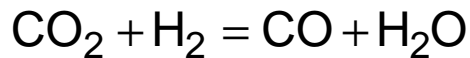ME 410   Day 13

Topics
- Chemical Equilibrium - Theory
- Chemical Equilibrium Example #1
- Equilibrium Constants
- Chemical Equilibrium Example #2
- Chemical Equilibrium of Hot Burned Gas

1. Chemical Equilibrium

We have already referred to a certain reaction, which takes place at high temperature after rich combustion.

$$CO_2 + H_2 = CO + H_2O$$

What is meant by equilibrium? The products are turning into reactants as well as the reactants turning into products. The reaction goes both ways at the same rate.

The consequence is that all species have reached constant concentrations in the mixture.

A more general case. M_i is a species involved in a reaction and υ_i is its molar coefficient.

$$\upsilon_1 M_1 + \upsilon_2 M_2 + \cdots = \upsilon_m M_m + \upsilon_n M_n + \cdots$$
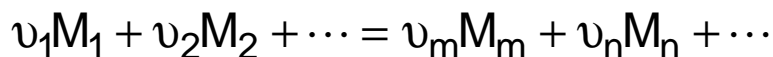
Again, the reaction goes both ways. Species reach constant concentrations.

This is the kind of situation we have at the end of combustion. The reaction rates are faster than the engine's kinematics, so we assume, at least to begin with that the burned gases are in equilibrium of this sort at the beginning of the power stroke.

Some theory...

Closed system of reacting gases. Only PV work may be exchanged with surroundings.

- We assume the gases in equilibrium are at temperature T.
- We also assume that the pressure, P, is constant.

Imagine an incremental process in which reactants go to products.

The first law of thermodynamics simplifies to

$$\Delta Q = \Delta H$$

The second law of thermodynamics simplifies to

$$\Delta Q \leq T\Delta S$$

So the combination reveals that

$$\Delta H - T\Delta S \leq 0$$

Recall from last time that the property G = H - T S is called the Gibbs Free Energy. The reaction taking place implies that

$$\Delta G \leq 0$$

That is the system lowers its G by reacting. Consequently, we have found a handy measure for establishing equilibrium. That is when the change in G is zero.
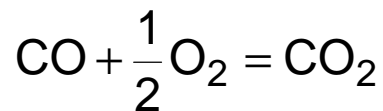
$$\Delta G = 0$$

At the temperature and pressure specified, the Gibbs free energy of the products will match that of the reactants.

2. Example Problem

This is a variation of Example 3.4 (p. 88-89)

A stoichiometric mix of carbon monoxide and oxygen was burned.

$$CO + \frac{1}{2}O_2 = CO_2$$

The combustion product CO_2 will then disassociate back into the original species. So, in a state of chemical equilibrium, all three species are present. The challenge is to find the mole fractions of each. Assume that we have T_{eq} = 2500 K and p_{eq} = 5.76 atm.

The solution will be done in EES. We assume that the product is

$$\alpha CO + n_2 O_2 + n_3 CO_2$$
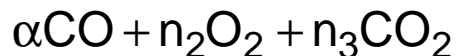
The variable α is used to facilitate comparison with the text. We also write two element balance equations

$$1 = \alpha + n_3$$

$$2 = \alpha + 2n_2 + 2n_3$$

The total moles of disassociated mixture is $n_T = \alpha + n_2 + n_3$. So we can set up the following molar fractions

$$y_1 = \frac{\alpha}{n_T} \qquad y_2 = \frac{n_2}{n_T} \qquad y_3 = \frac{n_3}{n_T}$$

In EES we work on a per mole unit basis. Note that when we want to get the entropy of a species we have to supply a pressure as well as a temperature.

Due to the way entropy is calculated, this must be the partial pressure of the species. So for CO we supply the pressure

$$p = y_1\, P_{eq}$$

Remember that the partial pressure of a gas is obtained by multiplying the total pressure by the mole fraction.

The EES solution can now be demonstrated. Please download it from the website.

3. Use of Equilibrium Constants

Here is a more complete explanation of chemical equilibrium.

Think of the reaction involving 1 mole of some species. Not important which. We divide out the molar coefficient of that species. We also subtract the reactant side from the product side.

I.e., think of writing the equation describing equilibrium as follows:

$$\upsilon_n M_n + \upsilon_{n+1} N_{n+1} + \cdots - \upsilon_1 M_1 - \upsilon_2 M_2 - \cdots = 0$$

So if a molar amount, δn, of our species reacted (i.e. changed), the number of moles of each of the other species that changed would be proportional to it,

$$\delta n_i = \upsilon_i\, \delta n$$

The total change in Gibbs free energy if we let these molar composition changes take place would be

$$\Delta G = g_n \delta n_n + g_{n+1}\delta n_{n+1} + \cdots - g_1 \delta n_1 - g_2 \delta n_2 - \cdots$$

$$\Delta G = \sum_{\text{all } \upsilon} g_i \delta n_i = \left(\sum_{\text{all } \upsilon} \upsilon_i \, g_i \right) \delta n$$

The "g's" are specific Gibbs Free Energies, the G per mole of each species at the temperature and pressure where equilibrium is occurring.

The text refers to these as the chemical potentials. Symbol μ. I'll keep it g in these notes.

It can be shown, (the text suggests how) that for ideal gases we can write the following expression for g

$$g_i = g_i^0 + RT \ln\left(\frac{p_i}{p_0} \right)$$

(Remember we are giving these quantities on a molar basis.)

The quantity g_i^0 is evaluated at the temperature of interest and standard pressure of 1 atm. It is the Gibbs Free Energy of formation of the substance i.

$$\Delta G = \left(\sum_{\text{all } \upsilon} \upsilon_i \left(g_i^0 + RT \ln\left(\frac{p_i}{p_0} \right) \right) \right) \delta n$$

Now for ΔG to be zero the sum must be zero. Remeber δn is arbitrary.

R is the universal gas constant, p_0 is standard 1 atm.

$$\sum_{\text{all } \upsilon} \upsilon_i \, g_i^0 = -RT \sum_{\text{all } \upsilon} \upsilon_i \, \ln\left(\frac{p_i}{p_0}\right)$$

Let ΔG^0 be the Gibbs free energy of the reaction as it takes place under standard conditions (1 atm and the desired temperature). It can be regarded as a constant, actually.

$$\Delta G^0 = \sum_{\text{all } \upsilon} \upsilon_i \, g_i^0$$

See how it's based on the specific Gibbs Free Energy of Formation for each species.

$$\sum_{\text{all } \upsilon} \upsilon_i \, \ln\left(\frac{p_i}{p_0}\right) = \sum_{\text{all } \upsilon} \ln\left(\frac{p_i}{p_0}\right)^{\upsilon_i} = -\frac{\Delta G^0}{RT}$$

Let

$$\ln(K_p) = -\frac{\Delta G^0}{RT}$$

where we will call Kp the equilibrium constant at constant pressure and temperature T. We then find that the sum is converted into a product.

$$K_p = \prod_{\text{all } \upsilon} \left(\frac{p_i}{p_0}\right)^{\upsilon_i}$$

Equilibrium constants like this are tabulated in JANAF tables. We will need them to understand our next challenge:

Equilibrium of Burned Gas Just AFTER Combustion

This later.

Right now another example.

Example 3.5 (p. 89-90)

In fuel-rich combustion product mixtures, equilibrium between the species CO2, H_2O, CO and H_2 is often assumed to determine the burned gas composition. For ϕ = 1.2, for C_8H_{18} combustion products determine the mole fractions of the product species at 1700 K.

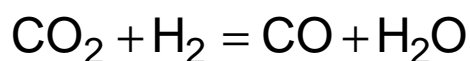I cite here the author's combustion equation using his own notation. It is based on a mole of C_8H_{18}.

$$C_8H_{18} + \frac{12.5}{1.2}(O_2 + 3.773N_2) \rightarrow aCO_2 + bH_2O + cCO + dH_2$$
$$+ 39.30N_2$$
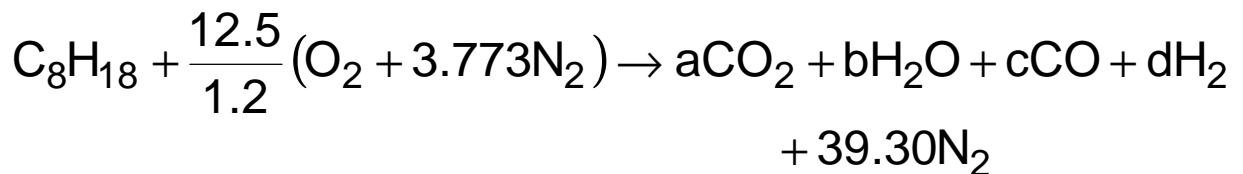
Balance

C: $\quad 8 = a + c$

H: $\quad 18 = 2b + 2d$

O: $\quad 25/1.2 = 2a + b + c$

N: $\quad$ already done.

This describes the situation incompletely. What's going on in the products is

$$CO_2 + H_2 = CO + H_2O$$

This reaction is deemed to be in chemical equilibrium. We will employ EES to calculate the Gibbs free energies of products and reactants.

Please see the EES document on the Website.