General Method for Calculating Chemical Equilibrium Composition

1) For given initial conditions (e.g., for given reactants), **choose the species** to be included in **the products**.

As an example, for combustion of hydrogen with air we might chose the following products: H_2O, H_2, O_2, N_2, NO, OH, H, and NO_2. In terms of a conversion reaction, we would write:

$$\phi H_2 + \frac{1}{2}(O_2 + 3.76N_2) \rightarrow n_{H_2O}H_2O + n_{H_2}H_2 + n_{O_2}O_2 + n_{N_2}N_2 + n_{NO}NO + n_{OH}OH + n_H H + n_{NO_2}NO_2$$

where ϕ represents an arbitrary number of moles of the fuel (and also in the way this equation was chosen to be written it is also called the **equivalence ratio**, where a value of ϕ=1 represents just the right number of moles of fuel to react with the oxygen to form only the most stable combustion products, H_2O in this case).

2) For a mixture of M species, there are generally M+2 unknowns: M concentrations, n_i, and two intensive properties, e.g., T and P. For a mixture consisting of R atoms, e.g. R=4 for the C/H/O/N system, we can write R atom conservation equations. You can think of each of the conservation equations as initial conditions or constraints. (Note, these R equations may not be independent, in which case we can only use as many as are independent.) If we further specify two thermodynamic properties, we typically have M-R unknowns. One could specify the T and P of the products, or for example in adiabatic flame temperature calculations, you would specify H and P of the products.

We solve for the M-R unknowns using stoichiometric reaction relationships to give us enough independent K_p. To come up with the M-R reactions, one method is to **write formation reactions for each species** present, except for the "element" species. (*Note: this method is not so helpful if one of the element species in not part of the mixture.*)

In our example (M=8,R=3), we need 5 formation reactions:

$$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$$
$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \Leftrightarrow NO$$
$$\frac{1}{2}H_2 + \frac{1}{2}O_2 \Leftrightarrow OH$$
$$\frac{1}{2}H_2 \Leftrightarrow H$$
$$\frac{1}{2}N_2 + O_2 \Leftrightarrow NO_2$$

3) Next, **write equilibrium relationships** for each formation reactions using the $Kp_{f,i}$ for each.

For our hydrogen/air example, we have:

$$X_{H_2O} = K_{P_{f,H_2O}} X_{H_2} X_{O_2}^{1/2} P^{1/2}$$
$$X_{NO} = K_{P_{f,NO}} X_{N_2}^{1/2} X_{O_2}^{1/2}$$
$$X_{OH} = K_{P_{f,OH}} X_{H_2}^{1/2} X_{O_2}^{1/2}$$
$$X_H = K_{P_{f,H}} X_{H_2}^{1/2} P^{-1/2}$$
$$X_{NO_2} = K_{P_{f,NO_2}} X_{N_2}^{1/2} X_{O_2} P^{1/2}$$

4) Now, we include the (independent) **atom conservation equations**.

Again for our example, we get:

$$n_{H\,atoms} = 2\phi = (2X_{H_2O} + 2X_{H_2} + X_H + X_{OH})n_{tot}$$
$$n_{O\,atoms} = 1 = (X_{H_2O} + 2X_{O_2} + X_{OH} + X_{NO} + 2X_{NO_2})n_{tot}$$
$$n_{N\,atoms} = 3.76 = (2X_{N_2} + X_{NO} + X_{NO_2})n_{tot}$$

where n_{tot} is the total number of product moles per ϕ moles of H_2 and is unknown at this point.

5) To remove the n_{tot} dependence, we use atom balance ratios (physically, it is these ratios, not the total number of moles, which are most important), and we add the constraint that the mole fractions must sum to unity, e.g.,

$$\frac{n_{H\,atoms}}{n_{O\,atoms}} = \frac{2\varphi}{1} = \frac{(2X_{H_2O} + 2X_{H_2} + X_H + X_{OH})}{(X_{H_2O} + 2X_{O_2} + X_{OH} + X_{NO} + 2X_{NO_2})}$$
$$\frac{n_{N\,atoms}}{n_{O\,atoms}} = \frac{3.76}{1} = \frac{(2X_{N_2} + X_{NO} + X_{NO_2})}{(X_{H_2O} + 2X_{O_2} + X_{OH} + X_{NO} + 2X_{NO_2})}$$
$$1 = X_{H_2O} + X_{H_2} + X_{OH} + X_{O_2} + X_H + X_{N_2} + X_{NO} + X_{NO_2}$$

6) Now **given two thermodynamic properties**, we have enough information to solve for the unknown X_i. If T and P of the products are known, the solution simply consists of determining the $Kp_{f,i}$ from a source such as the JANNAF tables.

If the final temperature is unknown, for example in an adiabatic flame temperature calculation, then the solution is iterative: guessing T, finding the product composition, then calculating its associated T and using it to improve your guess at T. As an alternative for calculating the final temperature, one can realize that most of the energy is associated with the presence of the "major" (largest X_i) species. Therefore you can ignore all the other/"minor" species on your first iteration and get a very close estimate of T using the major species only. Then go back and reiterate, now including the minor species. For rough estimates of product compositions, you can simply take the temperature and the species mole fractions found from the major species product calculations and use them, along with stoichiometric reactions that form the minor species from the major species (i.e., appropriate K_p), to calculate the minor species concentrations. This approach is known as the *major-minor model or major-minor species approximation*. In some cases, like the hydrogen/air example described above, one can get a simple algebraic solution for the mole fractions of the major products using the major species model (see below).

Of course, the easiest way to solve the problem is to use a chemical equilibrium computer code/tool. You still have to determine the products to be included in the calculation, and the initial conditions, e.g., initial atom ratios, but then the computer can perform the thermodynamic property evaluations and the iterations!!

7) **Major-Minor Model**: To illustrate the use of the major-minor model, let's estimate the flame temperature for the hydrogen/air combustion example. First, we choose the major species; we let the products be H_2O, N_2 and either O_2 (for lean mixtures) or H_2 (for rich mixtures). Writing the reactions for the two cases and denoting the stoichiometric coefficients for the products in terms of ϕ from simple atom balances, we have

$$for\,\phi<1: \quad \phi H_2+\frac{1}{2}\left(O_2+3.76N_2\right)\rightarrow \phi H_2O+\frac{1-\phi}{2}O_2+1.88N_2$$

$$for\,\phi>1: \quad \phi H_2+\frac{1}{2}\left(O_2+3.76N_2\right)\rightarrow H_2O+(\phi-1)H_2+1.88N_2$$

Major Species Mole Fractions: From the above reaction equations and with algebra, we get:

X_i	ϕ<1 (lean)	ϕ>1 (rich)
H_2O	$\phi\Big/\left(\frac{\phi+1}{2}+1.88\right)$	$1/(\phi+1.88)$
N_2	$1.88\Big/\left(\frac{\phi+1}{2}+1.88\right)$	$1.88/(\phi+1.88)$
O_2	$\left(\frac{1-\phi}{2}\right)\Big/\left(\frac{\phi+1}{2}+1.88\right)$	
H_2		$(\phi-1)/(\phi+1.88)$

Thus simply given ϕ (the H:O ratio), we know the product composition and can calculate the final temperature. For example with ϕ=1.3 (rich combustion), we get,

$$X_{H_2O}=0.3145$$
$$X_{N_2}=0.5912$$
$$X_{H_2}=0.0943$$

Adiabatic Flame Temperature: Assuming an initial temperature of -55 °C (218 K) for the reactants, we find the adiabatic flame temperature using $\Delta P=0$ and $\Delta H_R=0$, i.e.,

$$H_{\text{Products}}(T_{ad})=H_{\text{Reactants}}(218K)$$
$$\sum_{\text{Products}} n_i\left[\left(\bar{h}_{T_{ad}}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_i=\sum_{\text{Reactants}} n_i\left[\left(\bar{h}_{218K}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_i$$

Writing out the summation for each product and reactant, and using the number of moles of each for our ϕ=1.3 flame we have,

$$1mol_{H_2O}\left[\left(\bar{h}_{T_{ad}}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_{H_2O}+1.88mol_{N_2}\left[\left(\bar{h}_{T_{ad}}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_{N_2}+0.3mol_{H_2}\left[\left(\bar{h}_{T_{ad}}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_{H_2}$$
$$=1.3mol_{H_2}\left[\left(\bar{h}_{218K}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_{H_2}+0.5mol_{O_2}\left[\left(\bar{h}_{218K}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_{O_2}+1.88mol_{N_2}\left[\left(\bar{h}_{218K}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_{N_2}$$

Since the enthalpy of formation for elements is zero, we get

$$1mol_{H_2O}\left[\left(\bar{h}_{T_{ad}}-\bar{h}_{T_{ref}}\right)+\Delta\bar{h}_{f,T_{ref}}\right]_{H_2O}+1.88mol_{N_2}\left[\left(\bar{h}_{T_{ad}}-\bar{h}_{T_{ref}}\right)\right]_{N_2}+0.3mol_{H_2}\left[\left(\bar{h}_{T_{ad}}-\bar{h}_{T_{ref}}\right)\right]_{H_2}$$
$$=1.3moles_{H_2}\left[\left(\bar{h}_{218K}-\bar{h}_{T_{ref}}\right)\right]_{H_2}+0.5moles_{O_2}\left[\left(\bar{h}_{218K}-\bar{h}_{T_{ref}}\right)\right]_{O_2}+1.88moles_{N_2}\left[\left(\bar{h}_{218K}-\bar{h}_{T_{ref}}\right)\right]_{N_2}$$

Data for Δh_f of water and the sensible enthalpy changes for each species* can be found in a number of sources, e.g., the JANNAF tables. Using this data, one finds $T_{ad}\approx$2300K.

<u>Minor Species Mole Fractions:</u> We can write the following stoichiometric relationships between the minor species and the major species of our rich hydrogen/air flame (for emphasis, the minor species are written in bold letters). Each reaction represents a method for producing the minor species using only the major products of our hydrogen/air flame.

$$2H_2O \Leftrightarrow \mathbf{O_2} + 2\mathrm{H_2}$$
$$\frac{1}{2}N_2 + H_2O \Leftrightarrow \mathbf{NO} + \mathrm{H_2}$$
$$H_2O \Leftrightarrow \mathbf{OH} + \frac{1}{2}\mathrm{H_2}$$
$$\frac{1}{2}H_2 \Leftrightarrow \mathbf{H}$$
$$\frac{1}{2}N_2 + 2H_2O \Leftrightarrow \mathbf{NO_2} + 2\mathrm{H_2}$$

Now we can write the following expressions for the mole fractions of the minor species in terms of the major species X_i:

$$X_{O_2} = K_{P_{f,H_2O}}^{-2} X_{H_2O}^{2} X_{H_2}^{-2} P^{-1}$$
$$X_{NO} = K_{P_{f,NO}} K_{P_{f,H_2O}}^{-1} X_{N_2}^{1/2} X_{H_2O} X_{H_2}^{-1} P^{-1/2}$$
$$X_{OH} = K_{P_{f,OH}} K_{P_{f,H_2O}}^{-1} X_{H_2O} X_{H_2}^{-1/2} P^{-1/2}$$
$$X_{H} = K_{P_{f,H}} X_{H_2}^{1/2} P^{-1/2}$$
$$X_{NO_2} = K_{P_{f,NO_2}} K_{P_{f,H_2O}}^{-2} X_{N_2}^{1/2} X_{H_2O}^{2} X_{H_2}^{-2} P^{-1/2}$$

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*It is not reasonable to assume that c_p is constant in $h_T - h_{T\,ref} = \int_{T_{ref}}^{T} c_p(T')dT'$ for our large temperature range.

where we have used the fact that K_p for each of the stoichiometric reactions is simply a function of the formation equilibrium constants of the species in the reaction. For example for the reaction

$$2H_2O \Leftrightarrow O_2 + 2H_2$$

the equilibrium constant is given by

$$K_p = \frac{K^2_{p_{f,H_2}} K_{p_{f,O_2}}}{K^2_{p_{f,H_2O}}} = \frac{1}{K^2_{p_{f,H_2O}}}$$

since the formation equilibrium constant K_{pf} of an element is unity (by definition).

Using the Kp_f from the JANNAF tables at 2300 K, the estimated X_i for the major species, and assuming a pressure of 1 bar, we get the values for the minor species X_i listed in the table below. As a comparison, the table below also includes results from a complete solution obtained with the STANJAN chemical equilibrium code. While not completely accurate, the major-minor model does a good job of predicting the flame temperature (+25 K or ~1% relative error) and the major species' mole fractions (<1% relative error), and gives a reasonable estimate of the minor species' mole fractions (within a 40% relative error, and certainly better than one order-of-magnitude). Thus for rough approximations, the major-minor model is simple and reasonably accurate.

Species/T_{ad}	Major-Minor Model	Full Calculation	Error(%)
T_{ad}	2300 K	2275 K	1.1
N_2	59.1%	59.0%	0.17
H_2O	31.5%	31.2%	0.96
H_2	9.4%	9.4%	0
H	0.30% (3000 ppm)	0.26% (2600 ppm)	15
OH	0.16% (1600 ppm)	0.13% (1300 ppm)	23
NO	220 ppm	180 ppm	22
O_2	49 ppm	36 ppm	39
NO_2	3.4 ppb	2.5 ppb	36

ppm=parts per million ($\times 10^{-6}$), ppb=parts per billion ($\times 10^{-9}$)