THE CHEMICAL EQUILIBRIUM PROBLEM

BY

JAMES H. BIGELOW

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I. Formulation

Consider a beaker, into which we will put known amounts of various atoms, ions, radicals, molecules, or other chemical entities. These entities, called 'inputs' will have the property that no combination of more than one can react together to form other inputs. Thus if we were to load the beaker with H^+ ion and OH^- ion, we could not also use H_2O as an input. i.e. We assume that the entities when expressed as vectors are linearly independent. We order the inputs $i = 1,2,\ldots,m$ and enter the amount in moles of the i^{th} input into the i^{th} component of a vector b.

These inputs may react with one another in fixed proportions to form various chemical species. If we number the species $j = 1,2,\ldots,n$ then species j may be represented by a vector P_j with m compenents, specifying in its i^{th} component how moles of the i^{th} input are consumed in the reaction which forms one mole of species j. Then, if x_j = the number of moles of species j in the solution, conservation of mass demands that the following vector equation be satisfied:

$$\sum_{j=1}^{n} P_j x_j = b \qquad (1.1)$$

If we define:

$$\bar{x} = \sum_{j=1}^{n} x_j \qquad (1.2)$$

then $x_j/\bar{x}$ is the concentration, in mole fractions, of the j^{th} species.

There is a function, called the Gibbs Free-Energy function, which expresses the total electro-chemical potential of the solution. This function in the single compartmented case is proportional to z ; where

$$z = \sum_{j=1}^{n} x_j \quad c_j + \log {}^{x_j}/\bar{x} \qquad (1.3)[1]$$

1. Theory tells us that for an ideal chemical solution, the partial molar electro-chemical potential of a species j takes the form:

$$\mu_j = \mu_j + RT \log c_j + z_j \; FX$$

where c_j is the molar concentration of species j , z_j the electric charge on each molecule of species j , and X the electrical potential. R, T and F have their usual meanings.

On the range of concentrations for which ideality is a good approximation to the real world, there is a constant α , approximately the same for each species, such that: $c_j \simeq \alpha \, {}^{x_j}/\bar{x}$ (to be read 'approximately equal to '). Clearly then,

$$\mu_j = RT \left[\left\{ \frac{\mu_j^o + z_j \; FX}{RT} + \log \alpha \right\} + \log {}^{x_j}/\bar{x} \right]$$

We let:

$$c_j = \frac{\mu_j^o + z_j \; FX}{RT} + \log \alpha$$

Then the actual Gibbs free-energy function becomes

$$\begin{aligned} G &= \sum RT \, x_j \left(c_j + \log {}^{x_j}/\bar{x} \right) \\ &= RT \, z \end{aligned}$$

Thus z is indeed proportional to the Gibbs free-energy.

Also, our constants c_j include any electrical potential impressed from outside upon the compartment. The number μ_j^o is the standard partial molar free-energy, and can be found in the literature. The constant α converts mole fractions to molar concentrations. In dilute aqueous solutions α will be approximately 55.5 moles/liter.

Willard Gibbs showed that our beaker will be at equilibrium when the chemical solution achieves the composition $x = (x_1,\ldots,x_n)$ and Min z satisfying:

$$\begin{aligned}
&\sum_{j=1}^{n} x_j \left(c_j + \log {}^{x_j}/\bar{x} \right) &&= && z(x)\,(\mathrm{Min}) \\
\text{s.t. } &\sum_{j=1}^{n} P_j\, x_j &&= && b \qquad (1.4) \\
& x_j &&\geq && 0\ ,\ j = 1,2,\ldots,n. \\
&\text{where } \bar{x} = \sum_{j=1}^{n} x_j
\end{aligned}$$

Methods for finding equilibrium solutions to chemical problems based on this formulation have had much success. R. J. Clasen [1] at Rand Corporation, for example, has devised several procedures for solving (1.4). However, all such methods have so far run into trouble whenever degeneracy has occurred during the computational procedure, i.e. whenever some x_j becomes zero or nearly zero. This paper will propose a method not at all discommoded by degeneracy.

II. Method of solution

Suppose we had an initial feasible solution $\underline{x} = (x_1,\ldots,x_n)$ to (1.4) with the property that each component x_j of $\underline{x}$ were strictly positive.* Then by following the stops given below, one can successively improve the solution, and ultimately find a solution as close to the optimal solution as desired.

---

* Before the method in this Section can be applied it is necessary to have at hand an initial solution with all $x_j > 0$. How to find such a solution when it exists is discussed in Appendix 1. If for certain j, x = 0 must hold, Appendix 1 gives an algorithm for determining which x_j must be dropped so that the above algorithm can be initiated on a subset of the variables.

Step 1:

$$\text{Letting} \quad \theta_j = \frac{1}{x_j}, \qquad j = 1,2,\ldots,n,$$

$$\text{and} \quad \bar{\theta} = \frac{1}{\bar{x}},$$

find the unique y satisfying the quadratic program: Find $y_j \geq 0$, Min z:

$$\frac{1}{2} \sum \theta_j y_j^2 + \sum \left[c_j - 1 - \log (\theta_j/\bar{\theta}) \right] y_j = z$$

$$\sum P_j y_j = b$$

This is equivalent to solving

$$\begin{array}{c}
\begin{array}{cccc|c} y_1 & y_2 & \cdots & y_n & \Pi \end{array} \\
\left[\begin{array}{cccc|c}
\theta_1 & & & & -P_1^T \\
 & \theta_2 & & & -P_2^T \\
 & & \ddots & \theta_n & -P_n^T \\
\hline
P_1 & P_2 & \cdots & P_n &
\end{array}\right]
\end{array}
+
\left[\begin{array}{c}
c_1 - 1 - \log {}^{\theta_1}/_{\bar{\theta}} \\
c_2 - 1 - \log {}^{\theta_2}/_{\bar{\theta}} \\
\vdots \\
c_n - 1 - \log {}^{\theta_n}/_{\bar{\theta}} \\
-b
\end{array}\right]
=
\left[\begin{array}{c}
\sigma_1 \\
\sigma_2 \\
\vdots \\
\sigma_n \\
0
\end{array}\right] \qquad (2.1)$$

$$y_j \geq 0, \quad \sigma_j \geq 0, \qquad j = 1,2,\ldots,n.$$

$$\text{and} \quad \sum_{j=1}^{n} y_j \sigma_j = 0$$

Step 2:

Form the weighted average solution μ,

$$u = \lambda x + (1 - \lambda) y \qquad (2.2)$$

where λ is chosen to minimize the value of $z(\mu(\lambda))$ for all values of λ for which (2.2) is non-negative. Notice from (2.1) that y is a feasible solution to (1.4), and since x is feasible, so must μ be feasible.

Now compute $\eta_j = \left(\delta_j + \frac{x_j - y_j}{x_j}\right)$. If each $|\eta_j|$ is small enough then μ is a close approximation to the optimal solution. If not, go to Step 3. We can decide if each $|\eta_j|$ is small enough by the following.

It will be shown that $x^o = (x_1^o, \ldots, x_n^o)$ is an optimal solution to problem (1.4),

$$\begin{aligned} \text{Min } z(x) &= \sum x_j \left(c_j + \log {}^{x_j}/\bar{x}\right) \\ \text{s.t.} \quad \sum P_j x_j &= b \\ x_j &\geq 0 \end{aligned}$$

if and only if there is a vector Π^o satisfying:

$$c_j + \log {}^{x_j^o}/\bar{x}^o - \Pi^o P_j = 0 \qquad j = 1,\ldots,n.$$

We have assumed here that $x_j^o > 0$, $j = 1,2,\ldots,n$.

Let $x^1 = (x_1^1, \ldots, x_n^1)$ be the optimal solution to the similar problem.

$$\begin{aligned} \text{Min } w(x) &= \sum x_j \left(c_j^1 + \log {}^{x_j}/\bar{x}\right) \\ \text{s.t.} \quad \sum P_j x_j &= b \\ x_j &\geq 0 \end{aligned}$$

Clearly, the feasible solution x of both problems are the same. Furthermore, if x is feasible, then:

$$|w(x) - z(x)| \leq \sum x_j |c_j^1 - c_j|$$

Suppose that we have a bound $^{\varepsilon}/_2$ on the right-hand side of the above, or:

$$\sum x_j |c_j^1 - c_j| < {}^{\varepsilon}/_2$$

for all feasible x.

Then

$$|w(x) - z(x)| < {}^{\varepsilon}/_2$$

Furthermore, recalling that x^o yielded the minimum value of $z(x)$, and x^1 the minimum value of $w(x)$ for all feasible x, it is easy to see that:

$$|w(x^1) - z(x^o)| < {}^{\varepsilon}/_2$$

Thus:

$$\begin{aligned} |z(x^1) - z(x^o)| &= |z(x^1) - w(x^1) + w(x^1) - z(x^o)| \\ &\leq |z(x^1) - w(x^1)| + |w(x^1) - z(x^o)| \\ &< \varepsilon \end{aligned}$$

Now notice from eqn. (2.1) that since $\theta_j = {}^1/x_j$, $\bar{\theta} = \frac{1}{\bar{x}}$, we have that:

$$\begin{aligned} & c_j - \left(\delta_j + 1 - \frac{y_j}{x_j}\right) + \log \frac{x_j}{\bar{x}} - \Pi P_j = 0 \\ = & \left[c_j - \eta_j\right] + \log {}^{x_j}/\bar{x} - \Pi P_j \end{aligned}$$

If we let:

$$c_j^1 = c_j - \eta_j ,$$

then the current solution x is the optimal solution to:

$$\text{Min } w(x) = \sum x_j \left(c_j^1 + \log {}^{x_j}/\bar{x} \right)$$
$$\text{s.t.} \quad \sum P_j x_j = b$$
$$x_j \geq 0$$

Hence, by the foregoing:

$$|z(x) - z(x^o)| \leq B ,$$

where B is any bound which satisfies:

$$2 \sum t_j |c_j - c_j| = 2 \sum t_j |\eta_j| \leq B$$

for all feasible solutions $t = (t_1, \ldots, t_n)$.

Such bounds are not usually hard to find. For example, one can usually determine a bound $\bar{t}_m$ on $\bar{t} = \sum t$; by inspection. If the inputs may combine together but in no species does an input split into two or more parts, then the sum of the inputs is such a bound $\bar{t}_m$ on $\bar{t}$. Then if $\eta_m = \max_j |\eta_j|$, we can let:

$$B = 2\bar{t}_m \eta_m$$

Alternately, a separate upper bound on each species may be found by:

$$m_j = \min_j \left\{ {}^{b_i}/a_{ij} \mid b_i a_{ij} \geq 0 , \quad a_{ij} \neq 0 \right\}$$
$$= \infty \text{ if no such } b_i \text{ and } a_{ij}$$

where a_{ij} is the i^{th} component of the vector P_j . If all these numbers m_j are finite, then we can set

$$B = 2 \sum m_j | \eta_j |$$

Whatever B is finally decided upon, the following will be true:

$$z(x^o) \geq z(x) - B \quad .$$

Hence we will be able to estimate how close the solution $u = \lambda x + (1-\lambda)y$ is to the optimum.

Step 3.

In theory, since x is strictly positive, then u will also be strictly positive (see Section 3). If the computations are made in practice, it may be that some component of u, say u_j, is so small as to be negligible. In this case, set u_j at some small lower bound and continue the computations. If there are several such u_j, they can be made all small and at the same time proportional to $\exp(\Pi P_j - c_j)$.

Alternatively, column j could be deleted from the problem entirely. This of course, means that the j^{th} species will not appear at all in the final solution, and so it is treated as if it were zero in the final solution to the original problem.

Step 4.

Let the strictly positive solution u, modified as in step 3, take the place of x in step 1 and in (2.1).

One will repeatedly cycle through these four steps until the convergence criterion of step 2 is satisfied. At that point, the last solution found will closely approximate the actual optimal solution to (1.4).

III. Derivation:

The chemical equilibrium problem (1.4 or 3.1 below) is difficult to solve because its objective, the function $z(x)$, is non-linear. Linear problems being easy to solve, we will attempt to replace this problem with a linear one. We do this in two stages: first, we find an approximating problem with a non-linear separable objective which in turn is approximated by a quadratic program with a convex separable objective. The first step is accomplished by theorem 1.

Theorem 1   Consider the following two problems:

$$\text{Min } z = \sum_{j=1}^{n} x_j \left(c_j + \log {}^{x_j}/\bar{x} \right)$$

$$\text{s.t.} \quad \sum_{j=1}^{n} P_j x_j = b \tag{3.1}$$

$$x_j \geq 0$$

$$\text{where} \quad \bar{x} = \sum_{j=1}^{n} x_j$$

and:

$$\text{Min } w = \sum x_j \left(c_j + K + \log x_j \right)$$

$$\text{s.t.} \quad \sum P_j x_j = b \tag{3.2}$$

$$x_j \geq 0$$

Then there is a particular value of K for which the optimal solution $x^o = (x_1^o, \ldots, x_n^o)$ to (3.2) is also optimal for (3.1).

Proof: Look at the optimality conditions for the two problems: x^o is optimal for (3.2) if there exists a vector $\Pi^o = (\Pi_1^o, \ldots, \Pi_m^o)$ such that (x^o, Π^o) satisfies:

$$\frac{\partial \left[w(x^o) - \Pi^o \left(\sum_k P_k x_k - b \right) \right]}{\partial x_j} = c_j + 1 + K + \log x_j - \Pi^o P_j$$

$$\begin{cases} \geq 0 & j = 1, \ldots, n \\ = 0 & \text{if } x_j^o > 0 \end{cases} \tag{3.3}$$

Similarly, it is optimal for (3.1) if there is a $\Pi^1 = (\Pi^1_1,\ldots,\Pi^1_m)$ such that (x^o, Π^1) satisfies:

$$\frac{\partial\left[z(x^o) - \Pi^1\left(\sum_k P_k x_k - b\right)\right]}{\partial x_j} = c_j + \log x^o_j/\bar{x}^o - \Pi^1 P_j$$

$$\begin{cases} \geq 0 & j = 1,\ldots,n \\ = 0 & \text{if } x^o_j > 0 \end{cases} \qquad (3.4)$$

Now let:

$$K = -1 - \log \bar{x}^o \qquad (3.5)$$

Substitution of (3.5) into (3.3) shows that (x^o, Π^o), for this value of K, satisfies the optimality conditions (3.4) of problem (3.1). Of course this also shows that:

$$\Pi^1 = \Pi^o \qquad (3.6)$$

QED.

If we did happen to know the value of $\bar{x}^o$, then theorem 1 states that the solution to problem (3.2), with K as in (3.5) would be the desired solution to (3.1). In addition, (3.2) is separable, as we wished.

Unfortunately, $\bar{x}^o$ is not known. Instead, we will use the value of $\bar{x}$ in the current solution to (3.1) to approximate K in (3.5) and (3.2).

If our current feasible (but non-optimal) solution to (3.1) is $\hat{x} = (\hat{x}_1,\ldots,\hat{x}_n)$, so that $\hat{\bar{x}} = \sum \hat{x}_j$, we let:

$$d_j = c_j - 1 - \log \hat{\hat{x}} \tag{3.7}$$

and then consider the problem:

$$\begin{aligned} \text{Min } w = \textstyle\sum x_j\ (d_j + \log x_j) & \\ \text{s.t.} \quad \textstyle\sum P_j x_j &= b \\ x_j &\geq 0 \end{aligned} \tag{3.8}$$

The approximating quadratic program could be obtained by expanding $\mu \log \mu$ into a Taylor series about $\mu = \mu_o$. However, it is also possible to "linearize" (3.8) by replacing it with an equivalent generalized linear program:

$$\begin{aligned} \text{Min } \phi(x,\theta) = \textstyle\sum x_j(d_j - \log \theta_j) & \\ \text{s.t.} \quad \textstyle\sum P_j x_j &= b \quad : \Pi \\ \theta_j x_j &\leq 1 \quad : (-y_j) \\ x_j &\geq 0 \end{aligned} \tag{3.9}$$

where $\theta_j \geq 0$ is a variable that can be chosen independently of x_j .

It is easy to show that from any feasible solution of either (3.8) or (3.9), a feasible solution to the other can be found. Furthermore, the same holds true for optimal solutions.

A moments thought will convince one that if (x,θ) is a solution to (3.9) which does not satisfy:

$$\theta_j x_j = 1 \tag{3.10}$$

for each $x_j > 0$, then it can be improved by increasing their respective θ_j's.

The Π and $-y_j$ appearing to the right of the constraints of (3.9) are Lagrange Multipliers. The multipliers Π corresponding to equality constraints, are unrestricted in sign, but the $-y_j$ corresponding to inequalities of the sort $\leq$ must satisfy:

$$y_j \geq 0 \tag{3.11}$$

We will assume that the current solution $(\hat{x}, \hat{\theta}) = (\hat{x}_1,\ldots,\hat{x}_n ; \hat{\theta}_1,\ldots,\hat{\theta}_n)$ is strictly positive, and that (3.10) is satisfied for each j. Now consider the $\hat{\theta}_j$ as constants. For the given $\hat{\theta}$ assume $x = x^*$ is an optimal solution to (3.9); then, there must exist multiplier $(\hat{\Pi}, \hat{y}_j)$ which satisfy the Lagrangian conditions (3.11) and:

$$\frac{\partial \left[\phi(x^*, \theta) - \hat{\Pi}\left(\sum_k P_k x_k^* - b \right) + \sum_k \hat{y}_k \left(\theta_k x_k^* - 1 \right) \right]}{\partial x_j} = f(\hat{\theta}_j)$$

$$= d_j - \log \hat{\theta}_j - \hat{\Pi} P_j + \hat{y}_j \hat{\theta}_j = 0 \qquad j = 1,2,\ldots,n. \tag{3.12}$$

We will show that we can find an improved solution to (3.9) if and only if we can find a new vector of constants $\theta^1 = (\theta_1^1,\ldots,\theta_n^1)$, which satisfy:

$$f(\theta_j^1) \leq 0 \qquad j = 1,2,\ldots,n \tag{3.14}$$

for which the inequality is strict for at least one j .

If we are trying to satisfy (3.14), we look for that value of θ_j which minimizes $f(\theta_j)$. Since $f(\theta_j)$ is strictly convex, it has a unique minimum, occuring at $\theta_j = \theta_j^1$ where

$$f^1(\theta_j) = 0 = -\frac{1}{\theta_j} + y_j$$

Thus we pick

$$\theta_j^1 = \begin{cases} \dfrac{1}{y_j} & \text{if } y_j > 0 \text{ , otherwise} \\ \beta & \text{(some arbitrary large number)} \end{cases} \tag{3.15}$$

So far, we have only asserted the existance of multipliers $(\hat{\Pi}, \hat{y})$ satisfying (3.11) and (3.12). Conditions (3.11) and (3.12) in general are too few to determine their values. But equations (3.15) suggest that y_j be interpreted as an amount of species j , which together with $\theta_j^1 = \frac{1}{y_j}$ would correspond to a new feasible solution to (3.9). Thus we ask that in addition to (3.11) and (3.12), the multipliers satisfy:

$$\sum P_j y_j = b \tag{3.16}$$

Writing (3.12) and (3.16) in matrix form gives:

$$
\begin{array}{cccc|c}
y_1 & y_2 & \cdots & y_n & \Pi \\
\end{array}
$$

$$
\left[\begin{array}{cccc|c}
\hat{\theta}_1 & & & & -P_1^T \\
& \hat{\theta}_2 & & & -P_2^T \\
& & \ddots & & \vdots \\
& & & \hat{\theta}_n & -P_n^T \\
\hline
P_1 & P_2 & & P_n &
\end{array}\right]
+
\begin{bmatrix}
d_1 - \log \hat{\theta}_1 \\
d_2 - \log \hat{\theta}_2 \\
\vdots \\
d_n - \log \hat{\theta}_n \\
-b
\end{bmatrix}
=
\begin{bmatrix}
0 \\ 0 \\ \vdots \\ 0 \\ 0
\end{bmatrix}
\qquad (3.17)
$$

If the matrix $[P_1, P_2, \ldots, P_n]$ has rank m, it is easy to show that there is a unique solution $(\Pi_1 y)$ to (3.17). However, that solution need not satisfy $y_j \geq 0$. Thus we relax the restrictions slightly.

$$
\begin{array}{cccc|c}
y_1 & y_2 & \cdots & y_n & \Pi \\
\end{array}
$$

$$
\left[\begin{array}{cccc|c}
\hat{\theta}_1 & & & & -P_1^T \\
& \hat{\theta}_2 & & & -P_2^T \\
& & \ddots & & \vdots \\
& & & \hat{\theta}_n & -P_n^T \\
\hline
P_1 & P_2 & \cdots & P_n &
\end{array}\right]
+
\begin{bmatrix}
d_1 - \log \hat{\theta}_1 \\
d_2 - \log \hat{\theta}_2 \\
\vdots \\
d_n - \log \hat{\theta}_n \\
-b
\end{bmatrix}
=
\begin{bmatrix}
\delta_1 \\ \delta_2 \\ \vdots \\ \delta_n \\ 0
\end{bmatrix}
\qquad (3.18)
$$

$$y_j \geq 0 , \quad \delta_j \geq 0 , \quad j = 1,2,\ldots,n$$

$$\sum y_j \delta_j = 0$$

It can be shown by the application of complementary pivot theory, or by noting that (3.18) is equivalent to a positive definite quadratic program, that (3.18) has a unique solution (Π, y) .

Theorem 2: If the feasible solution to (3.8) $y \neq \hat{x}$ found by solving (3.18) then y yields a lower value of w than the current solution $\hat{x} = (\hat{x}_1, \ldots, \hat{x}_n)$.

Proof: Taking (Π, y) from (3.18), we have that:

$$f(\hat{\theta}_j) = d_j - \log \hat{\theta}_j - \Pi P_j + \hat{\theta}_j y_j = \delta_j \geq 0$$

We have shown that

$$-\log \theta_j + y_j \theta_j \geq \log y_j + 1$$

Now:

$$0 \leq \sum \hat{x}_j \delta_j = \sum \hat{x}_j (d_j - \log \hat{\theta}_j - \Pi P_j + y_j \hat{\theta}_j)$$

$$= w(\hat{x}) - \Pi b + \sum y_j$$

since $\hat{\theta}_j = \frac{1}{\hat{x}_j}$. Similarly, summing all j for which $y_j > 0$,

$$0 = \sum y_j \delta_j = \sum y_j (d_j - \log \hat{\theta}_j - \Pi P_j + y_j \hat{\theta}_j)$$

$$\geq \sum y_j (d_j + \log y_j - \Pi P_j + 1)$$

$$\geq w(y) - \Pi b + \sum y_j$$

Thus: $\qquad w(\hat{x}) - \Pi b + \sum y_j \geq w(y) - \Pi b + \sum y_j$

Or: $\qquad w(y) \leq w(\hat{x})$

And the inequality is strict if there is any $y_j > 0$ such that $\hat{\theta}_j \neq \frac{1}{y_j}$.

Q.E.D.

However, problem (3.8) is not the problem we are interested in. We must show:

<u>Theorem 3</u>: y found by (3.18) yields a lower value of z in (3.1) than does the current solution $\hat{x}$.

<u>Proof</u>: Inserting d_j from (3.7) into $f(\hat{\theta}_j)$,

$$f(\hat{\theta}_j) = c_j - 1 - \log \hat{\bar{x}} - \log \hat{\theta}_j - \Pi P_j + y_j \hat{\theta}_j = \delta_j$$

Evaluating $\sum x_j f(\hat{\theta}_j)$ and $\sum y_j f(\frac{1}{y_j})$, we find

$$\sum \hat{x}_j f(\hat{\theta}_j) = z(\hat{x}) - \hat{\bar{x}} + \sum y_j - \Pi b = \sum \hat{x}_j \delta_j \geq 0$$

$$\sum y_j f(\frac{1}{y_j}) = z(y) - \Pi b + \bar{y} \log (\bar{y}/\hat{\bar{x}}) \leq 0$$

In theorem 2, we expressed $\sum \hat{x}_j f(\hat{\theta}_j)$ and $\sum y_j f(\frac{1}{y_j})$ in terms of $w(\hat{x})$ and $w(y)$. Simple algebra shows that:

$$\begin{aligned} z(\hat{x}) - z(y) &= w(\hat{x}) - w(\bar{y}) + \bar{y}\left[\frac{\hat{\bar{x}}}{\bar{y}} - 1 - \log \frac{\hat{\bar{x}}}{\bar{y}}\right] \\ &= w(\hat{x}) - w(y) + \bar{y} g\left(\frac{\hat{\bar{x}}}{\bar{y}}\right) \end{aligned} \qquad (3.19)$$

where $g(\mu) = \mu - 1 - \log \mu$ is defined for $\mu \geq 0$.

It is easy to check that the strictly convex functions $g(\mu)$ has a minimum at $\mu = 1$ of $g(1) = 0$.

Thus: $$g(\mu) \geq 0$$

Since: $$\bar{y} = \sum y_j > 0 ,$$

and from theorem 2, $w(\hat{x}) - w(y) \geq 0$, we have

$$z(y) \leq z(\hat{x})$$

As in theorem 2, the inequality is strict if for any $y_j > 0$, the corresponding $\hat{\theta}_j \neq \frac{1}{y_j}$.

Q.E.D.

So far then, we have a procedure for finding an improved solution y for (3.1), starting from a non-degenerate solution x . In order to apply the method again, we must find a new non-degenerate solution.

<u>Theorem 4</u>: If y is a degenerate solution to (3.1), and $\hat{x}$ is a non-degenerate solution to (3.1), then there exists $\lambda > 0$ such that the solution μ defined by:

$$\mu_j = (1-\lambda)y_j + \lambda\hat{x}_j$$

satisfies $z(\mu) < z(y)$, $A\mu = b$, $n > 0$.

(μ is non-degenerate since $\hat{x}$ is , and $\lambda > 0$.)

Proof: Consider z a function of λ. Then:

$$z(\lambda) = \sum_j u(\lambda)_j(\lambda) \left(C_j + \log \frac{u_j(\lambda)}{\bar{u}(\lambda)} \right) .$$

Taking the derivative, and evaluating at $\lambda = 0$ (i.e. $u = y$),

$$\frac{dz(u(\lambda))}{d\lambda} = \sum_j (x_j - y_j) \left(C_j + \log {}^{y_j}/\bar{y} \right)$$

Since y is degenerate, we will suppose $y_k = 0$. Then

$$\hat{x}_k - y_k > 0 , \quad \text{and} \quad \log {}^{y_k}/\bar{y} = -\infty$$

Thus:

$$\left. \frac{dz(u(\lambda))}{d\lambda} \right|_{\lambda = 0} = -\infty$$

Since z and $\frac{dz}{d\lambda}$ are continuous functions of λ, for $1 \geq \lambda > 0$, there will be an interval $(0, \beta)$ in which $\frac{dz}{d\lambda}$ is negative. Thus:

$$z(u(\beta)) < z(0) = z(y) .$$

Q.E.D.

<u>Corr</u>: If there exists a non-degenerate feasible solution to (3.1), then the optimal solution will be non-degenerate.

We would like to show that the value of z in (3.1) computed using the solution u is strictly lower than z computed using $\hat{x}$.

__Theorem 5__: Either $y = \hat{x}$, in which case $\hat{x}$ is the optimal solution to (3.1), or $y \neq \hat{x}$, in which case there is a solution of the form (3.20) which yields a value of z strictly less than z evaluated at $\hat{x}$.

__Proof__: If $y = \hat{x}$, then:

$$f(\hat{\theta}_j) = C_j - 1 - \log \hat{\theta}_j - \log \hat{\bar{x}} - \Pi P_j + y_j \hat{\theta}_j$$

$$= C_j + \log \hat{x}_j/\hat{\bar{x}} - \Pi P_j = \delta_j ,$$

remembering that $\hat{\theta}_j = \frac{1}{\hat{x}_j}$. Since $\hat{x}$ is non-degenerate, so is y .

Thus

$$\sum y_j \delta_j = 0 \Rightarrow \delta_j = 0 , \quad j = 1,2,\ldots,n.$$

Hence:

$$C_j + \log \hat{x}_j/\hat{\bar{x}} - \Pi P_j = 0 , \quad j = 1,2,\ldots,n. \tag{3.21}$$

But (3.21) are the optimality conditions for (3.1).

Thus if $y = \hat{x}$, then $\hat{x}$ is optimal.

If $y \neq \hat{x}$, and y is degenerate, we have from theorems 3 and 4 that there is a u of the form (3.20) satisfying:

$$z(u) < z(y) \leq z(\hat{x})$$

If $y \neq \hat{x}$ and y is non-degenerate, then the concluding remark of theorem 3 holds, so that

$$z(y) < z(\hat{x})$$

In this case the best value of λ might be either $\lambda > 0$ or $\lambda = 0$.

Our process, then, is an iterative one. We start with a non-degenerate solution $\hat{x} = (\hat{x}_1, \ldots, \hat{x}_n)$ to (3.1) and find (y, Π) satisfying (2.1), which is repeated here as (3.22);

$$
\begin{array}{c}
\begin{array}{cccccc} y_1 & y_2 & --- & y_n & & \Pi \end{array} \\
\left[\begin{array}{cccc|c}
\theta_1 & & & & -P_1^T \\
& \theta_2 & & & -P_2^T \\
& & \ddots & & \\
& & & \theta_n & -P_n^T \\ \hline
P_1 & P_2 & & P_n &
\end{array}\right]
\end{array}
+
\left[\begin{array}{c}
c_1 - 1 - \log \theta_1/\bar{\theta} \\
c_2 - 1 - \log \theta_2/\bar{\theta} \\
\vdots \\
c_n - 1 - \log \theta_n/\bar{\theta} \\
\\
-b
\end{array}\right]
+
\left[\begin{array}{c}
\delta_1 \\ \delta_2 \\ \vdots \\ \delta_n \\ \\ 0
\end{array}\right]
\tag{3.22}
$$

$$y_j \geq 0, \quad \delta_j \geq 0, \qquad j = 1, 2, \ldots, n$$

$$\sum y_j \delta_j = 0$$

where $\theta_j = \frac{1}{\hat{x}_j}$, $\theta = \frac{1}{\hat{x}}$.

Problem (3.22) can be easily derived by replacing the constants d_j in (3.18) by their values given in equations (3.7).

Then we form the new non-degenerate solution u to (3.1) by equations (3.20), choosing λ to minimize the value of the function $z(u(\lambda))$. The new solution u replaces $\hat{x}$, and the process is repeated. Each iteration produces a strict improvement in z , or, if $\hat{x}$ is optimal reproduces the current solution $\hat{x}$ and the corresponding value of z . (See Sec. 2)

The only remaining question is whether the process converges, and if it converges to the optimal solution.

<u>Theorem 6</u> This process converges to the optimal solution.

<u>Proof</u>: For any real chemical problem, the set of feasible solutions x to (3.1) is bounded. Thus the possible values of z are bounded. In particular, z is bounded from below, by z^o, the optimum.

Suppose successive applications of the method yielded a sequence $x^1, x^2, \ldots, x^m, \ldots$ of solutions to (3.1) with corresponding values of z ,

$$z^{(1)} > z^{(2)} > \ldots > z^{(n)} > \ldots$$

Since the sequence $\{z^{(k)}\}$ is monotone decreasing and bounded from below, it must converge. Suppose it converges to $\hat{z} > z^o$.

The sequence $\{x^{(n)}\}$ has elements taken from a compact subset of n-space. Thus it possesses a subsequence $\{x^{(n_k)}\}$ which converges, and of course, $\{z^{(n_k)}\}$ also converges, to $\hat{z}$.

Let $\lim_k x^{(n_k)} = \hat{x}$. Clearly, since z is a continuous function of x , we can say that

$$\hat{z} = z(\hat{x}) \; .$$

And since $\hat{z} > z^o$, $\hat{x}$ cannot be optimal.

Thus, by Theorem 5, if we apply our method to $\hat{x}$, we will find a solution $\hat{u}$ to (3.1) such that $z(\hat{u}) < z(\hat{x})$.

Let $z(\hat{u}) = z(\hat{x}) - h$, for some $h > 0$.

I claim however, that $\hat{u}$ is a continuous function of $\hat{x}$.

Let $\hat{x}$ be as in (3.26). Clearly $\hat{y}$ is a continuous function of $\hat{x}$. And:

$$\hat{u} = \lambda_o \hat{x} + (1-\lambda_o)\, \hat{y}$$

where λ_o is that value of λ at which:

$$z(\hat{u}(\lambda)) = \text{Min.}$$

By a theorem by Dantzig, et al [2] on the continuity of the minimum set of a function, $\hat{u}$ is a continuous function of $\hat{x}$. Thus $z(\hat{u})$ is a continuous function of $z(\hat{x})$.

Thus it is possible to pick a k so large that the solution u^{n_k} derived by our method from x^{n_k} is as close as desired to u, since x^{n_k} will be close to $\hat{x}$; and the value $z(u^{n_k})$ will be as close as desired to $z(\hat{u})$. Let $z(u^{n_k}) < z(\hat{u}) + \varepsilon$, for some small $0 < \varepsilon < h$. Then:

$$z(u^{n_k}) < z(\hat{u}) + \varepsilon < z(\hat{x}) - h + \varepsilon < z(\hat{x}) .$$

But $u^{n_k} = x^{n_k+1}$, and $z(x^{n_k+1}) > z(\hat{x})$...contradiction.
Thus z^n converges to z^o.

Since the optimal solution x^o to (3.1) is unique, $\{x^n\}$ must converge to x^o.

Q.E.D.

APPENDIX 1

AN INITIAL NON-DEGENERATE SOLUTION

Before the method given in section 2 can be applied, an initial non-degenerate feasible solution to the problem must be found. That is, we must find $x = (x_1,\ldots,x_n)$ such that:

$$\begin{aligned} \sum P_j x_j &= b \\ x_j &> 0 \end{aligned} \qquad \text{(A1.1)}$$

To do this, first define the vector Q , where:

$$Q = \sum P_j \qquad \text{(A1.2)}$$

Then consider the problem:

$$\begin{aligned} &\text{Max } y \\ &\text{s.t. } Qy + \sum P_j \mu_j = b \quad : \lambda \\ &\qquad\qquad \mu_j \geq 0 \end{aligned} \qquad \text{(A1.3)}$$

This is a simple linear program, and therefore easily solved. Let $(y^o, \mu_1^o,\ldots,\mu_n^o)$ be the optimal solution.

Suppose $y^o > 0$. Then a strictly positive solution to (A1.1) would be:

$$x_j = \mu_j^o + y^o \qquad \text{(A1.4)}$$

If, on the other hand, there were no feasible solution to (A1.3), or if $y^o < 0$, then there would be no feasible solution to (A1.1). This statement is clear since if there were a feasible x to (A1.1), then by setting $\mu_j = x_j$ in (A1.3), we would have a feasible solution with $y = 0$ to (A1.3).

Finally, suppose $\operatorname{Max} y^o = 0$. We must find at least one μ_j which is constrained to be zero by the equations (A1.1), (for otherwise we could reduce all μ_j by $\Delta = \operatorname{Min} \mu_j$ and replace y^o by $y^o + \Delta$, implying y^o is not maximum.) Now let λ^o be the vector of multipliers associated with the optimal solution (y^o, μ^o) to (A1.3). Pricing out,

$$1 + \lambda^o Q = 0 \qquad \text{(A1.5)}$$

$$\lambda^o P_j \leq 0 \qquad (\lambda^o P_j)\mu_j = 0 \quad \text{and} \quad j=1,2,\ldots,n.$$

From the duality theorem $\lambda^o b = -y^o$, hence the equation:

$$(\lambda^o Q)y + \sum (\lambda^o P_j)\ _j = -y^o \qquad \text{(A1.6)}$$

is an equation which must be satisfied by all solutions to (A1.3). Since $y^o = 0$, and $\lambda^o Q = -1$, we have:

$$-y + \sum (\lambda^o P_j)\ \mu_j = 0 \qquad \text{(A1.7)}$$

But $$\sum_j \lambda^o P_j = \lambda^o Q = -1, \text{ by } \quad \text{(A1.2)},$$

so that for at least one j we can say that:

$$\lambda^o P_j < 0 \qquad \text{(A1.8)}$$

Letting $\alpha_j = -\lambda^o P_j$, we have from (A1.7),

$$y + \sum \alpha_j \mu_j = 0 \qquad \text{(A1.9)}$$

We have argued that we should only consider solutions to (A1.3) which satisfy $y \geq 0$, so that (A1.9) becomes:

$$\sum \alpha_j \mu_j \leq 0 \qquad \text{(A1.10)}$$

where $\alpha_j \geq 0$ for each j, and $\alpha_j > 0$ for at least one j. That is, a positively weighted partial sum of non-negative variables must be less than or equal to zero. This can only occur when those variables are zero.

Thus we delete those columns j from (A1.1) for which $\lambda^o P_j < 0$, and again apply the method. The process will continue either until we have found a reduced problem (A1.3) with $y^o > 0$, or until we have deleted all but m of the columns of (A1.1). If the latter occurs, then there is only the one feasible solution to the original problem, and it must be optimal.

APPENDIX 2

MULTIPLE COMPARTMENTS

Suppose that our beaker, in section 1, were divided into several different compartments, each set off from the others by semi-permeable membranes. Some species would exist in all compartments, others would be excluded from some of the compartments.

This method can readily be extended to find the equilibrium distribution of the inputs among the various species in the different compartments. The mass balance equations, while still taking the form:

$$\sum P_j x_j = b \qquad \text{(A2.1)}$$

are by species into the various compartments, thus:

$$\sum_{j=1}^{n_1} P_j^1 x_j^1 + \sum_{j=1}^{n_2} P_j^2 x_j^2 + \ldots + \sum_{j=1}^{n_k} P_j^k x_j^k = b \qquad \text{(A2.2)}$$

where species j in compartment i has vector description P_j^i in terms of the inputs. Now, however, an extra equation must be added to the system (A2.2) for each compartment beyond the first. This new equation will state that the net electrical charge within a compartment is zero;

$$\sum_{j=1}^{n_i} a_{\varepsilon j}^i \; x_j^i = 0 \;, \quad i = 2,3,\ldots,k \qquad \text{(A2.3)}$$

where $a_{\varepsilon j}^i$ is the charge per mole of the j^{th} species in compartment i. Equations (A2.3) can be appended to (A2.2) by including the charge per mole of species j in compartment i as another component of P_j^i.

An equation of the sort (A2.3) is not needed for one of the compartments because presumably the inputs b are themselves neutral, forcing the entire system to electrical neutrality. If all but one compartment are individually neutral, and all compartments together are neutral, then the remaining compartment must also be neutral.

Remember also that if a species, say water (H_2O), is permitted to enter more than one compartment, its vector representation P_{H_2O} must be reproduced in each compartment where it is allowed. If a species is represented by its column P_j in only one compartment, it will never occur in any other.

The entire multi-compartment formulation becomes:

$$\text{Min } z = \sum_{j=1}^{n_1} x_j^1 \left(C_j^1 + \log \frac{x_j^1}{\bar{x}^1} \right) + \sum_{j=1}^{n_2} x_j^2 \left(C_j^2 + \log \frac{x_j^2}{\bar{x}^2} \right) + \ldots + \sum_{j=1}^{n_k} x_j^k \left(C_j^k + \log \frac{x_j^k}{\bar{x}^k} \right)$$

$$\text{s.t. } \sum P_j^1 x_j^1 + \sum P_j^2 x_j^2 + \ldots + \sum P_j^k x_j^k = b$$

$$x_j^i \geq 0 \;, \quad i = 1,\ldots,n_j, \quad i = 1,\ldots,k. \qquad \text{(A2.4)}$$

Now, of course, as well as reflecting the relative free energies of the various species with respect to the inputs, the c_j^i must reflect any forces applied to the entire compartment. A voltage inposed from outside on one compartment but not another, or a difference in mechanical pressure between compartments or the outside will alter the c_j^i .

Once the problem is formulated, the method for solving it becomes the same as in section 2. Now, however, we let:

$$\theta_j^i = \frac{1}{x_j^i} \qquad \text{(A2.5)}$$

$$\bar{\theta}^i = \frac{1}{\bar{x}^i}$$

where

$$\bar{x}^i = \sum_{j=1}^{n_i} x_j^i$$

Then (2.1) becomes: Find (y, Π) satisfying:

$$
\begin{array}{c}
\begin{array}{ccccc}
y^1_1 y^1_2 \text{ -- } y^1_{n_1} & y^2_1 \text{ --- } y^2_{n_2} & \text{---} & y^k_1 \text{ --- } y^k_{n_k} & \Pi
\end{array} \\
\left[\begin{array}{c|c|c|c|c}
\begin{matrix} \theta^1_1 & & \\ & \theta^1_2 & \\ & & \ddots \ \theta^1_{n_1} \end{matrix} & & & & \begin{matrix} -(P^1_1)^T \\ -(P^1_2)^T \\ \vdots \\ -(P^1_{n_1})^T \end{matrix} \\ \hline
 & \begin{matrix} \theta^2_1 & \\ & \ddots \ \theta^2_{n_2} \end{matrix} & & & \begin{matrix} -(P^2_1)^T \\ \vdots \\ -(P^2_{n_2})^T \end{matrix} \\ \hline
 & & \ddots & & \\ \hline
 & & & \begin{matrix} \theta^k_1 & \\ & \ddots \ \theta^k_{n_k} \end{matrix} & \begin{matrix} -(P^k_1)^T \\ \vdots \\ -(P^k_{n_k})^T \end{matrix} \\ \hline
P^1_1 \ P^1_2 \ \ P^1_{n_1} & P^2_1 \text{ --- } P^2_{n_2} & \text{---} & P^k_1 \text{ --- } P^k_{n_k} &
\end{array}\right]
\end{array}
+
\left[\begin{array}{c}
\begin{matrix} C^1_1 - 1 - \log \theta^1_1/\bar{\theta}^1 \\ C^1_2 - 1 - \log \theta^1_2/\bar{\theta}^1 \\ \vdots \\ C^1_{n_1} - 1 - \log \theta^1_{n_1}/\bar{\theta}^1 \end{matrix} \\ \hline
\begin{matrix} C^2_1 - 1 - \log \theta^2_1/\bar{\theta}^2 \\ \vdots \\ C^2_{n_2} - 1 - \log \theta^2_{n_2}/\bar{\theta}^2 \end{matrix} \\ \hline
\vdots \\ \hline
\begin{matrix} C^k_1 - 1 - \log \theta^k_1/\bar{\theta}^k \\ \vdots \\ C^k_{n_k} - 1 - \log \theta^k_{n_k}/\bar{\theta}^k \end{matrix} \\ \hline
-\ b
\end{array}\right]
=
\left[\begin{array}{c}
\begin{matrix} \delta^1_1 \\ \delta^2_2 \\ \vdots \\ \delta^1_{n_1} \end{matrix} \\ \hline
\begin{matrix} \delta^2_1 \\ \vdots \\ \delta^2_{n_2} \end{matrix} \\ \hline
\\ \hline
\begin{matrix} \delta^k_1 \\ \vdots \\ \delta^k_{n_k} \end{matrix} \\ \hline
0
\end{array}\right] , \qquad \text{(A2.6)}
$$

$$y^i_j \geq 0 \ , \quad \delta^i_j \geq 0 \ , \qquad j = 1,\ldots,n_i;\ i = 1,\ldots,k$$

$$\sum_{i=1}^{k} \sum_{j=1}^{n_i} y^i_j \ \delta^i_j = 0$$

The modifications of the theorems in section 3 and their proofs necessary to handle the multi-compartment case are obvious, except perhaps in the case where all quantities in a compartment vanish.

For example, consider the case below:

Compartment 1		Compartment 2		RHS
H_2O	Sugar	H_2O		
1		1	=	10
	1			10

with all free energy constants $c_j = 0$. The second compartment vanishes in the optimal solution for this problem. However, it is important to note that the concentration of H_2O in the second compartment is never zero. In any solution in which there is a positive amount of H_2O in compartment 2, the compartment 2 concentration of H_2O is 1. Thus in the limit, as we tend toward the optimal solution, the concentration of H_2O in compartment 2 is still 1.

In general, if a given compartment has not vanished, then the sum of the concentrations of the species in that compartment will be unity. Thus, in the limit as the compartment vanishes, the concentration of species in the compartment must still sum to unity. The problem is only to apportion this total concentration of one among the species.

Suppose, at some iteration, all the quantities y_j^1 in (A2.6) either vanish or become so small that they may be considered to have vanished. That is, all of compartment 1 is gone.

Harking back to the optimality conditions to the original problem, we would like the concentrations of species in compartment 1 to satisfy:

$$C_j^1 + \log \eta_j - \Pi P_j^1 \geq 0 \ , \ j = 1,2,\ldots,n_1 \qquad \text{(A2.7)}$$

where η_j is the concentration of the j^{th} species in the first compartment, and the Π we use in the one we have available--the one computed in (A2.6). In addition, of course, we demand that:

$$\sum_{j=1}^{n_1} \eta_j = 1 \qquad \text{(A2.8)}$$

and

$$\eta_j \geq 0 \ , \ j = 1,2,\ldots,n_1 \qquad \text{(A2.9)}$$

Suppose we let:

$$\eta_j = \exp\,[\Pi P_j^1 - C_j^1]/S \qquad \text{(A2.10)}$$

where

$$S = \sum_{k=1}^{n_1} \exp[\Pi P_k^1 - C_k^1] \qquad \text{(A2.11)}$$

Then clearly (A2.8) and (A2.9) are satisfied. Furthermore, from (A2.6) every species in compartment 1 must satisfy:

$$C_j^1 - 1 + y_j^1\theta_j - \log \theta_j^1/\bar{\theta}^1 - \Pi P_j^1 \geq 0 \qquad \text{(A2.12)}$$

Since the compartment has just vanished, every species must have either decreased in amount (if it were above the minimal allowed level previously) or at least not increased (if it were at the minimal allowed level). Thus for each j , we have $y_j^1\theta_j^1 \leq 1$ so that:

$$-\log \theta_j^1/\bar{\theta}^1 \geq \Pi P_j^1 - C_j^1$$

Exponentiating and summing:

$$1 = \sum_{k=1}^{n_1} \frac{\bar{\theta}^1}{\theta_j^1} \geq \sum_{k=1}^{n_1} \exp[\Pi P_j^1 - C_j^1] = s \tag{A2.13}$$

Thus, substituting (A2.10) into (A2.7) and using (A2.13) we find:

$$C_j^1 + \log \eta_j - \Pi P_j^1 = -\log S \geq 0$$

Equations (A2.7) are also satisfied.

The rest is simple. To enter a new iteration of (A2.6), compute the new θ_j^1 by choosing an appropriately small quantity for $1/\bar{\theta}^1$, and using η_j as in (A2.10) in the equation:

$$\frac{\bar{\theta}^1}{\theta_j^1} = \eta_j \tag{A2.14}$$

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13. ABSTRACT

It has long been known that the problem of determining the equilibrium composition of a solution of chemically reacting species could be formulated as a constrained minimum problem. Previous methods for solving the chemical equilibrium problem in this form have had much success. However, all such methods run into trouble whenever degeneracy or near-degeneracy occurs during the computational procedure.

This paper shows that the constrained minimum formulation of the chemical equilibrium problem is equivalent to a generalized linear program which can in turn be replaced by a quadratic program. In these alternative forms, degeneracy is more easily accomodated than in previous methods.

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