

## 16.50 Lecture 11

**Subject: Reacting Gases (continued); Temperature dependence of specific heats.**

Reacting gases (continued)

We were at the point in the last lecture of solving for the composition in the combustion chamber.

If we set  $T_c$  and  $P_c$ , we can solve for the set of six relations outlined for  $\alpha, \beta, \delta, \nu, \dots$ , and the gas composition is known. But how do we find  $T_c$  and  $p_c$ ? As indicated earlier the pressure is determined by the mass flow and the nozzle throat area:

$$\dot{m} = \frac{P_c A_t}{c^*(T_c)}$$

We regard the pressure as prescribed for now.

To find  $T_c$  we go back to the definition of  $\Delta H_f^0$  and write conservation of energy as

$$\begin{aligned} h_{H_2}(T_o) + nh_{O_2}(T_o) &= \alpha[\Delta h_{H_2O}(T_c) + \Delta H_{f_{H_2O}}^0] \\ &+ \beta[h_{H_2}(T_c)] + \delta[\Delta h_{OH}(T_c) + \Delta H_{f_{OH}}^0] \\ &+ \nu[\Delta h_H(T_c) + \Delta H_{f_H}^0] + \epsilon[h_{O_2}(T_c)] \\ &+ \eta[\Delta h_O(T_c) + \Delta H_{f_O}^0] \end{aligned} \quad (7)$$

where the symbol  $\Delta h_{H_2O}(T_c)$  means the excess specific enthalpy of  $H_2O$  at  $T_c$ , over and above that at the reference temperature  $T_f=298.16K$ . For species like  $H_2$  and  $O_2$  the  $\Delta$  is omitted, because the enthalpy at  $T_f$  is zero, by convention. These excess enthalpies are tabulated vs.  $T$  in standard data sets.

If the  $\alpha, \beta \dots$  are known we can solve this for  $T_c$ .

In general, we have to represent the  $K_p(T_c)$ 's and the  $h(T_c)$ 's and solve this system numerically. This is no problem but requires iteration and some care to ensure that the numerical procedures converge.

The primary constituents in the products are  $H_2O$  and  $H_2$ , so as a first estimate, assume  $\delta=0, \nu=0, \epsilon=0, \eta=0$ . Then  $\alpha \approx 2n$ ,  $\alpha + \beta \approx 1$ ,  $\beta \approx 1 - 2n$  and we can now estimate the magnitudes of  $\delta$  and  $\nu$ . The quantities  $\epsilon$  and  $\eta$  will be henceforth neglected, because of the fuel-rich nature of the mixture. For example from (5') of the previous lecture,

$$\frac{K_{p_{H_2O}}^2}{K_{p_{OH}}} = \frac{\left(\frac{\alpha}{\sigma} p_c\right)^2}{\left(\frac{\beta}{\sigma} p_c\right)\left(\frac{\delta}{\sigma} p_c\right)^2} = \frac{\alpha^2}{\beta \delta^2} \left(\frac{\sigma}{p_c}\right)$$

$$\delta^2 = \frac{\alpha^2}{\beta} \left( \frac{\sigma}{p_c} \right) \frac{K_{pOH}}{K_{pH_2O}^2}$$

and for  $\sigma = \alpha + \beta = 1$  and the above estimates for  $\alpha$  and  $\beta$ ,

$$\delta^2 = \frac{(2n)^2}{1-2n} \frac{1}{p_c} \frac{K_{pOH}}{K_{pH_2O}^2}$$

We now need an estimate of  $T_c$ . From (7), and using constant specific heats,

$$h_{H_2}(T_o) + nh_{O_2}(T_o) \approx 2n[\Delta h_{H_2O}(T_c) + \Delta H_{fH_2O}^0] + (1-2n)[h_{H_2}(T_c)]$$

where we read from tables

$$\Delta H_{fH_2O}^0 = -57.8 \frac{kcal}{gmole}$$

and we approximate for now

$$c_{pH_2} = 7.5 \text{ cal/mole/K} \quad c_{pH_2O} = 10.6 \text{ cal/mole/K}$$

Let  $h(T_o) = 0$  (as noted above this is arbitrary: we assume we are injecting gaseous  $H_2$  and  $O_2$  at  $t_0 = 298K$ ). The energy balance then becomes

$$0 = 2n[(10.6)(T_c - 298) - 57,800] + (1-2n)[7.5(T_c - 298)]$$

and we can solve this for  $(T_c - 298)$ :

$$T_c - 298 = \frac{2n(57,800)}{2n(10.6) + (1-2n)7.5} = \frac{1.15 \times 10^5 n}{7.5 + 6.20n}$$

To proceed further we must specify  $n$ . Let us take  $n = 0.25$ , or half the stoichiometric value of 0.5. This corresponds to an Oxygen/Hydrogen mass ratio of 4. A more usual value is about 5. Then we find  $T_c = 3480 K$  as a first estimate.

Now we have to check to see what the actual composition is for this temperature. Using the methods explained before, the values of  $K_{pOH}$  and  $K_{pH_2O}$  at the estimated temperature are:

n	$T_c$	$K_{p,OH}$	$K_{p,H_2O}$ atm <sup>1/2</sup>
<u>0.25</u>	<u>3480</u>	<u>1.70</u>	<u>4.93</u>

And from our previous result for  $\delta$ ,  $p_c^{1/2} \delta = 0.19$ , so now if  $p_c = 100 \text{ atm}$ ,  $\delta = .019$  as a second estimate, compared to the original estimate of 0.

What about  $v$ ? From Eq. (4) of the previous lecture,

$$K_{pH} = \frac{p_H^2}{p_{H_2}} = \frac{\left(\frac{v}{\sigma}\right)^2 p_c^2}{\left(\frac{\beta}{\sigma}\right) p_c} = \frac{v^2 p_c}{\beta \sigma}$$

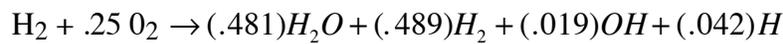
$$v^2 \approx \beta K_{pH}(T_c) \left(\frac{\sigma}{p_c}\right)$$

For  $n = .25$ ,  $T_c = 3480^\circ\text{K}$ , we calculate from the standard chemical potentials  $K_{pH} = .35$  atm,

so 
$$v^2 = (0.5)(.35) \frac{1}{p_c}; \quad v = \frac{.42}{p_c^{1/2}}$$

For  $p_c = 100$  atm, and the estimated temperature, we now have  $v = .042$  as a second estimate.

So, using Eqs. (2) for  $\alpha$  and (1) for  $\beta$ , we find  $\alpha = 2 \times 0.5 - 0.019 = 0.481$ , and  $\beta = 1 - 0.481 - (0.019 + 0.042)/2 = 0.489$ :



With this composition we can now go back and calculate  $T_c$  more accurately:

$$0 = h_{\text{H}_2}(T_o) + .25 h_{\text{O}_2}(T_o) = .481 [10.6(T_c - 298) - 57,800]$$

$$+ .489 [7.5(T_c - 298)] + .019 [7.8(T_c - 298) + 10.06]$$

$$+ .042 [5(T_c - 298) + 52.09]$$

$$T_c - 298 = \frac{.481(57,800) - .019(10.06) - .042(52.09)}{.481(10.6) + .489(7.5) + .019(7.8) + .042(5)} = 3047$$

$$T_c = 3345 \text{ K}$$

We stop the iteration here. A useful observation is that, just as the first approximation for  $T_c$  was too high because it ignored the endothermic dissociations, the second is likely to be too low, because it must have over-estimated these dissociations, since the equilibrium shifts in favor of dissociation when the temperature is high. It is a good idea to under-relax the temperature, as for example using for the next estimate the average of the previous two:

$$T_c \approx \frac{1}{2}(3480 + 3345) = 3413 \text{ K}$$

### Temperature dependence of specific heats

In working through the above example, we assumed for simplicity that the specific heats of the gases were constant. In fact they vary with temperature, generally increasing with increasing temperature. Generally we account for this by taking the specific heat or the enthalpy from tables of thermodynamic properties. But it is desirable for you to understand qualitatively why the specific heat varies, hence the following discussion.

For a full understanding of this subject one must have recourse to Statistical Mechanics, which deals with the thermal behavior of matter from a microscopic viewpoint, drawing on quantum mechanics. There is not time for such a discussion here, so we must be content with a summary of some of the results.

A key concept is that of active degrees of freedom. This is the number of terms in the classical expression for total energy that are quadratic in a coordinate or a velocity component. According to the Law of Equipartition of Energy each of these states if fully excited will contain an energy per mol of  $\mathfrak{R}T/2$  where  $\mathfrak{R}$  is the ideal molar gas constant.

Real molecules behave quantically, so at low enough temperatures, where the quantum of energy is greater than the available thermal energy per molecule, a quantum degree of freedom may not be "active". Generally, translational and rotational quanta are small enough that translational degrees of freedom are regarded as active in all cases of interest to us, but vibrational freedoms become active only at temperatures of the order of 2,000-3,000K. Taking the simplest case first:

a) Monoatomic gases

The molecule of a monoatomic gas can be thought of as a point mass, and as such it has three translational degrees of freedom. So the Internal Energy (per mol) is  $3\mathfrak{R}T/2$ , so we find a molar Specific Heat at Constant Volume

$$c_v = 12.47 \text{ Joule/mole/K ( Monoatomic)}$$

The ideal gas constant being  $\mathfrak{R} = 8.32 \text{ J/mole/K}$ , the Specific Heat at Constant Pressure is

$$c_p = c_v + \mathfrak{R} = 20.79 \text{ Joule/kg mole/K}$$

and the ratio of specific heats is  $\gamma = 5/3 = 1.667$ .

All of these values are independent of temperature because the translational degrees of freedom are fully excited at normal temperatures.

b) Diatomic molecules.

The simplest non-trivial case, the diatomic molecule, may be thought of as a "dumbbell" with in general unequal weights on the two ends, connected by a spring that can extend along the line of their common centers.

Like the monoatomic molecule, the diatomic molecule as a whole has 3 translational degrees of freedom, each containing energy  $\mathfrak{R}T/2$  per mol. In addition it has 2 rotational degrees of freedom (note that the moment of inertia about the line of centers is very small, so this degree of freedom does not count). Each of these rotational degrees of freedom is fully excited at the temperatures of interest here (though not at very low T) and contains  $\mathfrak{R}T/2$ . So at "low" temperatures (near room temperature) the Internal Energy per mole is  $5\mathfrak{R}T/2$  and the Specific Heat at Constant Volume is

$$c_v = 20.79 \text{ Joule/mole/K ( Diatomic at low T)}$$

It follows that

$$c_p = c_v + \mathfrak{R} = 29.11 \text{ Joule/mole/K (Diatomic at low T)}$$

and  $\gamma = 7/5 = 1.4$ .

At higher temperatures, the vibration of the molecule along its line of centers is excited, introducing two more degrees of freedom. This happens gradually between room temperature and the maximum temperatures encountered in propulsion devices. It is this variation that causes the variations of  $c_v$  of interest to us here. If the vibrational degrees of freedom are fully excited, the Internal energy per mole is  $7\mathfrak{R}T/2$  and

$$c_v = 37.41 \text{ Joule/mole/K ( Diatomic at high T)}$$

Correspondingly,

$$c_p = c_v + \mathfrak{R} = 45.73 \text{ Joule/mole/K (Diatomic at high T)}$$

and  $\gamma = 9/7 = 1.286$ .

### c) Polyatomic Molecule

Most polyatomic molecules are non-linear, so they have an additional rotational degree of freedom as compared to diatomic molecules. Thus at low temperatures, the Internal Energy is  $6\mathfrak{R}T/2 = 3\mathfrak{R}T$ . It follows that

$$c_v = 24.94 \text{ Joule/mole/K (Polyatomic at low T)}$$

$$c_p = c_v + \mathfrak{R} = 33.260 \text{ Joule/mole /K (Polyatomic at low T)}$$

and the ratio of specific heats is  $\gamma = 4/3 = 1.333$ .

The behavior of the vibrational degrees of freedom of polyatomic molecules can be very complex if the number of atoms is large. A useful rule for estimating their energy content is to compute the number of vibrational degrees of freedom as the difference of the total for the molecule minus the translational and rotational degrees of freedom. Thus if N is the number of atoms, Vibrational Degrees of Freedom =  $3N - 6$ , and the Internal Energy per molecule if they are all excited is  $3kT + (3N - 6)kT = (3N - 3)kT$ . The ratio of specific heats then becomes

$$\gamma = \frac{3N - 2}{3N - 3} \text{ (Polyatomic at high T)}$$

and it is clear that this can be close to 1 for N large.

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