General Gibbs Minimization as an Approach to Equilibrium

Most of us have used the equilibrium constant approach to find equilibrium compositions for simple systems. This requires you to hypothesize equilibrium reactions. While the approach can be done by hand calculations, it has never been successfully generalized to large systems. During the late 1960's, researchers at NASA developed a general Gibbs minimization approach for finding the equilibrium composition of arbitrarily large systems without the need to write equilibrium reactions. The algorithm is so successful that it has been adopted as the basis for most equilibrium codes developed since.

While the equilibrium constant approach is well documented in almost every thermodynamics text, the generalized Gibbs approach appears almost nowhere. The NASA documentation (Gordon and McBride, 1994) contains a complete but terse development which is fine if you already understand the approach, but not very useful as a learning tool. The goal of the writeup that follows is to take the reader in some detail from thermodynamic first principles through to the method of application of application of the Gibbs minimization approach.

1.0   General Theory

The general idea behind thermochemical equilibrium is that all spontaneous reactions occur in the direction that increases the overall entropy of the universe (meaning both the system under consideration and the surroundings that represent the rest of the universe). When the composition of the system arrives at a point where the total entropy for the system plus surroundings reaches a maximum, it becomes "stuck" since movement in any direction in composition space involves an entropy decrease, and thus cannot spontaneously occur without violating the second law. Thus, the equilibrium state we seek is this end state, which is reached by all spontaneously reacting systems if given enough time.

There are several kinds of equilibrium problems. A few of the more important ones are the following:

- The system can be a box that is fixed in volume and is adiabatic. In this case, as the reactions progress, both the temperature and pressure within the box will change. Thus, both the final temperature and the pressure are unknowns and these are provided by the solution. This system is an idealization of what occurs in a calorimetry bomb.
- The system can be fixed in volume, but be in contact with an environment at a known temperature. As the reaction progresses, any energy released by the reaction will be carried away as heat to keep the box at the same temperature. The pressure will change in response to the change in the total number of moles as the reaction progresses. Thus, the final temperature is known, but the final pressure is provided as part of the solution.
- The system can be adiabatic, but is allowed to expand or contract as the reaction progresses to keep the pressure constant (*e.g.,* an adiabatic piston/cylinder system). In this case, the final pressure is known but the final temperature is part of the solution. Many common combustion systems most closely approach this model, *e.g.,* Bunsen burners, combustion in boilers, gas turbine combustors. In these systems the combustion is approximately adiabatic and the pressure is constant (here the specific volume of the gas expands to accommodate the increase in temperature and any changes in mole numbers).
- The system is a box that is in contact with an environment at a known temperature and the volume expands or contracts to keep the pressure constant. Here, both the final temperature and pressure are known, and the box undergoes both a heat and work interaction with the surroundings while the reaction progresses. This case is important when you know both the final temperature and pressure of a process and you are looking for the corresponding equilibrium composition. An example might be the composition at

the tail pipe of a car, where you have measured the exhaust temperature and you know the pressure is atmospheric.

We will focus on the latter case. The approach for the others is similar.

The starting point is the increase in entropy principle, which says:

$$S_{gen} = \Delta s_{system} + \Delta s_{surroundings} \qquad (1)$$

For any spontaneous process, $S_{gen} \geq 0$. Since the environment is assumed to be at a constant temperature, $\Delta s_{surroundings} = q/T$, where T is the temperature of the surroundings and q is the heat flow into the surroundings (if you have forgotten why this is true, remember, this is the formal definition of s). This means that for any spontaneous process:

$$0 \leq \Delta s_{system} + q_{surroundings}/T_{surroundings} \qquad (2)$$

or in differential form: $0 \leq ds_{system} + \delta q_{surroundings}/T_{surroundings}$

The differential first law for our box is:

$$\delta q - \delta w = du \qquad (3)$$

For a reversible process, the work term is Pdv. From equation 2, q can be expressed as $\delta q_{system} \leq Tds_{system}$ (note that we have changed our reference point for q from the surroundings to the system, which involves a change of sign for q). Substituting these into the first law gives: Tds-Pdv $\geq$ du, or

$$0 \geq du+Pdv-Tds \qquad (4)$$

Note that this equation holds for any of the four types of equilibrium systems noted above. The definition of Gibbs free energy is:

$$g \equiv u+Pv-Ts \qquad (5)$$

Taking the derivative, we get:

$$dg=du+Pdv+vdP-Tds-sdT \qquad (6)$$

We are following an equilibrium process that occurs at constant pressure and temperature (case 4 from above). In this case, dP=dT=0, so the equation becomes:

$$dg=du+Pdv-Tds \qquad (7)$$

Comparing this to equation 4, we see that for a spontaneous chemical reaction at constant T and P, the change in Gibbs energy must be negative (*i.e.,* a positive change violates the second law):

$$0 \geq dg \qquad (8)$$

This means that spontaneous reaction will occur at a fixed temperature and pressure until the Gibbs free energy reaches a minimum point in composition space, and then it will become "stuck". This will be the equilibrium point.

The Gibbs free energy is a function of pressure, temperature, and composition (*i.e.,* the moles of the various components that are present, *e.g.,* H_2O, CO_2, *etc.*). This functionality can be formally written as:

$$g=g(T,P,N_1,N_2,...N_{NS}) \tag{9}$$

Here, N_j is the number of moles of species j in the box, and the index NS is the total number of species in the system. Taking the total derivative of g gives:

$$dg = \left(\frac{\partial g}{\partial T}\right)_{P,N} dT + \left(\frac{\partial g}{\partial P}\right)_{T,N} dP + \sum_{j=1}^{NS} \left(\frac{\partial g}{\partial N_j}\right)_{P,T,N_i} dN_j \tag{10}$$

Here the summation is over all the species present. Since T and P are fixed, these terms drop out. This leaves our equilibrium condition as:

$$dg = 0 = \sum_{j=1}^{NS} \mu_j dN_j \tag{11}$$

Here μ_j is the chemical potential, which is defined as:

$$\mu_j \equiv \left(\frac{\partial g}{\partial N_j}\right)_{T,P,N_i} \tag{12}$$

The chemical potential can be thought of as the change of Gibbs free energy of a mixture caused by the addition of a differential amount of species j when the T, P, and other mole numbers are held constant. For ideal gases, this is the Gibbs free energy of the individual species since they do not interact in a mixture:

$$g_j = u_j + Pv_j - Ts_j = h_j - Ts_j \tag{13}$$

Now we can expand h in terms of enthalpy of formation and also expand s to express the pressure correction for ideal gases:

$$g_j = h_{f,j}^0 + (h_j - h_{0,j}) - T[s_j^0 - R \ln\left(\frac{P_j}{P_0}\right)] \tag{14}$$

Here, $h_{f,j}^0$ is the enthalpy of formation at 298 K, h_j is the enthalpy at the target temperature, $h_{j,0}$ is the enthalpy at 298 K, s_j^0 is the 1 atm entropy at the target temperature, R is the gas constant, P_j is the partial pressure of the component, and P_0 is 1 atm (all of these are simple look-up values from standard thermodynamics tables). It is usually customary to separate out the properties that depend just on temperature, so:

$$g_j = h_{f,j}^0 + (h_j - h_{0,j}) - Ts_j^0 + RT \ln\left(\frac{P_j}{P_0}\right) \tag{15}$$

Next, we define:

$$g_j^* = h_{f,j}^0 + (h_j - h_{0,j}) - Ts_j^0 \tag{16}$$

We also split up the pressure term as follows:

$$\ln\left(\frac{P_j}{P_0}\right) = \ln\left(\frac{P_j}{P}\frac{P}{P_0}\right) = \ln\left(\frac{N_j}{N}\frac{P}{P_0}\right) = \ln\left(\frac{N_j}{N}\right) + \ln\left(\frac{P}{P_0}\right) \tag{17}$$

Here, P is the system pressure and N is the total number of moles in the system. This leads us to an operational equation for calculating g_j:

$$g_j = g_j^* + RT\ln N_j - RT\ln N + RT\ln\left(\frac{P}{P_0}\right) \tag{18}$$

If you know T and P, you can get g^*, and the only unknowns are the mole numbers of species j and the total number of moles in the system. Substituting this into equation 11 gives us the operational equation for the minimization:

$$dg = 0 = \sum_{j=1}^{NS} g_j dN_j = \sum_{j=1}^{NS} [g_j^* + RT\ln N_j - RT\ln N + RT\ln\left(\frac{P}{P_0}\right)]dN_j \tag{19}$$

This is the point of departure for the equilibrium constant approach. In that approach, an equilibrium reaction is hypothesized, and this is used to reduce all the dN_j to one variable, which is then divided into the zero. The resulting equation contains (within the g_j terms) the variables N_j and N. Using algebraic manipulation and atom balances, the N_j and N terms are reduced to a single variable, which is solved (this approach is detailed in most standard thermodynamics texts, *e.g.,* Çengal and Boles (1998), and is not discussed further here). This approach is essentially impossible to execute for complex systems, so we move to the general Gibbs minimization approach which is the basis for all the equilibrium codes.

2.0   Solution via Lagrange Multipliers

It is key to recognize that the N_j in equation 19 are not independent variables. They are constrained such that the number of moles of each element in the system must remain constant (*i.e.,* if you start with 4 moles of oxygen atoms, this must stay constant as the reaction progresses). These constraint equations are best developed by example. Assume a system starts with 1 mole CO_2 and 2 moles H_2O (for a total of 4 moles of O-atom going in). We assume the equilibrium mixture contains CO_2, H_2O, OH and O_2. The constraint equation for oxygen atoms is an expression of the fact that there must be 4 moles of O-atom in the products:

$$4 = 2N_{CO2} + N_{H2O} + N_{OH} + 2N_{O2} \tag{20}$$

One approach to such constrained optimization problems is the method of Lagrange (or undetermined) multipliers. (A simple application of the approach is to constrain a cylinder to contain a certain volume, and find the length and diameter dimensions that minimize the total external surface area.)

We start by generalizing the constraint condition as:

$$0 = \sum_{j=1}^{NS} a_{i,j} N_j - b_i \qquad (21)$$

Here, b_i is the number of moles of element i in the system, and $a_{i,j}$ is number of atoms of element i in one molecule of species j (*e.g.,* there are 2 atoms of O in one molecule of CO_2, so $a_{i,j}=2$). There will be one of these equations for each element in the system (i=1,2,…NE), where NE is the total number of elements in the system). If we generalize these equations as functions:

$$0 = \varphi_i(N_1, N_2, ... N_{NS}) \qquad (22)$$

Here we have one constraint equation for each element. We can take the total derivative of this:

$$d\varphi_i = 0 = \left(\frac{\partial \varphi_i}{\partial N_1}\right) dN_1 + \left(\frac{\partial \varphi_i}{\partial N_2}\right) dN_2 + ... + \left(\frac{\partial \varphi_i}{\partial N_{NS}}\right) dN_{NS} \qquad (23)$$

Now we make a linear combination of equation 23 (one for each element) with the differential dg from equation 10 (with the P and T derivatives already set to 0):

$$dg + \lambda_1 d\varphi_1 + \lambda_2 d\varphi_2 + ... = \left[\frac{\partial g}{\partial N_1} + \lambda_1 \frac{\partial \varphi_1}{\partial N_1} + \lambda_2 \frac{\partial \varphi_2}{\partial N_1} + ...\right] dN_1 +$$

$$\left[\frac{\partial g}{\partial N_2} + \lambda_1 \frac{\partial \varphi_1}{\partial N_2} + \lambda_2 \frac{\partial \varphi_2}{\partial N_2} + ...\right] dN_2 + ... \qquad (24)$$

The λ_i's can be anything, and we define them such that all the bracketed terms simultaneously go to zero (but we do not yet have any way of calculating their values yet):

$$0 = \left[\frac{\partial g}{\partial N_j} + \lambda_1 \frac{\partial \varphi_1}{\partial N_j} + \lambda_2 \frac{\partial \varphi_2}{\partial N_j} + ...\right] \qquad (25)$$

According to the discussion following equation 12, the "g" differential is just g_j. The terms involving the constraint equations are obtained by differentiating equation 21:

$$\lambda_i \frac{\partial \varphi_i}{\partial N_j} = \lambda_i a_{i,j} \qquad (26)$$

Substituting into equation 25 yields:

$$0 = g_j + \sum_{i=1}^{NE} \lambda_i a_{i,j} \qquad (27)$$

This gives a system of "j" equations (equation 27), one for each species. We also have "i" constraint equations, one for each element:

$$0 = \sum_{j=1}^{NS} a_{i,j} N_j - b_i \qquad (21)$$

Finally, we have the condition that the total number of moles in the system must equal the sum of the individual mole numbers:

$$0 = \sum_{j=1}^{NS} N_j - N \qquad (28)$$

Equations 21, 27, and 28 form a system of NS+NE+1 equations. Note that g_j is defined by equation 18 and it contains the unknowns N_j and N. Thus the unknowns are the N_j (there are NS of these), the λ_i (there are NE of these), and N. Thus, the number of unknowns match the number of equations and we have a closed algebraic system. Note that it is not necessary to hypothesize any equilibrium reactions; all you need to do is specify the species you expect to appear in your system and you can find the equilibrium solution.

3.0 Numerical Solution

The approach used by the code is to solve equations 21, 27, and 28 via a Newton Raphson method for non-linear equations. The method is outlined by Press *et al.* (1986). This involves some art in addition to the mathematics.

We search for the zeros of a function f:

$$0 = f(x_1, x_2, \ldots x_N) = f(\mathbf{X}) \qquad (29)$$

To do this we first expand f as a Taylor series:

$$f(\mathbf{X} + \delta\mathbf{X}) = f(\mathbf{X}) + \sum_{i=1}^{N} \frac{\partial f}{\partial x_i} \delta x_i + O(\mathbf{X}^2) + \ldots \qquad (30)$$

Next, you neglect the higher-order terms. We are looking for the point where $f(\mathbf{X})=0$, so you want to choose your corrections (δx_i) such $f(\mathbf{X}+\delta\mathbf{X}) \rightarrow 0$. Setting the left side of equation 30 to zero, you obtain:

$$\sum_{i=1}^{N} \frac{\partial f}{\partial x_i} \delta x_i = -f(\mathbf{X}) \qquad (31)$$

The idea is that you have a system of f equations (N in number) and equation 31 then expands into a matrix whose solution yields the correction values (δx_i). These are then applied to the original estimates:

$$x_{new} = x_{old} + \delta x \qquad (32)$$

The process is repeated until you converge. Now we enter into the art part of the problem. First, we take equation 27 and expand to open up the g_j term:

$$0 = g_j^* + RT \ln\left(\frac{P}{P_0}\right) + RT \ln N_j - RT \ln N + \sum_{i=1}^{NE} \lambda_i a_{i,j} \qquad (33)$$

Next, we divide by RT to non-dimensionalize the equation:

$$0 = \frac{g_j^*}{RT} + \ln\left(\frac{P}{P_0}\right) + \ln N_j - \ln N + \sum_{i=1}^{NE} \frac{\lambda_i a_{i,j}}{RT} \tag{34}$$

To apply equation 31 in as linear a way as possible, we choose non-linear correction variables. These are $\Delta \ln N_j$, $\Delta \ln N$, and $\pi_i = -(\lambda_i/RT)$.[1] This makes the derivatives in equation 31 become:

$$\frac{\partial f_j}{\partial (\ln N_j)} = 1 \tag{35a}$$

$$\frac{\partial f_j}{\partial (\ln N)} = -1 \tag{35b}$$

$$\frac{\partial f_j}{\partial (\pi_i)} = -a_{i,j} \tag{35c}$$

Substituting these into equation 31 yields:[2]

$$\Delta \ln N_j - \Delta \ln N - \sum_{i=1}^{NE} a_{i,j} \pi_i = -\frac{g_j}{RT} \tag{36}$$

There will be one of these equations for each species (j=1,2,…NS). Next we go after equation 21. Here we rewrite the equation in terms of $\ln N_j$:

$$0 = \sum_{j=1}^{NS} a_{i,j} \exp(\ln N_j) - b_i \tag{37}$$

The derivative from equation 31 becomes:

$$\frac{\partial f_i}{\partial (\ln N_j)} = \sum_{j=1}^{NS} a_{i,j} \exp(\ln N_j) = \sum_{j=1}^{NS} a_{i,j} N_j \tag{38}$$

Substituting into equation 31 yields:

$$\sum_{j=1}^{NS} a_{i,j} N_j \Delta \ln N_j = b_i - \sum_{j=1}^{NS} a_{i,j} N_j \tag{39}$$

We will have one of these equations for each element (i=1,2,…NE). Finally, we turn to equation 28. Again, we convert this to a log variable:

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[1] The question is why do we not use $\Delta \pi_i$? This is a very subtle point that is more art than science. It is argued (Gordon and McBride, 1994) that the iterations are uninfluenced by starting each new iteration with the Lagrange multipliers set equal to zero. Thus, $\pi_i = \Delta \pi_i$ for each iteration. This will influence the form of equation 36.

[2] Note that the right side of equation 36 would normally contain the summation of $a_{i,j} \pi_i$, but since $\pi_i = 0$ at the start of each iteration, these terms drop out (see footnote 1).

$$0 = \sum_{j=1}^{NS} \exp(\ln N_j) - \exp(\ln N) \tag{40}$$

Taking the derivatives in equation 31 yields:

$$\frac{\partial f}{\partial(\ln N_j)} = \sum_{j=1}^{NS} \exp(\ln N_j) = \sum_{j=1}^{NS} N_j \tag{40a}$$

$$\frac{\partial f}{\partial(\ln N)} = -\exp(\ln N) = -N \tag{40b}$$

So substituting these equations into equation 31 yields:

$$\sum_{j=1}^{NS} N_j \Delta \ln N_j - N\Delta \ln N = N - \sum_{j=1}^{NS} N_j \tag{41}$$

There will be one of these equations. Equations 36, 39, and 41 can be collected together into a matrix format. This is illustrated by an example in which the system contains 5 species and 3 elements:

$$
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 & -a_{11} & -a_{21} & -a_{31} & -1 \\
0 & 1 & 0 & 0 & 0 & -a_{12} & -a_{22} & -a_{32} & -1 \\
0 & 0 & 1 & 0 & 0 & -a_{13} & -a_{23} & -a_{33} & -1 \\
0 & 0 & 0 & 1 & 0 & -a_{14} & -a_{24} & -a_{34} & -1 \\
0 & 0 & 0 & 0 & 1 & -a_{15} & -a_{25} & -a_{35} & -1 \\
a_{11}N_1 & a_{12}N_2 & a_{13}N_3 & a_{14}N_4 & a_{15}N_5 & 0 & 0 & 0 & 0 \\
a_{21}N_1 & a_{22}N_2 & a_{23}N_3 & a_{24}N_4 & a_{25}N_5 & 0 & 0 & 0 & 0 \\
a_{31}N_1 & a_{32}N_2 & a_{33}N_3 & a_{34}N_4 & a_{35}N_5 & 0 & 0 & 0 & 0 \\
N_1 & N_2 & N_3 & N_4 & N_5 & 0 & 0 & 0 & -N
\end{bmatrix}
\begin{bmatrix}
\Delta \ln N_1 \\
\Delta \ln N_2 \\
\Delta \ln N_3 \\
\Delta \ln N_4 \\
\Delta \ln N_5 \\
\pi_1 \\
\pi_2 \\
\pi_3 \\
\Delta \ln N
\end{bmatrix}
=
\begin{bmatrix}
-g_1/RT \\
-g_2/RT \\
-g_3/RT \\
-g_4/RT \\
-g_5/RT \\
b_1^\circ \\
b_2^\circ \\
b_3^\circ \\
N^\circ
\end{bmatrix}
$$

Here:

$$b_i^0 = b_i - \sum_{j=1}^{NS} a_{i,j} N_j$$

$$N^0 = N - \sum_{j=1}^{NS} N_j$$

So the approach is to make reasonable initial guesses for N_j, calculate the g_j's from equation 18 (knowing P and T), solve the matrix for the correction factors, and use the correction factors to get the revised values of N_j. The process is repeated with, as mentioned in the footnotes, π_i reset to zero for each iteration.

4.0 A Slick Numerical Trick

The difficulty here is that practical calculations for hydrocarbon air systems can involve the order of 70 species and 4 elements, resulting in a 75x75 matrix. The sparseness of the upper left corner

of the matrix suggests that substitution may result in a smaller number of more complex equations to solve (also, as the systems grow, this sparse region becomes most of the matrix). With the following substitution, we can reduce this monster matrix to one that is NE+1 in size.

We start by solving equation 36 for $\Delta \ln N_j$:

$$\Delta \ln N_j = \Delta \ln N + \sum_{i=1}^{NE} a_{i,j}\pi_i - \frac{g_j}{RT} \qquad (42)$$

This is substituted into equation 39 in place of the $\Delta \ln N_j$ term:

$$\sum_{j=1}^{NS} a_{i,j}N_j\left[\Delta \ln N + \sum_{i=1}^{NE} a_{i,j}\pi_i - \frac{g_j}{RT}\right] = b_i - \sum_{j=1}^{NS} a_{i,j}N_j \qquad (43)$$

We recognize that the i that appears in the first and last summation terms, and the b_i relates to the equation itself, while the i in the middle summation term is actually summed. Calling the unsummed i (the equation index) as k, and rearranging gives:

$$\sum_{i=1}^{NE}\sum_{j=1}^{NS} a_{k,j}a_{i,j}N_j\pi_i + \left[\sum_{j=1}^{NS} a_{k,j}N_j\right]\Delta \ln N = b_k - \sum_{j=1}^{NS} a_{k,j}N_j + \sum_{j=1}^{NS} a_{k,j}N_j \frac{g_j}{RT} \qquad (44)$$

There will be k=1,2,…,NE of these equations. We also make the same substitution of equation 42 into equation 41:

$$\sum_{j=1}^{NS} N_j\left[\Delta \ln N + \sum_{i=1}^{NE} a_{i,j}\pi_i - \frac{g_j}{RT}\right] - N\Delta \ln N = N - \sum_{j=1}^{NS} N_j \qquad (45)$$

Rearranging this to put the correction variables on the left side yields:

$$\sum_{i=1}^{NE}\sum_{j=1}^{NS} a_{i,j}N_j\pi_i + \left(\sum_{j=1}^{NS} N_j - N\right)\Delta \ln N = N - \sum_{j=1}^{NS} N_j + \sum_{j=1}^{NS} N_j \frac{g_j}{RT} \qquad (46)$$

There will be one of these equations. Equations 44 and 46 can be cast into a matrix form as shown above, although now the matrix will be (NE+1)x(NE+1) in size and the solution vector will be: $(\pi_1, \pi_2,…, \pi_{NE}, \Delta \ln N)$.

The solution procedure is as follows. First, you make an initial guess for N_j and N. (The solution procedure is very robust, and the standard crude initial guesses are N=0.1, and N_j=0.1/NS. (N_{NS} is usually set a little off from the others in value to prevent a zero divide problem in the first iteration. From this convergence is almost always quickly achieved.) You use these, along with the known T and P to calculate g_j from equations 16 and 18. You solve the matrix represented by equations 44 and 46 to get the correction vector, $(\pi_1, \pi_2,…, \pi_{NE}, \Delta \ln N)$. Next, you use the values from the correction vector to calculate $\Delta \ln N_j$ using equation 42. Then you correct each of the variables:

$$\ln N_{j,new} = \ln N_{j,old} + e\Delta \ln N_j \qquad (47a)$$

$$\ln N_{new} = \ln N_{old} + e\Delta \ln N \qquad (47b)$$

You iterate until you locate the equilibrium point. The factor "e" is a self-adjusting underrelaxation parameter (it varies between 0 and 1). If e=1, the solution may numerically diverge for poor initial guesses, so e is calculated via an empirical procedure outlined in Gordon and McBride (1994) that is based on the existing N and N_j. In practice, e is much less than 1 at the start of a calculation and it reaches 1 as the problem approaches convergence.

The value e is calculated as follows:

Assign a parameter SIZE=-ln10^{-8}. Then define a parameter:

$$e_1 = \frac{2}{\max(5|\Delta \ln N|, |\Delta \ln N_j|)} \tag{48}$$

For those species where $\ln(N_j/N) \leq$-SIZE, and $\Delta \ln N_j \geq 0$, find a second parameter:

$$e_2 = \min \left| \frac{-\ln \frac{N_j}{N} - 9.2103404}{\Delta \ln N_j - \Delta \ln N} \right| \tag{49}$$

Finally:

$$e = \min(1, e_1, e_2) \tag{50}$$

5.0   References

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