ME 410 Day 14

Topics

- A More Comprehensive Equilibrium Model
- EES Implementation of this Model
- Web Applet of this Model
- EES Model with even More Species!
- Discussion

Remarks

- The general problem of chemical equilibrium may be stated in terms of the minimization of certain thermodynamic functions (e.g. the Gibbs Free Energy, or the Helmholtz Free Energy) subject to the constraints of the stoichiometry.
- This is a Lagrange Multiplier Problem.
- There are shortcuts. Here's one.

1. Chemical Equilibrium with Equilibrium Constants

Here's the main reaction.

$$C_\alpha H_\beta O_\gamma N_\delta + \frac{a_s}{\phi}\left(O_2 + 3.773N_2\right) \rightarrow \begin{aligned} & n_1CO_2 + n_2H_2O + \\ & n_3N_2 + n_4O_2 + \\ & n_5CO + n_6H_2 + \\ & n_7H + n_8O + \\ & n_9OH + n_{10}NO \end{aligned}$$

Note that we are allowing for disassociated H, O, OH as well as NO.

The a_s is the stoichiometric number for complete combustion of that particular fuel.

Let

$$N = \sum_{i=1}^{10} n_i \qquad \text{the total number of moles of product.}$$

We now balance the equation chemically.

Carbon: $\alpha = (y_1 + y_5)N$

Hydrogen: $\beta = (2y_2 + 2y_6 + y_7 + y_9)N$

Oxygen:

$$\gamma + \frac{2a_s}{\phi} = (2y_1 + y_2 + 2y_4 + y_5 + y_8 + y_9 + y_{10})N$$

Nitrogen: $\delta + \dfrac{2a_s(3.773)}{\phi} = (2y_3 + y_{10})N$

The quantities y are mole fractions: $y_i = \dfrac{n_i}{N}$

Hence $\displaystyle\sum_{i=1}^{10} y_i = 1$

Next we will look over a list of equilibrium reactions which are taking place in the mixture.

Apparently, this is a more sophisticated model that the water gas reaction we used yesterday. It is certainly more applicable at high temperatures.

The scheme will be to present the reaction, followed by the definition of the equilibrium constant that applies, written out in terms of the mole fractions y_i and the total pressure P, which must be given in atmospheres.

$$\frac{1}{2}H_2 = H \qquad K_1 = \frac{y_7 P^{0.5}}{y_6^{0.5}}$$

$$\frac{1}{2}O_2 = O \qquad K_2 = \frac{y_8 P^{0.5}}{y_4^{0.5}}$$

$$\frac{1}{2}H_2 + \frac{1}{2}O_2 = OH \qquad K_3 = \frac{y_9}{y_4^{0.5} y_6^{0.5}}$$

$$\frac{1}{2}O_2 + \frac{1}{2}N_2 = NO \qquad K_4 = \frac{y_{10}}{y_4^{0.5} y_3^{0.5}}$$

$$H_2 + \frac{1}{2}O_2 = H_2O \qquad K_5 = \frac{y_2}{y_4^{0.5} y_6 P^{0.5}}$$

$$CO + \frac{1}{2}O_2 = CO_2 \qquad K_6 = \frac{y_1}{y_5 y_4^{0.5} P^{0.5}}$$

The K's are like the equil. constants we studied earlier. They are temp. dependent. Olikara and Borman have used JANAF table data to fit the equilibrium constants with expressions of the form

$$\log_{10}(K_i) = A_i \ln\left(\frac{T}{1000}\right) + \frac{B_i}{T} + C_i + D_i T + E_i T^2$$

These coefficients are given in several places. The one I used is Table 3-6 on page 73 of Internal Combustion Engines, by Colin R. Ferguson and Allan T. Kirkpatrick. (Wiley, 2001)

(I need to give credit to these authors for the presentation on which these notes are based.)

There are 11 unknowns: 10 y's and N.

There are 11 equations: 4 mass balance, 6 K definitions and the constraint that the sum of the y's = 1.

We can solve these equations by Newton's Method which is incorporated into EES.

There are two places where software which solves the problem may be accessed.

- Our course website where the Equil. Solver is posted as a text file of EES commands. Down load and paste into EES. You will have to set the variable limits so it'll converge. Instructions are in the file.
- The CSU website linked. Look under Engine Thermodynamics and Combustion.

Classwork

Get to one of these pieces of software, or both, and try and get it / them running. Do the combustion of C_7H_{17} at a $\phi = 0.6$. What are the molar fractions of each of the 10 products.

More Sophisticated Solver

There is an even more advanced equilibrium solver which we can get free. Go to www.fChart.com and look under “Free EES Goodies!”

You have to do a download, but it’s not too hard to figure out. I have done it, and have posted an EES file which illustrates how to use the equilibrium solver.

Discussion:

- Review what we know how to do...
- Talk about where we go next.

One thing, we need to be able to calculate the properties of the mixture of gases, now that we know its composition.

Bring your computers with EES for Monday and we will practice.