Solving Equilibrium Problems Using the Conservation of Mass Equations

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Our purpose is to show how the familiar atom conservation equations may be combined with the equilibrium expression to yield a series of equations that solve the equilibrium problem: *given*, the algebraic mass action expression for a reacting system, its numerical value and the initial concentrations of reactants and products, *find* the equilibrium concentrations.

As a concrete example, consider the Haber reaction as presented in Table 6.1 of your text. The equilibrium system is

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$

The value of K for this system is given as 6.02 x 10^{-2}. The initial concentrations are

$$[N_2]_0,\ [H_2]_0,\ [NH_3]_0$$

The final concentrations at equilibrium are

$[N_2] = x$, $[H_2] = y$ and $[NH_3] = z$.

The equilibrium condition in terms of the unknowns is

$$K = \frac{z^2}{xy^3} \qquad (1)$$

The above is one (non-linear) equation in three unknowns. For this system, we need two more equations. The mass conservation equations are appropriate constraints to this system. We provide equations for conservation of nitrogen atoms and hydrogen atoms as follows:

$$\text{N:}\ \ 2[N_2]_0 + 3[NH_3]_0 = 2y + z \qquad (2)$$

$$\text{H:}\ \ 2[H_2]_0 + 3[NH_3]_0 = 2y + 3z \qquad (3)$$

Equations 1-3 represent a system of three equations in three unknowns. We solve this system for x by eliminating y and z from these equations.

Solve Equation 2 for z

$$z = 2[N_2]_0 + [NH_3]_0 - 2x \qquad (4)$$

Put Equation 4 into Equation 3

$$2[H_2]_0 + 3[NH_3]_0 - 3z = 2y \quad (5)$$

$$2[H_2]_0 + 3[NH_3]_0 - 6[N_2]_0 - 3[NH_3]_0 + 6x = 2y \quad (6)$$

$$[H_2]_0 - 3[N_2]_0 + 3x = y \quad (7)$$

Put Equations 4 and 7 into Equation 1. This results in a final polynomial equation in x alone

$$K = \frac{\left(2[N_2]_0 + [NH_3]_0 - 2x\right)^2}{x\left([H_2]_0 - 3[N_2]_0 + 3x\right)^3} \quad (8)$$

To clarify, make the following substitutions:

$$2[N_2]_0 + [NH_3]_0 = A \quad (9)$$

$$[H_2]_0 - 3[N_2]_0 = B \quad (10)$$

Then, Equation 8 becomes

$$K = \frac{(A - 2x)^2}{x(B + 3x)^3} \quad (11)$$

After expanding, Equation 11 becomes

$$K = \frac{A^2 - 4Ax + 4x^2}{B^3x + 9B^2x^2 + 27Bx^3 + 27x^4} \quad (12)$$

$$K\left(B^2x + 9B^2x^2 + 27Bx^3 + 27x^4\right) =$$

$$KB^3x + 9KB^2x^2 + 27KBx^3 + 27Kx^4 = A^2 - 4Ax + 4x^2 \quad (13)$$

Then rearrange Equation 13 in descending powers of x:

$$27Kx^4 + 27KBx^3 + \left(9KB^2 - 4\right)x^2 + \left(KB^3 + 4A\right)x - A^2 = 0 \quad (14)$$

The above is the polynomial to be solved for. This gives us x, but we also want y and z. These may be obtained by back substitution as

$$z = 2[N_2]_0 + [NH_3]_0 - 2x \quad (15)$$

and

$$y = (3[NH_3]_0 + 2[H_2]_0 - 3z \quad (16)$$

Now we have what is needed to make up a calculator problem that solves the Haber equilibrium problem once and for all!

Here is a basic program for the TI 83/84 that you can enter into your calculator:

```
Prompt K
Prompt N
Prompt H
Prompt A
2*N+AüC
H-3*NüD
solve(27*K*X^4+27*K*D*X^3+(9*K*D^2-4)*X^2+(K*D^3+4C)*X-C^2,X,4,{0,5})
Disp " N IS",Ans
AnsüM
2*N+A-2*MüZ
(3*A+2*H-3*Z)/2üY
Disp "H IS",Y
Disp "A IS",Z
Stop
```

You can also down load this program in ready to go format. To try it out, see if you can duplicate the results in Table 6.1 of your text book.