Ideal Gas Thermodynamic Properties in Chemkin Format

Thermodynamic properties for ideal gases are tabulated in a variety of locations in Chemkin format. This format involves two sets of seven constants a_1 through a_7. These constants are fits to specific heat, enthalpy, and entropy data (or calculations) according to the following formulae:

$$\frac{\hat{c}_p}{R_u} = \frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \tag{1}$$

$$\frac{\hat{h}}{R_u T} = \frac{h}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T} \tag{2}$$

$$\frac{\hat{s}^\circ}{R_u} = \frac{s^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7 \tag{3}$$

Note that all the parameters on the left hand side of equations (1) through (3) are dimensionless.

Three temperatures are given on the first line of the data, T_{low}, T_{high}, and T_{mid}. Usually, these values are 300, 5000, and 1000 K respectively. The first set of parameters a_1 through a_7 applies for the high temperature range (T_{mid} through T_{high}), while the second set applies for the low temperature range (T_{low} through T_{mid}).

Sample Data in Chemkin Format for Nitrogen (N_2)

```
N2                121286N   2             G   0300.00 5000.00 1000.00          1
 0.02926640E+02   0.14879768E-02  -0.05684760E-05   0.10097038E-09  -0.06753351E-13   2
-0.09227977E+04   0.05980528E+02   0.03298677E+02   0.14082404E-02  -0.03963222E-04   3
 0.05641515E-07  -0.02444854E-10  -0.10208999E+04   0.03950372E+02                    4
```

Format:

Symbol	Identifier #atoms	Phase	T_{low}	T_{high}	T_{mid}	
						1
a_1 (hi range)	a_2 (hi range)	a_3 (hi range)	a_4 (hi range)		a_5 (hi range)	2
a_6 (hi range)	a_7 (hi range)	a_1 (lo range)	a_2 (lo range)		a_3 (lo range)	3
a_4 (lo range)	a_5 (lo range)	a_6 (lo range)	a_7 (lo range)			4

Equilibrium Example: $O_2 \rightarrow 2O$ Composition at 3000 K and 0.1 and 1 atm.

Crunching the numbers.

Data Files in Chemkin Format

```
O                 L 1/90O   1    00    00    00G    200.000   3500.000   1000.000      1
 2.56942078E+00-8.59741137E-05 4.19484589E-08-1.00177799E-11 1.22833691E-15     2
 2.92175791E+04 4.78433864E+00 3.16826710E+00-3.27931884E-03 6.64306396E-06     3
-6.12806624E-09 2.11265971E-12 2.91222592E+04 2.05193346E+00 6.72540300E+03     4

O2                TPIS89O   2    00    00    00G    200.000   3500.000   1000.000      1
 3.28253784E+00 1.48308754E-03-7.57966669E-07 2.09470555E-10-2.16717794E-14     2
-1.08845772E+03 5.45323129E+00 3.78245636E+00-2.99673416E-03 9.84730201E-06     3
-9.68129509E-09 3.24372837E-12-1.06394356E+03 3.65767573E+00 8.68010400E+03     4
```

Molar specific heat at constant pressure (J/mol-K): O_2, 39.994; O, 20.935

Molar enthalpy (kJ/mol): O_2, 98.10; O, 305.73

Molar entropy @ 1 atm (J/mol-K): O_2, 284.4987; O, 209.6926

Molar Gibbs Free Energy @ 1 atm (kJ/mol): O_2,-755.39; O, -323.34

Enthalpy of Formation @ 1 atm, 298 K: O_2, 0; O, 249.16

$\Delta G° = 2\hat{\mu}_O - \hat{\mu}_{O2} = +108.71$ kJ/mol $K_p = \exp(-\Delta G°/RT) = 0.0128$,

using .008314 kJ/mol-K for R, and 3000 K for T.

$$\xi = \sqrt{\frac{K_p}{4(P/P_{ref}) + K_p}}$$

For 1 atm, P = P_{ref}, and $\xi = 0.0565$. Xo = No/NT = $2\xi/(1+ \xi) = 0.1069$

For 0.1 atm, P/P_{ref} = 0.1, and $\xi = 0.1761$. Xo = No/NT = $2 \xi /(1+ \xi) = 0.2994$

For a mixture of 1 mole of CO and 1 mole of O_2, it is desired to know the equilibrium composition at 3000 K. Consider CO, CO_2, O_2, and O as the possible species.

a) Choose an appropriate set of reactions and calculate K_p for each reaction at 3000 K from tabulated data.

b) Obtain K_p from another source for the chosen reactions (e.g. a thermo book, a combustion book, published papers, etc.) and compare results.

c) Calculate the equilibrium composition of a mixture of 1 mole CO and 1 mole O_2 at 3000 K and 1 atm. Give your results in the form of mole fractions for each species.

d) Repeat part c) for $P = 0.1$ atm.

Solution

For parts a) and b) the answers depend on what set of reactions that were chosen. For each reaction, $K_p = \exp\left(-\Delta G^\circ / \hat{R} T\right)$. $\Delta G^\circ = \sum_i \nu_i \hat{\mu}_i^\circ$, where $\hat{\mu}_i^\circ = \hat{u}_i(T, P_0) + \hat{R}T - T\hat{s}_i(T, P_0)$. The superscript '°' denotes that those quantities are evaluated at the reference pressure, which is typically 1 atmosphere.

Even though there are 4 species, we can only write two linearly independent reactions. For example:

$$CO + O \rightleftharpoons CO_2 \quad \text{and} \quad \frac{1}{2}O_2 \rightleftharpoons O \tag{1}$$
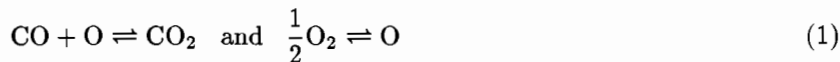
I call the advancement for the first reaction ξ_1 and that for the second reaction ξ_2. Then I can write the relations:

$$N_{CO} = 1 - \xi_1 \quad N_{CO_2} = \xi_1 \quad N_O = \xi_2 - \xi_1 \quad N_{O_2} = 1 - \xi_2/2 \tag{2}$$

Also, we note that the total number of moles is the sum over all the species or $N_T = 2 - \xi_1 + \xi_2/2$. These relations tell us that ξ_1 is between 0 and 1 and that ξ_2 is between ξ_1 and 2. Next, we write the expression for the equilibrium constants for these reactions. For the first reaction, $K_{p,1} = 27.16$ and for the second, $K_{p,2} = .1125$ at 3000 K (from an undergraduate thermodynamics text).

$$K_{p,1} = \frac{P_{CO_2}/P_0}{P_{CO}P_0/P_0^2} = \frac{X_{CO_2}}{X_{CO}X_O}\left(\frac{P_0}{P}\right) = \frac{N_T N_{CO_2}}{N_{CO}N_O}\left(\frac{P_0}{P}\right) \tag{3}$$

Where we have used the fact that $X_i = N_i/N_T$. Plugging in our relations for the N's gives us:

$$K_{p,1} = \frac{(2 - \xi_1 + \xi_2/2)\xi_1}{(1 - \xi_1)(\xi_2 - \xi_1)}\left(\frac{P_0}{P}\right) \tag{4}$$

Similarly for $K_{p,2}$ we get:

$$K_{p,2} = \frac{\xi_2 - \xi_1}{(2 - \xi_1 + \xi_2/2)^{1/2}(1 - \xi_2/2)^{1/2}}\left(\frac{P}{P_0}\right)^{1/2} \tag{5}$$

Now we have two equations for two unknowns, ξ_1 and ξ_2. Unfortunately, we can't isolate either variable, so we have to do a systematic search. I chose a value of ξ_1, and then solved for ξ_2 in $K_{p,2}$ using a Newton-Raphson method on a calculator. Then I plugged these values into $K_{p,1}$ and used the agreement there as a barometer for convergence. For the $P = 1$ atm case, I got $\xi_1 = .646$ and $\xi_2 = .763$. This gives me mole fractions as follows:

$$X_{CO} = .204 \quad X_{CO_2} = .372 \quad X_O = .067 \quad X_{O_2} = .357 \tag{6}$$

These values agree excellently with those obtained by a canned software routine which solves for equilibrium composition. For the low pressure case, $(P/P_0) = 0.1$, and I get $\xi_1 = .349$ and $\xi_2 = .749$ leading to the following mole fractions:

$$X_{CO} = .321 \quad X_{CO_2} = .172 \quad X_O = .198 \quad X_{O_2} = .309 \tag{7}$$

Note that the reduced pressure has increased N_T as expected due to Le Chatlier's principle.