Chemical Reaction Engineering - Part 3
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Stoichiometry

We can write a balance equation for all components in one reaction but we don't need to do that if we are dealing with what I call "simple" reactors. These are reactors in which the relative amounts of components change only by reaction. Batch reactors are simple reactors in this sense. Semi-batch reactors in which one or more components are fed or removed during the reaction are not simple reactors.

For a single reaction in a batch reactor, if we know the initial composition and the concentration of any one component at some later time, then we can compute the concentrations of the other components using a stoichiometric table or mole table. This is easy for the A=B reaction considered above but we have to do more work for more complex reactions.

Consider this form of a stoichiometric equation.

$$A + bB = cC + dD$$
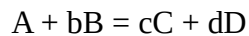
where b, c and d are numbers and A, B, C and D are the names or formulae of the components.

The equation is written so that the coefficient of the limiting or key (important) reactant is one. If you are given an equation where this is not the case, just divide by a constant to get this form.

Now move all the reactants to the right hand side.

$$0 = -A - bB + cC + dD$$

This is the general form of a stoichiometric equation:

$$0 = \sum \upsilon_i \mathcal{A}_i$$

where $\mathcal{A}_i$ are the names or formulae of the components, and υ_i are the "formal stoichiometric coefficients." Here,

$$\upsilon_1 = \upsilon_A = -1 \qquad \mathcal{A}_1 = A$$
$$\upsilon_2 = \upsilon_B = -b \qquad \mathcal{A}_2 = B$$
$$\upsilon_3 = \upsilon_C = c \qquad \mathcal{A}_3 = C$$
$$\upsilon_4 = \upsilon_D = d \qquad \mathcal{A}_4 = D$$

Note that the formal stoichiometric coefficients of the reactants are negative and those of the products are positive.

For a single reaction, the rates of the different components in the stoichiometric equation are related this way.

$$\frac{r_i}{\upsilon_i} = \frac{r_j}{\upsilon_j} = \frac{r_k}{\upsilon_k} = \text{constant for all components in one reaction}$$

Write a stoichiometric table by writing the following equation for each component in the stoichiometric equation.

$$N_i = N_{i0} + \upsilon_i N_{A0} X_A$$

where X_A is the conversion of the limiting or key reactant A

$$X_A = \frac{N_{A0} - N_A}{N_{A0}}$$

Conversions are dimensionless. If you are dealing with gases, also write a line for any inerts

$$N_{Inert} = N_{Inert 0}$$

and then sum all the columns in the table to get the total number of moles of gas N_{tot} to use in computation of gas volume or pressure. In this course, we will use the ideal gas law unless told otherwise.

You may remember the stoichiometric extent of reaction from your material balance course. The conversion can be related to the stoichiometric extent of reaction ξ and the stoichiometric table can be written in terms of the extent. We will need to use extents with multiple reaction systems but can stick with conversion for single reactions.

$$X_A = \frac{\xi}{N_{A0}} \quad ; \quad N_i = N_{i0} + \upsilon_i \xi$$

Here is an example for the gases CO, O_2, CO_2 and N_2 where CO is the limiting reactant A.

$$CO + 0.5\ O_2 = CO_2$$
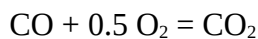
Stoichiometric table (mole table)

$$N_{CO} = N_{CO,0} - N_{CO,0} X_{CO}$$
$$N_{O_2} = N_{O_2,0} - 0.5\ N_{CO,0} X_{CO}$$
$$N_{CO_2} = N_{CO_2,0} + N_{CO,0} X_{CO}$$
$$N_{N_2} = N_{N_2,0}$$
$$\overline{\phantom{N_{tot} = N_{tot,0} - 0.5 N_{CO,0} X_{CO}}}$$
$$N_{tot} = N_{tot,0} - 0.5\ N_{CO,0} X_{CO}$$

For this example, the total number of moles of gas decreases as the conversion of CO increases. In a constant volume, isothermal batch reactor, this will result in decreasing gas pressure.

Let's say the rate equation is the following in a batch reactor. Since we don't show the reverse reaction, this would be true for conditions in which the equilibrium conversion of CO is almost complete, which is often the case.

$$r_{CO} = -k\, C_{CO}\, C_{O_2}$$

We say that a reaction is "essentially reversible" or, loosely, "irreversible" when the reactant conversion at equilibrium closely approaches one. In that case, we can neglect the back reaction, except when we want to get very close to equilibrium conversion.

$$\frac{d\, N_{CO}}{d\, t} = r_{CO}\, V = -k\, C_{CO}\, C_{O_2}\, V$$

For a batch reactor, the concentration of any component is given by

$$C_i = \frac{N_i}{V}$$

We can get any N_i in terms of X_{CO} from the stoichiometric table

$$\frac{d\, N_{CO}}{d\, t} = -N_{CO,0} \frac{d\, X_{CO}}{d\, t} = r_A\, V = -k\, C_{CO}\, C_{O_2}\, V$$

$$-N_{CO,0} \frac{d\, X_{CO}}{d\, t} = -k\, \frac{N_{CO}}{V}\, \frac{N_{O_2}}{V}\, V$$

$$\frac{d\, X_{CO}}{d\, t} = k(1 - X_A) \frac{N_{O_2}}{V}$$

For a variable volume reactor, we can use the ideal gas law and the expression for N_{tot} to get V as a function of X_{CO}.

Here, specify that the reactor volume V is constant.

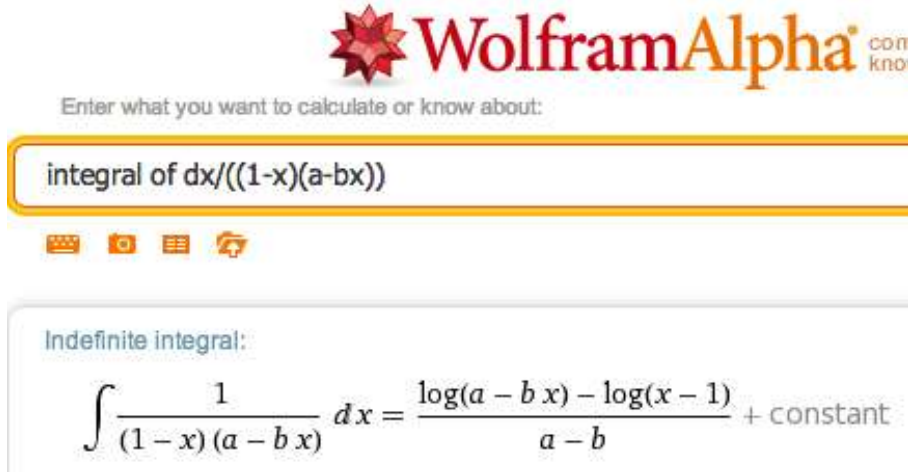$$\frac{d\, X_{CO}}{d\, t} = k(1 - X_{CO})(C_{O_2,0} - 0.5\, C_{CO,0}\, X_{CO})$$

Now we have written our equation in terms of the one dependent variable X_{CO} and can separate variables (separate X_{CO} and t).

$$\frac{d\, X_{CO}}{(1 - X_{CO})(C_{O_2,0} - 0.5\, C_{CO,0}\, X_{CO})} = k\, dt$$

Then we can integrate from our initial conditions, which are

$$t=0 \; ; \; X_{CO}(0)=0 \; ; \; C_{CO}(0)=C_{CO,0} \; ; \; C_{O_2}(0)=C_{O_2,0}$$

WolframAlpha.com is useful for problems like this. The "log" below is the natural log ("ln") as in Matlab, not log to the base 10 as in normal handwriting.

Important new terms

simple reactor
formal stoichiometric coefficients
stoichiometric table or mole table
stoichiometric extent of reaction
variable volume reactor

Additional resources

Schmidt's book - on library reserve & online via http://roger.ucsd.edu/record=b7179459~S9
        Chapter 2 - sections 7, 16, 17 [note: Schmidt uses χ for extent, not ξ]

Fogler's "Essentials" book - on library reserve for this course
        Chapter 4 - section 1

Fogler also has an older "Elements" book on reserve. Use the "Essentials" book if it is available.
Chapter 3 and 4 of "Essentials" is Chapter 3 of "Elements."