

16.512, Rocket Propulsion
 Prof. Manuel Martinez-Sanchez
Lecture 13: Examples of Chemical Equilibrium

13.1 Numerical Iteration Procedure

For the Shuttle main engine, we take $R = O/F = 6$, and $P = 210$ atm. To get started, we neglect n_{O_2} , n_O , n_H and n_{OH} , so that Eqs. (12.2-3) and (12.2-4) reduce to

$$2n_{H_2O} + 2n_{H_2} = \frac{8}{3}$$

$$n_{H_2O} = 1$$

which give $n_{H_2O} = 1$, $n_{H_2} = 1/3$ and (since all other n_i 's are taken to be zero, $n = 4/3$).

The enthalpy before reaction was (assuming very cold reactants, i.e. $T_i = 0^\circ K$),

$$H = \frac{4}{3}h_{H_2}(O) + \frac{1}{2}h_{O_2}(O) = -15,632 \text{ J (for the } \frac{4}{3} \text{ moles of } H_2, \frac{1}{2} \text{ mole of } O_2).$$

For the products to have the same enthalpy, the temperature must be very high. Using the table in Ref. 12.1 (pp. 692-693) we have the trial values tabulated below:

T(K)	3400	4000	4200
h_{H_2O} (J/mole)	-92,973	-58,547	-46,924
h_{H_2} (J/mole)	103,738	126,846	134,700
$h_{H_2O} + \frac{1}{3}h_{H_2}$	-58.394	-16,265	-2,024

Since we must obtain an enthalpy of -15,632 J, these values indicate a temperature very close to 4000 K. Linear interpolation between 4000 and 4200 K gives

$$T = 4009 \text{ K}$$

We can now use this temperature to calculate the four equilibrium constants K_1 through K_4 . These are given in Table 12 of Ref. 12.1. With some interpolation, we obtain:

$$K_1 = 0.974 \text{ (atm)}^{1/2} \quad K_2 = 2.61 \text{ (atm)}$$

$$K_3 = 0.589 \text{ (atm)}^{1/2} \quad K_4 = 2.286 \text{ (atm)}$$

At this point we can obtain our first nonzero estimate of the “minor” species concentrations. From Eqs. (12.2-14) through (12.2-17),

$$n_{\text{OH}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2}^{1/2}} \sqrt{\frac{n}{p}} K_1 = \frac{1}{\sqrt{1/3}} \sqrt{\frac{4/3}{200}} 0.974 = 0.138$$

$$n_{\text{H}} = \sqrt{\frac{nn_{\text{H}_2}}{p}} K_2 = \sqrt{\frac{4/3 \times 1/3}{200}} \times 2.61 = 0.076$$

$$n_{\text{O}_2} = \left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2}} \right)^2 \frac{n}{p} K_3^2 = \left(\frac{1}{1/3} \right)^2 \frac{4/3}{200} (0.589)^2 = 0.021$$

$$n_{\text{O}} = \sqrt{\frac{nn_{\text{O}_2}}{p}} K_4 = \sqrt{\frac{4/3 \times 0.021}{200}} \times 2.286 = 0.018$$

We are now at the end of the first loop of our iteration procedure. We can next re-calculate $n_{\text{H}_2\text{O}}$ and n_{H_2} from the atom conservation equations, including the new “minor” n_i 's we just computed. With the new complete set of n_i 's, we can re-calculate the enthalpy at a few temperatures and interpolate for a new set of K_j 's, etc. We will do one more cycle in some detail to illustrate the nature of the typical results and the way they may tend to oscillate or diverge. Beyond that, a tabulated summary of the succeeding results will suffice.

Corrected $n_{\text{H}_2\text{O}}$, n_{H_2} , n : From Eqs. (12.2-3) and (12.2-4),

$$n_{\text{H}_2\text{O}} + n_{\text{H}_2} = \frac{4}{3} - \frac{0.076 + 0.138}{2} = 1.226$$

$$n_{\text{H}_2\text{O}} = 1 - 2 \times 0.021 - 0.018 - 0.138 = 0.802$$

Hence $n_{\text{H}_2} = 1.226 - 0.802 = 0.424$

and $n = 1.226 + 0.138 + 0.076 + 0.021 + 0.018 = 1.480$

Corrected temperature:

Since the partial decomposition of H₂O and H₂ into the minor species is an endothermic process, the new temperature will be lower. Using the tables of enthalpies and the computed mole numbers we calculate

$$h(2800 \text{ K}) = 0.802 \times (-126,533) + 0.424 \times 81,370 + 0.138 \times 121,729 + 0.076 \times 269,993 + 0.021 \times 90,144 + 0.018 \times 301,587 = -22,338 \text{ J}$$

$$h(3000 \text{ K}) = 0.802 \times (-115,466) + 0.424 \times 88,743 + 0.138 \times 129,047 + 0.076 \times 274,148 + 0.021 \times 98,098 + 0.018 \times 305,771 = -8,769 \text{ J}$$

Since we still want $h = -15,632 \text{ J}$, linear interpolation gives a temperature

$$T = 2800 + \frac{200}{-8,769 + 22,338} (-15,632 + 22,338) = 2899 \text{ K}$$

It is clear that at this new, much lower temperature, there will be much less of the minor species, since the new equilibrium constants, (K_1 through K_4) will be smaller. Since it was the presence of these minor species that forced a reduction from 4009 K to 2889 K, we would next obtain a refined T again relatively high, and the process is likely to overshoot at each iteration step. This suggests that we can accelerate convergence by adopting as a new trial temperature the average of the last two:

$$T = \frac{4009 + 2899}{2} = 3454 \text{ K}$$

Corrected minor species: The new equilibrium constants (at 3480 K) are:

$$K_1 = 0.251(\text{atm})^{1/2} \quad K_2 = 0.316(\text{atm})$$

$$K_3 = 0.184(\text{atm})^{1/2} \quad K_4 = 0.454(\text{atm})$$

and, proceeding as before,

$$n_{\text{OH}} = 0.0250 \quad n_{\text{H}} = 0.0297 \quad n_{\text{O}_2} = 0.0079 \quad n_{\text{O}} = 0.00105$$

Table 13.1 summarizes these two iterations, and shows the next few iterations as well, leading to the practically converged values of the last line. The mole numbers are then converted to mole fractions by simply dividing each by n (Table 13.2). Notice that the numbers of mole given in Table 13.1 have been converted to mole/kg, by dividing the n numbers used so far (which correspond to

$$\frac{8}{3} \times 0.00108 + 1 \times 0.016 = 0.01869 \text{ Kg of reactants) by this mass } 0.01869 \text{ Kg.}$$

ITERATION	N _{H₂O} (mol/kg)	N _{O₂}	N _O	N _{H₂}	N _H	N _{OH}	T (K)	$\frac{T + T_{OLD}}{2}$	K ₁ (atm) ^{1/2}	K ₂ (atm)	K ₃ (atm) ^{1/2}	K ₄ (atm)
1	53.57	0	0	17.86	0	0	4009		0.974	2.610	0.589	2.286
2	42.96	1.125	0.964	22.71	4.071	7.393	2899	3454	0.236	0.281	0.173	0.190
3	52.09	0.423	0.056	17.87	1.591	1.339	3784	3619	0.356	0.587	0.259	0.432
4	50.42	0.199	0.172	18.76	1.912	2.587	3644	3632	0.370	0.619	0.267	0.458
5	50.48	0.182	0.171	18.66	2.025	2.555	3642	3637				

Revised Table 13.1

The mean molecular weight of the gas is then obtained from Table 13.2 by:

$$\bar{M} = \sum_i x_i M_i = 13.48 \text{ kg/Kmole}$$

An approximate molar, specific heat for each species can also be obtained as $c_{p_i} = [h(3800) - h(3400)] / 400$, and these can also be averaged to obtain

$$\bar{c}_p = \sum_i x_i c_{p_i} = 50.62 \frac{\text{J}}{(\text{mole})\text{K}} = 12.11 \frac{\text{cal}}{(\text{mole})\text{K}}$$

and then the "average" specific heat ratio is

$$\bar{\gamma} = \frac{\bar{c}_p}{c_p - R} = \frac{50.62}{5.62 - 8.31} = 1.196$$

Finally, for purposes of calculating the flow in the rocket nozzle, it is useful to determine the entropy of the reacted gaseous mixture. We can refer this to a unit of mass, or, alternatively, to the same arbitrary amount of mass we have so far worked with, i.e., $\frac{4}{3}$ moles of H₂ and $\frac{1}{2}$ mole of O₂ (we should not calculate it per mole, since the number of moles in this much mass may change from the present value $n = 1.384$, due to reactions occurring in the nozzle). Table A. 11 of Ref. 12.1 gives values of the specific entropies s^0 of the various species at 1 atm, as a function of temperature. We can easily correct these to the proper pressures by using

$$S_i(T, P_i) = S_i^0(T) - R \ln P_i \quad (13.1)$$

where $P_i = P x_i$ is the corresponding partial pressure. The results are summarized in Table 13.3.

TABLE 13.3 Entropies at 3630 K

Species	Entropy at 1 atm KJ / (Kmole)K	Partial Pressure atm	Entropy at own pressure KJ / (Kmole)K
H ₂ O	293.905	142.8	252.66
H ₂	210.070	52.9	177.08
OH	261.771	7.4	245.13
H	166.668	5.9	151.91
O ₂	292.223	0.58	296.75
O	213.715	0.48	219.82

The total entropy in our control mass (4/3 moles of H₂ plus 1/2 mole of O₂, in the form of the N_i's listed in the last line of Table 12.2.1) is then

$$S = \sum_i s_i N_i = 17.050 \text{ KJ / Kg / K}$$

Ref. 12.2 "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks and Chapman – Jongnet Decorations", by S. Gordon, NASA Accession No. M84-10621, NASA Lewis Research Center.