibrium ( hence the name "ICE" problem) Here's a little problem:

Given the reaction:

$$
\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \longleftrightarrow 2 \mathrm{NH}_{3(\mathrm{~g})}
$$

Some $\mathrm{H}_{2}$ and $\mathrm{N}_{2}$ are added to a container so that initially, the $\left[\mathrm{N}_{2}\right]=0.32 \mathrm{M}$ and $\left[\mathrm{H}_{2}\right]=0.66 \mathrm{M}$.
At a certain temperature and pressure, the equilibrium $\left[\mathrm{H}_{2}\right]$ is found to be 0.30 M .
a) Find the equilibrium $\left[\mathrm{N}_{2}\right]$ and $\left[\mathrm{NH}_{3}\right]$.
b) Calculate Keq at this temperature and pressure.

Let's look at the two "time-frames":

INITIALLY or [I] - We are given [ $\mathrm{N}_{2}$ ] and [ $\mathrm{H}_{2}$ ]. Since we are not told anything about $\mathrm{NH}_{3}$, we assume that initially, $\left[\mathrm{NH}_{3}\right]=0$.

AT EQULIBRIUM or [E] - We are given $\left[\mathrm{H}_{2}\right]$ once equilibrium is reached. We need to find the other two concentrations at equilibrium.

Note that we know $\left[\mathrm{H}_{2}\right]$ initially, and at equilibrium, so we can easily find the change in or [C] of the $\left[\mathrm{H}_{2}\right]$ as the system approaches equilibrium.

We start by making a table as follows: (NOTE: We sometimes call this an (ICE) table.)
(Notice that the Species in the top row are always written in the same order as they appear in the balanced equation. This prevents confusion and minimizes errors when transferring this information.)


Now we fill the table in with all the information we are given in the question. Study this for a couple of minutes and makesure you're convinced youknow exactly where everything goes in the chart and why. Ask if you don't understand at this pont!



If you look at the chart, you will see that we know $\left[\mathrm{H}_{2}\right]$ initially and at equilibrium. We can see that $\left[\mathrm{H}_{2}\right]$ has decreased. We show this by making [C] negative for $\left[\mathrm{H}_{2}\right]$.

To calculate how much it has gone down, we subtract 0.30 from 0.66 ( 0.36). So [C] (Change in Concentration) for $\left[\mathrm{H}_{2}\right]=\underline{-0.36}$. We can insert this in the proper place in the table:

| Initial conc. $\quad[\mathrm{I}]$ | 0.32 | $\mathbf{\mathbf { N } _ { 2 }}$ | $\mathbf{3 H}_{\mathbf{2}}$ |
| :--- | :---: | :---: | :---: |
| (change in conc.) $[\mathrm{C}]$ |  | 0.66 | 0 |
| Equilibrium conc $[\mathrm{E}]$ |  | $-\mathbf{2}] \mathbf{N H}_{\mathbf{3}}$ |  |

Now to find how the other concentrations have changed, we use the equation and the mole ratios.

To keep things consistent, I like to always put "[C]'s." on top of the equation. (The concentrations are in the same ratio as the moles)

To determine whether a $[\mathrm{C}]$ is negative or positive, we use what I call the "Teeter-Totter" rule.

If you are on the same side of the teeter-totter as someone going down, you will go down also, and the person on the other side will go up.

If you are on the same side of the teeter-totter as someone going up, you will go up also, and the person on the other side will go down.

The " $\rightleftarrows$ " in the middle of the equation is like the pivot of the teeter-totter.
If you don't care for teeter-totters or silly little analogies like this, just remember, if a reaction shifts right, all reactants go down and all products go up. If it shifts left, all products go down and all reactants go up.

Looking back at our table, we see that $\left[\mathrm{H}_{2}\right]$ went down by 0.36 moles/L. $([C]=-0.36)$
We find [C] for $\mathrm{N}_{2}$ like this:


Since $\left[\mathrm{H}_{2}\right]$ and $\left[\mathrm{N}_{2}\right]$ are going down, the reaction must be shifting to the right and $\left[\mathrm{NH}_{3}\right]$ must be going up. Hence it will have a positive [C] (change in concentration)

We can also find it by using mole ratios:


Now we use the changes in concentration ([C]'s) and the initial concentrations to find the equilibrium concentrations of each species.

| $\mathbf{N}_{\mathbf{2}}$ |  |  |  |  | $\mathbf{3} \mathbf{3 H}_{\mathbf{2}}$ | $\rightleftarrows$ | $\mathbf{2 N H}_{\mathbf{3}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Initial conc. $\quad[\mathrm{I}]$ | 0.32 | 0.66 | 0 |  |  |  |  |
| (change in conc.) $[\mathrm{C}]$ | -0.12 | -0.36 | +0.24 |  |  |  |  |
| Equilibrium conc $[\mathrm{E}]$ | $0.32-0.12=\mathbf{0 . 2 0}$ | $\mathbf{0 . 3 0}$ | $0+0.24=\mathbf{0 . 2 4}$ |  |  |  |  |

Now we can answer question "a". The equilibrium $\left[\mathrm{N}_{2}\right]=\mathbf{0 . 2 0} \mathrm{M}$ and $\left[\mathrm{NH}_{3}\right]=0.24 \mathrm{M}$
The " $b$ " part of the question asked us to calculate the value of Keq for this reaction at these conditions.

First we write the expression for Keq : $\quad \mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \longleftrightarrow 2 \mathrm{NH}_{3(\mathrm{~g})}$

$$
\mathrm{Keq}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}
$$

To calculate Keq, we plug in the values for the equilibrium concentrations of all the species.
These are in the last row of the table above (the [E]'s (Equilibrium conc.))

$$
K e q=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}=\frac{(0.24)^{2}}{(0.20)(0.30)^{3}}=10.7=11\left(2 S D^{\prime} s\right)
$$

Try this:
3. Consider the following equilibrium system:

$$
2 \mathrm{NO}_{(\mathrm{g})}+\mathrm{Cl}_{2(\mathrm{~g})} \rightleftarrows 2 \mathrm{NOCl}_{(\mathrm{g})}
$$

0.80 moles of NO and 0.60 moles of $\mathrm{Cl}_{2}$ are placed into a 1.0 L container and allowed to establish equilibrium. At equilibrium $[\mathrm{NOCl}]=0.56 \mathrm{M}$.
a) Calculate the equilibrium [ NO ]
b) Calculate the equilibrium $\left[\mathrm{Cl}_{2}\right]$
c) Determine the value of Keq at this temperature. NOTE: In a 1.0 Litre container, concentration is moles/ 1.0 litre, so concentration is the same as the moles. In other words, if 0.80 moles of NO are placed in a 1.0 L container, the initial concentration of $N O=0.80 \mathrm{M}$

| $[$ I] |  |  |  |
| :--- | :--- | :--- | :--- |
| $[\mathrm{C}]$ |  |  |  |
| $[\mathrm{E}]$ |  |  |  |

a). The equilibrium $[\mathrm{NO}]=$ $\qquad$ M
b). The equilibrium $\left[\mathrm{Cl}_{2}\right]=$ $\qquad$ M
c). The value of $\mathrm{Keq}=$ $\qquad$
In another variation of Type 2 Problems, we are sometimes given the initial moles when we have something other than a 1.0 L container. In this case, you must find initial concentrations [I]. by using the familiar formula:

$$
\operatorname{Molarity}(M)=\frac{m o l}{L}
$$

Let's do an example:
Consider the equilibrium system: $\mathrm{A}+3 \mathrm{~B} \rightleftarrows 2 \mathrm{C}$
0.20 moles of $A$ and 0.60 moles of $B$ are placed in a 2.0 L container. When equilibrium is reached, the $[\mathrm{A}]$ is found to be 0.08 M . Calculate the equilibrium [B] and the equilibrium [C]
$\left.\left.\begin{array}{|l|}\hline \text { Initial }[A]=\frac{0.20 \mathrm{~mol}}{2.0 \mathrm{~L}}=0.10 \mathrm{M} \\ \hline \text { Initial }[B]=\frac{0.60 \mathrm{~mol}}{2.0 \mathrm{~L}}=0.30 \mathrm{M}\end{array}\right\} \begin{array}{l}\text { These are now ready to be plugged } \\ \text { into the [I] row of the ICE table }\end{array}\right\}$

Notice that in this case the equilibrium concentration (not moles!) of A is given. This can go right in the table under equilibrium concentration [E] of A.

| $\mathbf{A}$ |  |  |  |  | $\mathbf{3 ~ B}$ | $\mathbf{2 ~ C}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| Initial conc.(M=mol/L) $[\mathrm{I}]$ | $\mathbf{0 . 2 0} \div \mathbf{2 = \mathbf { 0 . 1 0 }}$ | $\mathbf{0 . 6 0} \div \mathbf{2 = 0 . 3 0}$ | $\mathbf{0}$ |  |  |  |
| (change in conc. $)$ | $[\mathrm{C}]$ |  |  |  |  |  |
| Equilibrium conc. | $[\mathrm{E}]$ | $\mathbf{0 . 0 8}$ |  |  |  |  |

We can see that [A] goes from 0.10 M down to 0.08 M (see column "A" in Table)
So the (change in conc. or $[\mathrm{C}]$ ) for " A " is -0.02
Use this and the mole ratios to calculate the [C]'s for B and C.
(If [A] goes down, $[\mathrm{B}]$ must also go down and $[\mathrm{C}]$ must go up (Shifting to the Right))


These can now be inserted into the " $[\mathrm{C}]$ " row in the table, and the equilibrium concentrations can be determined:

| $\mathbf{A}$ |  |  |  |  | $\mathbf{3 ~ B}$ | $\rightleftarrows$ | $\mathbf{2 ~ C}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Initial conc.(M=mol/L) <br> $[\mathrm{I}]$ | $0.20 \div 2=0.10$ | $0.60 \div 2=0.30$ | 0 |  |  |  |  |
| (change in conc.) $[\mathrm{C}]$ | -0.02 | -0.06 | +0.04 |  |  |  |  |
| Equilibrium conc. | $[\mathrm{E}]$ | $\mathbf{0 . 0 8}$ | $0.30-0.06=\mathbf{0 . 2 4}$ |  |  |  |  |

In one more variation of "Type 2", they may give you initial moles and equilibrium moles (not equilibrium concentration) in something other than a 1.0 L container.

In this case, you would have to calculate the [E] (Equilibrium concentration) from the equilibrium moles and the volume of the container using: $\quad M=\frac{m o l}{L}$
Here's an example:
Given the equilibrium: $\mathrm{X}+2 \mathrm{Y} \rightleftarrows 2 \mathrm{Z}$
When 2.0 moles of X and 3.5 moles of Y are placed in a 5.0 L container at $25^{\circ} \mathrm{C}$, an equilibrium is established in which there are 2.5 moles of $Z$.

Calculate $[\mathrm{X}],[\mathrm{Y}]$ and $[\mathrm{Z}]$ at equilibrium.
Notice that moles of Z (not [Z]) is given at equilibrium. We can find the Equilibrium [Z] using the formula: $\quad M=$ moles $/ L$. This can then be placed in the table and the rest of the calculations can be done:

Equilibrium $[Z]=\frac{2.5 \mathrm{~mol}}{0.50 \mathrm{~L}}=0.50 \mathrm{M}$

| $\mathbf{X}$ |  |  |  |
| :--- | :---: | :---: | :---: |
| $[\mathrm{I}]$ | $2.0 \div 5.0=0.40$ | $3.5 \div 5.0=0.70$ | $\mathbf{2 Y}$ |
| $[\mathrm{C}]$ |  |  | 0 |
| $[\mathrm{E}]$ |  |  | $2.5 \div 5.0=0.50$ |

Change in concentration [C], for Z must be $=+\mathbf{0 . 5 0}$ (since it started at 0 and ended up as 0.50 M )
Using mole ratios, we can find the [C]'s for X and Y : (make sure you understand how this is done!)


These are then plugged into the [C] row on the table and the rest of the calculations are performed:

| $\mathbf{X}$ |  |  |  |
| :--- | :---: | :---: | :---: |
| $[\mathrm{I}]$ | $2.0 \div 5.0=0.40$ | $\mathbf{2 Y}$ | $\mathbf{2} 5 \div 5.0=0.70$ |
| $[\mathrm{C}]$ | -0.25 | -0.50 | 0 |
| $[\mathrm{E}]$ | $0.40-0.25=0.15$ | $0.70-0.50=0.20$ | $2.5 \div 5.50$ |

We now have the answers to the question:
$[\mathrm{X}]=0.15 \mathrm{M}, \quad[\mathrm{Y}]=0.20 \mathrm{M}$, and $[\mathrm{Z}]=0.50 \mathrm{M}$ at equilibrium.

NOTE: If you were ever asked for the Equilibrium Moles of a substance (like X in this example), you would just take the equilibrium concentration and the litres given and use:

$$
\text { moles }=\boldsymbol{M} \boldsymbol{x} \text { Litres } \quad \text { eg. }) \text { moles } \mathrm{X}=0.15 \mathrm{M} \times 5.0 \mathrm{~L}=\underline{0.75} \text { moles of } \mathrm{X}
$$

**********************************************************
Here's an example for you:
4. Given the equilibrium equation:

$$
\mathrm{A}+2 \mathrm{~B} \rightleftarrows \mathrm{C}
$$

When 2.0 moles of A and 4.0 moles of B are added to a 10.0 L container, an equilibrium established in which 1.4 moles of C are found.

Find the equilibrium concentrations of $\mathrm{A}, \mathrm{B}$ and C .
(Notice that you do NOT have a 1.0 L container! Also notice that the amount of C found at equilibrium is given in moles, not in concentration. Any moles you are given in the question must be changed into concentration. And this time, you can make your own ICE table!

The equilibrium [A] = $\qquad$
The equilibrium $[\mathrm{B}]=$ $\qquad$
The equilibrium $[\mathrm{C}]=$ $\qquad$

## Type 3 - Determining What a Reaction Will Do, Given Initial Concentrations of all Species and Keq.

The ratio of [Products] to [Reactants] with the initial concentrations is called the Trial Keq.

By the "ratio", we mean the initial concentrations plugged in to the Keq expression.
For example: For the reaction $\quad \mathrm{A}_{(\mathrm{g})}+2 \mathrm{~B}_{(\mathrm{g})} \rightleftarrows 3 \mathrm{C}_{(\mathrm{g})}$
TrialKeq $=\frac{[C]^{3}}{[A][B]^{2}} \longleftarrow$ plug INITIAL concentrations into this expression to get Trial Keq
(NOTE: This is the same expression that is used for the Keq. The only difference is that the Keq has equilibrium concentrations, while the Trial Keq has initial concentrations.)

The value of the Trial Keq (initial concentrations) is then compared with the value for Keq (at equilibrium).

If Trial Keq $<\mathbf{K e q}$ the reaction will shift to the right. (a higher [products] is needed to bring the ratio up so that it does equal Keq )

If Trial Keq > Keq the reaction will shift to the left. (a lower [products] and a higher [reactants] is needed to bring down the ratio of products to reactants to make it equal the Keq .)

If Trial Keq $=$ Keq, the reaction will not shift at all. (It is already at equilibrium and no macroscopic properties, like concentration will change unless the equilibrium is disturbed.)

Let's do an example:
For the equilibrium reaction:

$$
\mathrm{CO}_{(\mathrm{g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \rightleftarrows \mathrm{CO}_{2(\mathrm{~g})}+\mathrm{H}_{2(\mathrm{~g})}
$$

The value of $\mathrm{Keq}=10.0$ at a temperature of $600^{\circ} \mathrm{C}$.
A reaction mixture is analyzed and found to contain $0.80 \mathrm{M} \mathrm{CO}, 0.050 \mathrm{M} \mathrm{H}_{2} \mathrm{O}$, $0.50 \mathrm{M} \mathrm{CO}_{2}$ and $0.40 \mathrm{M} \mathrm{H}_{2}$.

Determine which direction (left, right or not at all) the reaction will have to shift in order to reach equilibrium.

Here is how we would do this:

It doesn't say that the concentrations given are at equilibrium, so we call them initial concentrations.

We write the equilibrium equation and the expression for Keq :

$$
\mathrm{CO}_{(\mathrm{g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \rightleftarrows \mathrm{CO}_{2(\mathrm{~g})}+\mathrm{H}_{2(\mathrm{~g})}
$$

$\mathrm{Keq}=\frac{\left[\mathrm{CO}_{2}\right]\left[\mathrm{H}_{2}\right]}{\{\mathrm{CO}]\left[\mathrm{H}_{2} \mathrm{O}\right]}$
If we plug in INITIAL CONCENTRATIONS, the value for this is called the Trial Keq :

$$
\text { TrialKeq }=\frac{\left[\mathrm{CO}_{2}\right]\left[\mathrm{H}_{2}\right]}{[\mathrm{CO}]\left[\mathrm{H}_{2} 0\right]}=\frac{(0.50)(0.40)}{(0.80)(0.050)}=5.0
$$

Now in the question, they gave the actual Keq as $\underline{10.0}$ (See the $3^{r^{d} \text { line of this question.) }}$
So, in this case the Trial $\boldsymbol{K e q}<\boldsymbol{K e q}$ so this means that the reaction will have to shift to the right in order to reach equilibrium. (In other words, the ratio (5.0) is lower than it has to be at equilibrium (10.0). In order to make the ratio bigger, the reaction has to shift to the right to give a higher [products] and a lower [reactants].)

Here's a question for you to try:
5. The equilibrium equation: $\mathrm{PCl}_{5(\mathrm{~g})} \rightleftarrows \mathrm{PCl}_{3(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})}$ has a $\mathrm{Keq}=0.50$ at $25^{\circ} \mathrm{C}$.

If 0.60 moles of $\mathrm{PCl}_{3}, 0.45$ moles of $\mathrm{Cl}_{2}$ and 0.26 moles of $\mathrm{PCl}_{5}$ are all placed in a 1.0 L container, will the reaction move to the left, right or not at all in order to reach equilibrium?

Keq expression:

Trial $\mathrm{Keq}=$ $\qquad$ Actual Keq = $\qquad$ . Reaction will $\qquad$
As equilibrium is approached, what will happen to the $\left[\mathrm{PCl}_{5}\right]$ ? $\qquad$
As equilibrium is approached, what will happen to the $\left[\mathrm{PCl}_{3}\right]$ ? $\qquad$
As equilibrium is approached, what will happen to the $\left[\mathrm{Cl}_{2}\right]$ ? $\qquad$

## Type 4-Given Initial Concentrations Only and Keq and asked to Calculate the Equilibrium Concentrations of the Species.

This type of problem gives you the initial concentrations but it does NOT give you any concentrations or moles at equilibrium.

## Example:

At a particular temperature, for the reaction:

$$
\mathrm{H}_{2}+\mathrm{I}_{2} \rightleftarrows 2 \mathrm{HI} \quad \text { The Keq }=55.6
$$

If the initial $\left[\mathrm{H}_{2}\right]=0.200 \mathrm{M}$ and $\left[\mathrm{I}_{2}\right]=0.200 \mathrm{M}$, what is the equilibrium $[\mathrm{HI}]$ ?
The first thing we need to determine is,

## Which way does it have to shift in order to reach equilibrium?

To do this, we look at the value for the ratio:

$$
\frac{[H I]^{2}}{\left[H_{2}\right]\left[I_{2}\right]}
$$

when the initial values are put in (the Trial Keq) and then we compare with what the ratio has to be at equilibrium (which is, the value for Keq !)

Initially, we have no (0) HI , and $\left[\mathrm{H}_{2}\right]$ and $\left[\mathrm{I}_{2}\right]$ are both 0.200 M , so the Trial Keq is:

$$
\frac{[H I]^{2}}{\left[H_{2}\right]\left[I_{2}\right]}=\frac{(0)^{2}}{(0.200)(0.200)}=0
$$

At equilibrium, this ratio must be equal to the Keq which is $\mathbf{5 5 . 6}$. (Given at beginning of question.)
So, obviously, the ratio must go $u p$ (from 0 to 55.6) as the system approaches equilibrium.
In order for the ratio of product $(\mathrm{HI})$ to reactant $\left(\mathrm{H}_{2} \& \mathrm{I}_{2}\right)$ to go $\boldsymbol{u p}$, the reaction must shift to the right!

$$
\mathrm{H}_{2}+\mathrm{I}_{2} \longleftrightarrow 2 \mathrm{HI} \quad \text { will shift RIGHT in order to reach equilibrium. }
$$

This means $\left[\mathrm{H}_{2}\right]$ and $\left[\mathrm{I}_{2}\right]$ will go down, while $[\mathrm{HI}]$ will go up as equilibrium is approached.
OK. Now we've answered the first question, we can continue with the question:
The table for type 4 is similar but with one difference. You need the 3 important ones, namely Initial Concentration [I], $\Delta$ Conc. [C], and Equilibrium Concentration [E]

This time, however, we will leave three rows for Equilibrium Concentration. You will see why as we go through the problem.(I'm going to re-state the question here so you don't have to look back!)
At a particular temperature, for the reaction:

$$
\mathrm{H}_{2}+\mathrm{I}_{2} \rightleftarrows 2 \mathrm{HI} \quad \text { The Keq }=55.6
$$

If the initial $\left[\mathrm{H}_{2}\right]=0.200 \mathrm{M}$ and $\left[\mathrm{I}_{2}\right]=0.200 \mathrm{M}$, what is the equilibrium $[\mathrm{HI}]$ ?


Since you are not given anything at equilibrium, how do you know what [C] is going to be for any of them? Well, you don't!

But what you DO know is that the reaction will shift to the right in order to reach equilibrium. (Remember we calculated that using a Trial Keq!)

So $\left[\mathrm{H}_{2}\right]$ and $\left[\mathrm{I}_{2}\right]$ will go down and $[\mathrm{HI}]$ will go up!

$$
\mathrm{H}_{2}+\mathrm{I}_{2} \longleftrightarrow 2 \mathrm{HI}
$$

What we don't know is HOW MUCH these will go up or down!
So what we do is let the amount that $\left[\mathrm{H}_{2}\right]$ goes down $=\mathrm{x}\left(\mathrm{So}[\mathrm{C}]\right.$ for $\mathrm{H}_{2}$ is $\left.-x\right)$
(negative because it is going down!)
We can then determine [C]'s for the other species using mole ratios:


NEVER forget the coefficients to get the $\underline{\underline{2 x}}$ !!
(Of course [HI] goes up by 2 x because of the coefficient "2" DON’T FORGET THIS!!!!)

These can now be put into the table and the equilibrium concentrations can be figured out in terms of "x":

| $\mathbf{H}_{\mathbf{2}}$ | $\mathbf{+}$ | $\mathbf{I}_{\mathbf{2}}$ | $\rightleftarrows$ |
| :--- | :---: | :---: | :---: |
| $\mathbf{~} \mathrm{I}]$ | 0.200 | 0.200 | 0 |
| $[\mathrm{C}]$ | $-x$ | $-x$ | $+2 x$ |
| $[\mathrm{E}]$ | $\mathbf{0 . 2 0 0}-\mathbf{x}$ | $\mathbf{0 . 2 0 0}-\mathbf{x}$ | $\mathbf{0}+\mathbf{2 x}=\mathbf{2 x}$ |
| $[\mathrm{E}]$ |  |  |  |
| $[\mathrm{E}]$ |  |  |  |

So, how does this help us? Well, remember these are equilibrium concentrations and we have something that relates equilibrium concentrations....

Yes, friends, the Keq expression!
We know the value of Keq ( 55.6 in this case), so we plug the values from the table into the Keq expression and solve for $\boldsymbol{x}$ !

$$
\begin{aligned}
& \mathrm{H}_{2}+\mathrm{I}_{2} \rightleftarrows 2 \mathrm{HI} \\
& \mathrm{Keq}=\frac{[\mathrm{HI}]^{2}}{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]}=55.6
\end{aligned}
$$

Plugging in values for equilibrium concentrations from the [E] row of the ICE Table:

$$
K e q=\frac{(2 x)^{2}}{(0.200-x)(0.200-x)}=55.6
$$

This looks an awful lot like a quadratic, but relax! (we don't use those in Chem. 12)

$$
K e q=\frac{(2 x)^{2}}{(0.200-x)(0.200-x)}=55.6
$$

or

$$
K e q=\frac{(2 x)^{2}}{(0.200-x)^{2}}=55.6
$$

We can simplify this by taking the square root of both sides of the equation:
$\sqrt{\frac{(2 x)^{2}}{(0.200-x)^{2}}}=\sqrt{55.6}$
$\frac{2 x}{(0.200-x)}=7.4565$
We can now continue with our algebra to solve for "x". By cross multiplying:

$$
2 \mathrm{x}=7.4565(0.200-\mathrm{x})
$$

Working out the right side:

$$
2 \mathrm{x}=1.4913-7.4565 \mathrm{x}
$$

Adding 7.4565 x to both sides:

$$
2 \mathrm{x}=1.4913-7.4565 \mathrm{x}
$$

Adding 7.4565 x to both sides:

$$
\begin{aligned}
& 2 x+7.4565 x=1.4913 \\
& \text { or }
\end{aligned}
$$

$$
(2+7.4565) x=1.4913
$$

or

$$
9.4565 \mathrm{x}=1.4913
$$

or
$x=\frac{1.4913}{9.4565}=0.1577$

So we finally have that $\mathrm{x}=0.1577$, but what the heck was " x " (It was so long ago, you might not remember:)
"x" was the amount that the $\left[\mathrm{H}_{2}\right]$ went down during the shift.
Now to find out the equilibrium concentrations, we plug the value for "x" back into the table:
$\mathrm{x}=0.1577$

| $\mathbf{H}_{\mathbf{2}}$ | $\mathbf{+}$ | $\mathbf{I}_{\mathbf{2}}$ | 2HI |
| :--- | :---: | :---: | :---: |
| $[\mathrm{I}]$ | 0.200 | 0.200 | 0 |
| $[\mathrm{C}]$ | $-x$ | $-x$ | $+2 x$ |
| $[\mathrm{E}]$ | $0.200-\mathrm{x}$ | $0.200-\mathrm{x}$ | $0+2 \mathrm{x}=2 \mathrm{x}$ |
| $[\mathrm{E}]$ | $\mathbf{0 . 2 0 0 - 0 . 1 5 7 7}$ | $\mathbf{0 . 2 0 0 - 0 . 1 5 7 7}$ | $\mathbf{2 ( 0 . 1 5 7 7 )}$ |
| $[\boldsymbol{E}]$ | $\mathbf{0 . 0 4 2 3}$ | $\mathbf{0 . 0 4 2 3}$ | $\mathbf{0 . 3 1 5}$ |

Now we can answer the final question: "What is the equilibrium [HI]" We see from the table that it is 0.315 M .

Notice our answer is 3SD's (like our data) but we use more than 3 sd's when working through the algebra. Don't round much until the very end!

Final NOTE: We've done a lot of work here and there is always the possibility of a mistake. We can actually check to see if our answer is correct.

We can do this by plugging the final "Equilibrium Concentrations" into the Keq expression. If we've done everything right, the value should come out very close to the given value of Keq , which is 55.6 in this case. Let's try it!

$$
\text { Keq } \left.=\frac{[\mathrm{HI}]^{2}}{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]}=\frac{(0.315)^{2}}{(0.0423)^{2}}=55.45 \quad \text { (close enough }\right)
$$

Here's a question for you to try:
6. Consider the reaction:

$$
\mathrm{H}_{2(\mathrm{~g})}+\mathrm{CO}_{2(\mathrm{~g})} \longleftrightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}+\mathrm{CO}_{(\mathrm{g})}
$$

At a certain temperature the $\mathrm{K}_{\mathrm{eq}}$ for this reaction $=1.50$
If the initial concentration of all four species $=0.500 \mathrm{M}$, calculate the equilibrium concentration of $\mathrm{CO}_{2}$ and CO .
Remember to determine which way the reaction has to shift in order to reach equilibrium using a Trial Keq (Sometimes this can be done in your head)
(Look at the example given before this to help you find this out.)

Answer $\quad[\mathrm{CO}]=$ $\qquad$
$\left[\mathrm{CO}_{2}\right]=$ $\qquad$

Try these questions:

1. Given the equilibrium: $3 \mathrm{~A}_{(\mathrm{g})}+\mathrm{B}_{(\mathrm{g})} \rightleftarrows 2 \mathrm{C}_{(\mathrm{g})}$

If 4.0 moles of A and 2.0 moles of B are added to a 2.0 L container, an equilibrium is established in which the $[\mathrm{C}]=0.40 \mathrm{M}$.
a) Calculate the equilibrium $[\mathrm{A}]$ and $[\mathrm{B}]$

Equilibrium $[\mathrm{A}]=$ $\qquad$
Equilibrium $[\mathrm{B}]=$ $\qquad$
b) Calculate the value of Keq at the temperature at which this was carried out.

$$
\mathrm{Keq}=
$$

$\qquad$
2. Given the equilibrium equation:

$$
\mathrm{A}_{(\mathrm{g})}+\mathrm{B}_{(\mathrm{g})} \rightleftarrows \mathrm{C}_{(\mathrm{g})}+\mathrm{D}_{(\mathrm{g})}
$$

The value of Keq for this reaction at $25^{\circ} \mathrm{C}$ is 34.6
0.200 moles of $\mathrm{A}, \mathrm{B}, \mathrm{C} \& \mathrm{D}$ are all added to a 1.0 L container.

Calculate the $[B]$ at equilibrium.
HINT: The reaction will have to shift to the $\qquad$ in order to reach equilibrium. (more room on next page...)

Equilibrium $[\mathrm{B}]=$
3. Consider the equation:

$$
2 \mathrm{X}_{(\mathrm{g})}+3 \mathrm{Y}_{(\mathrm{g})} \longleftrightarrow 2 \mathrm{Z}_{(\mathrm{g})}
$$

An equilibrium mixture is analyzed and $[\mathrm{X}]$ is $0.030 \mathrm{M},[\mathrm{Y}]=0.500 \mathrm{M}$ and $[\mathrm{Z}]=0.600 \mathrm{M}$

Calculate the value of Keq for this reaction.

$$
\mathrm{Keq}=
$$

4. The Keq for the reaction: $\mathrm{A}_{(\mathrm{g})}+\mathrm{B}_{(\mathrm{g})} \rightleftarrows 2 \mathrm{C}_{(\mathrm{g})}$ is $\mathbf{1 . 2 0}$

A mixture of $\mathrm{A}, \mathrm{B}$ and C is analyzed and found to contain $3.0 \mathrm{M} \mathrm{A}, 0.40 \mathrm{M} \mathrm{B}$ and 2.50 M C .

This reaction will shift which way (left, right or not at all) in order to reach equilibrium?

Trial $\mathrm{Keq}=$ $\qquad$ The reaction will shift to the $\qquad$
As equilibrium is approached, the [A] will $\qquad$ , [B] will $\qquad$ and the [C] will $\qquad$

