Method of Successive Approximations

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General Chemistry II

Goal:	To learn an advanced technique for calculating equilibrium concentrations.
Previous Skills:	An understanding of the equilibrium equation. An understanding of the equilibrium constant. Simple equilibrium calculations using an ICE table.

At this level, many of the chemical equations we use when solving for equilibrium concentrations are fairly simple. We do this in order to get the basic idea across without making it too difficult. For example, let's look at the steam conversion of carbon monoxide to carbon dioxide and hydrogen gas at 1000 K.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If $K_C = 1.4$ (at 1000 K) and the initial concentrations of carbon monoxide and water vapor are 0.0500 M, what are the equilibrium concentrations of all the reactants and products? Here's the ICE table (remember what we did in class to determine the direction for the change)-

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
I	0.0500		0.0500		0		0
C	- x		- x		+ x		+ x
E	0.0500 - x		0.0500 - x		x		x

Using the equilibrium equation we get-

$$\left(\frac{[CO_2][H_2]}{[CO][H_2O]}\right) = 1.4 \quad \text{or} \quad \left(\frac{(x)(x)}{(0.0500 - x)(0.0500 - x)}\right) = 1.4$$

The initial values and the type of chemical equation allow us to make an easy simplification when solving for x.

$$\sqrt{\left(\frac{x^2}{(0.0500 - x)^2}\right)} = \sqrt{1.4} \qquad \left(\frac{x}{(0.0500 - x)}\right) = \sqrt{1.4}$$

Upon solving for x we get then determine the equilibrium concentrations for everything.

$$[CO(g)] = [H_2O(g)] = 0.023\text{ M} \qquad [CO_2(g)] = [H_2(g)] = 0.027\text{ M}$$

Let's check our answer by plugging the equilibrium concentrations back into the equilibrium equation and see how close it is to the given equilibrium constant.

$$\left(\frac{(0.027)^2}{(0.0500-0.023)^2}\right)=1.0 \qquad \text{which is fairly close to 1.4}$$

Let's now look at the steam conversion of methane, CH_4, to carbon dioxide and hydrogen gas.

$$CH_4(g)+2H_2O(g) \rightleftharpoons CO_2(g)+4H_2(g)$$

If $K_C = 7.4 \times 10^{-3}$ (at 1000 K) and the initial concentration of methane is 1.20 M and that of water vapor is 1.00 M, what are the equilibrium concentrations of all the reactants and products?

	$CH_4(g)$	+	$2H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$4H_2(g)$
I	1.20		1.00		0		0
C	- x		- 2x		+ x		+ 4x
E	1.20 - x		1.00 - 2x		x		4x

Using the equilibrium equation we get-

$$\left(\frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}\right)=0.0074 \quad \text{or} \quad \left(\frac{(x)(4x)^4}{(1.20-x)(1.00-2x)^2}\right)=0.0074$$

Since we won't be solving for x as done in the previous problem, we'll use a different technique called the "**method of successive approximations**." The idea is to get a value for x such that when we plug it back into the previous equation, we'll get a value that's "close enough" to 0.0074. This usually involves multiple steps but we have to start with something as or initial guess for x. Pick something that's reasonable with respect to the initial concentrations and the denominator. We'll try 0.25 as the initial guess.

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<u>(1) Initial Guess</u>: x = 0.25

$$\left(\frac{(0.25)(4(0.25))^4}{(1.20-0.25)(1.00-2(0.25))^2}\right)=1.05$$

The result is larger than 0.0074. We'll try a value for x less than 0.25 and see what happens.

<u>(2) New Guess</u>: x = 0.20

$$\left(\frac{(0.20)(4(0.20))^4}{(1.20-0.20)(1.00-2(0.20))^2}\right)=0.227$$

This value is closer to 0.0074 so our new, smaller guess was a better one. We'll make it smaller and see what happens.

<u>(3) New Guess</u>: x = 0.15

$$\left(\frac{(0.15)(4(0.15))^4}{(1.20-0.15)(1.00-2(0.15))^2}\right)=0.0378$$

This value is closer to 0.0074 than our previous guess. We'll make it smaller and see what happens.

<u>(4) New Guess</u>: x = 0.10

$$\left(\frac{(0.10)(4(0.10))^4}{(1.20-0.10)(1.00-2(0.10))^2}\right)=0.00364$$

Hmm. This guess for x resulted in value less than 0.0074 which means our guess was too small. We'll try again but use a guess for x that's a little larger.

<u>(5) New Guess</u>: x = 0.12

$$\left(\frac{(0.11)(4(0.11))^4}{(1.20-0.11)(1.00-2(0.11))^2}\right)=0.00622$$

This new value is closer to 0.0074. At what point do we stop? Well, when we are "close enough". Let's calculate the equilibrium values based on our value for x:

$$[CH_4] = 1.20 - 0.11 = 1.09 \text{ M} \qquad [CO_2] = 0.11 \text{ M}$$
$$[H_2O] = 1.00 - 2(0.11) = 0.78 \text{ M} \qquad [H_2] = 4(0.11) = 0.44 \text{ M}$$

Now, let's check the percent deviation:

$$\left(\frac{0.0062 - 0.0074}{0.0074}\right)(100) = 16\%$$

This method is commonly used but it's not typically done by hand anymore. It makes more sense these days to write a computer program. Once you've seeded the program with a reasonable initial guess for x, the program iterates the procedure until a value for x gives a result that's close to 0.0074 (in this case) using a user-defined tolerance for "close enough". This iterative method is extremely powerful but it can produce some strange results and there are some pitfalls to avoid.