THE MATHEMATICAL DUALITY FOR THE DETERMINATION OF CHEMICAL EQUILIBRIUM COMPOSITION

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ABSTRACT

Describe a simple, dual method which is applicable to all equilibrium reactions and requires only basic mathematics. The duality theorem is based on minimization of free energy and maximization of admissible energy contributed by the atoms of the species to approach chemical equilibrium. The energy calculation can predict the course of complicated reactions and the components of the reaction mixture from which an atom constituent matrix is formed. The minimum number of possible chemical reactions is the difference between the matrix rank and the number of total components. The rank itself represents the number of the principal components of the mixture. The reaction between methane and steam is used to illustrate this method.

INTRODUCTION

As more complicated chemical reactions are brought under consideration, it is desirable to develop a simpler and more general method for the equilibrium calculation. Where several reactions occur among a given group of reactants, the composition of the products at equilibrium depends on the simultaneous equilibria of all the separate reactions. Thus a number of certain independent reactions which include all reactants and products present to an appreciable extent in all phases of the equilibrium system must be considered and the formation of each product from the reactants must be accounted for. The old method for equilibrium computation made use of equilibrium constants to express the concentration of certain chosen species in terms of other chosen species.

However, the dual method based on mathematical convex (Dorn, 1960) which is applicable to all equilibrium reactions makes no distinction among the species. This is possible if the chemical potentials of the species

involved are used and numerical solutions are obtained by minimizing Gibb's free energy of the system and maximizing the admissible energy contributed by the atoms of the species. The dual of the equilibrium problem can be then formed, using mass balance constraints to relate these two energy functions. This method requires only simple algebraic operations and little chemical intuition in carrying out the calculation. The calculation of free energy can predict the course of complicated reactions and the species content of the mixture from which an atom constituent matrix can be formed. The minimum number of possible chemical reactions is determined by the rank of the matrix and the number of the total species. The rank itself represents the number of independent components by which the composition of the mixture is described.

Dantzig (1958) developed a classical method to approach chemical equilibrium by steepest descent and linear programming techniques. His basic concept is minimization of Gibb's free energy to determine equilibrium composition. The mathematical convex is a method to determine equilibrium composition by dual technique. It may be considered as an extension of Dantzig's (1958) work. It requires simpler initial trial value of x_j/x and less calculation iterations which gives faster convergence to the computation.

The reaction between methane and steam is used as an example to illustrate this method. The mixture components are found to be CO_2, CO, H_2, H_2O, CH_4 by the energy calculation. Thus the atom-matrix is 3x5 and the minimum number of possible chemical reactions is 2. The results from this method are presented in Tables 1 and 2, and highly comparable to the works by Dodge (1944) and Hougen (1954). This indicates that the application of dual and matrix theories to the computation of chemical equilibrium composition is mathematically verified

TABLE 1:
Possible Feasible Components

No.	Species	y_j	H	O	C	$f(x_j)$	x_j	(y_j)
*1	CO_2	0.550	—	1.10	0.55	—74.5232	0.6499	0.6000
2	CO	0.350	—	0.35	0.35	—38.2797	0.2655	0.3655
*3	H_2	3.250	6.50	—	—	—16.4760	3.5617	3.4058
*4	H_2O	3.550	7.10	3.55	—	—52.3990	3.4347	3.4927
5	CH_4	0.100	0.40	—	0.10	—32.0266	0.0018	0.0018
	Total	7.800	14.00	5.00	1.00			

* indicates principal components, y_j are assumed values of X_j and (y_j) = average values of previous iterations of x_j.

TABLE 2:
Optimal Feasible Solutions

		10th	11th	
Iteration		$u_1 = -8.6537$	$u_1 = -8.6546$	mole percent
Energy Contribution		$u_2 = -35.3921$	$u_2 = -35.6128$	
		$u_3 = -5.8593$	$u_3 = -6.8500$	

Species Moles		x_j	x_j	Wet basis	Dry basis
1	CO_2	0.6266	0.6338	8.04	14.44
2	CO	0.2743	0.2742	3.48	6.25
3	H_2	3.3631	3.4246	43.41	78.01
4	H_2O	3.4725	3.4987	44.35	—
5	CH_4	0.0572	0.0572	0.72	1.30
	Total	7.7937	7.8885	100.00	100.00
	$f(x)$	—304.0064,	—305.8765		
	$f(u)$	—304.0716,	—305.8862		

MATHEMATICAL THEORY

In many chemical processes, the process specifications are presented with maximum or minimum restrictions for a problem. The possible solutions which satisfy the restrictions form a convex region, and the optimal solutions always lie on the boundary of the convex region.

By convex region it means a collection of points in a space of N dimensions where N is arbitrary but fixed (James and James, 1949). The extreme points of a convex set are those points of the set which do not lie on a segment between any two other points of the set. It follows thus that, if the extreme points are known, then all the points of the set can be determined by drawing line segments between the extreme points and between all points lying on these line segments. For example, if the extreme points $P_1, P_2, \ldots, P_n$ of a convex set are finite in number, any other points may be expressed as

$$P = \sum k_j P_j, \quad j = 1, 2, \ldots, n$$

where

$$k_j \geq 0, \text{ and } \sum k_j = 1$$

The restriction is the boundary of the set. The feasible solutions are those solutions which lie in the region bounded by the restrictions. Theoretically, there may be an infinite number of feasible solutions, but only those optimal solutions are of more concern. The optimal solution is the solution at an extreme point of the convex set. In other words, solution need be sought only at the extreme points of the convex set which is bounded by the finite restrictions, and there will, in general, be a finite number of optimal solutions. Thus the problem is how to find the feasible solutions and optimal feasible solutions. This can be done by the expansion of P in terms of a linearly independent feasible solutions and optimal feasible solutions. This can be set of vectors (Hadley, 1962). If the coefficients are positive, then these coefficients are the components of the vector which is an extreme point of the convex set of feasible solutions. If a linear function is defined at every point of the convex set in the N-space, its minimum and maximum values are at the extreme points of the set. Therefore the function may be stated either as a maximum problem or as a minimum problem and the optimal solutions may be obtained from either (Clasen, 1963 and; Hadley, 1962). This is the normal mode of duality theorem. The mathematical formula of the theorem is

$$PX_o = \max(PX) = BY_o = \min(BY)$$

subject to $\quad AX = B \quad$ and $\quad AY = P$
$$X \geq O \quad \text{and} \quad Y \geq O$$

where X_o and Y_o are the solutions of the problem, respectively. Thus, along with the given maximum problem there arises quite naturally another problem called "the dual of the original problem". The dual of dual problem is the original problem. The dual of a maximizing problem is a minimizing one, and the dual of a minimizing problem is a maximizing problem. That is, the dual of the problem is to minimize (BY) when the original problem is to maximize (PX). To solve the minimum problem, we formulate the dual maximum problem and use the simplex method for the maximum. However, in computation, it is clear that one has a choice in the problem to solve numerically, either maximum or minimum, for one problem might be considerably easier than the other. It is said that if a series of problems must be solved in which the restrictions b_i are changed,

then it is apparent that the dual problem should be solved since, after the first solution, a feasible vector is available for succeeding problems. Changes in the original function do not affect the feasibility of a vector.

APPLICATION TO CHEMICAL EQUILIBRIUM

The chemical thermodynamics may be used to determine the number of independent components in an equilibrium system if the system contains a large number of chemically reacting species. This problem as frequently presented appears to be one which does not have a systematic method of solution. However, in general, the number of independent components in an equilibrium mixture is the minimum number of substances necessary to specify a phase. The minimum number of the substances may be determined by Gibb's energy calculation. Suppose that a phase at equilibrium contains x_j moles of a substance M_j. Each chemical substance M_j is made up of atoms of b_i and let the number of atoms of b_i in M_j be a_{ij}. An atom-constituent matrix equation can be formed as follows:

$$AX = B \qquad (1)$$

and thus the system of equations is

$$\sum a_{ij} x_j = b_i$$
$$i = 1, 2, 3, \ldots, m \text{ and } j = 1, 2, 3, \ldots, n$$

The chemical substance would then be written as

$$M = (b_1)_{a1j}(b_2)_{a2j} \ldots (b_m)_{amn} \qquad (2)$$

and the chemical formula for M is

$$M = a_{1j} a_{2j} \ldots a_{mj} \qquad (3)$$

In vector sense, Equation 3 is a row vector. If the rank of the atom-constituent matrix is r, then the number of independent vectors in the equilibrium space is r and each of the vector is a chemical reaction and may be represented as a linear combination of vectors such as

$$\sum_j S_i M_{ij} = O, \quad j = 1, 2, \ldots, n \qquad (4)$$

These vectors are called stoichiometric equations in the chemical literature and the S_i are called stoichiometric coefficients in the reactions. They count for all the chemical substances in the equilibrium mixture. The minimum number of independent reactions which can count for all the species is the (n-r) since each reaction contains a particular substance which the others do not. However, the minimal set of reactions is not necessary if the chemical equilibrium values are based on thermodynamic properties because the thermodynamic properties are state functions and their calculation is independent of the path followed by the formation of the substances themselves. Conventionally, these (n-r) equations must be solved simultaneously with r independent atomic balances in order to obtain the composition of the equilibrium mixture resulting from some initial composition. Therefore it is obvious that the (n-r) equilibrium relations can serve to define the (n-r) values of x_j in terms of r values of the remaining x_j so that the composition of the equilibrium mixture can be completely determined if the value is known. However, the equilibrium composition may be easily obtained without solving simultaneous equations if the chemical equilibrium problem is formulated as a dual program.

According to Gibb's principle, free energy is a thermodynamic property and depends only upon the initial and final states and not upon the particular path used to go from one set of substances to another. Hence values of the free energy do not depend upon the intermediate chemical reactions which have ben used to transform a set of reactants, under specified conditions, to a series of products. Thus the free energy of the mixture may be obtained from the substances of both reactants and products. At equilibrium the free energy is at minimum. However, since the molecule of a substance is made of atoms, if it is assumed that a given thermodynamic property of a substance may be resolved into contributions from each of the constituent atoms in the molecule, the free energy of the species can be also estimated from atom-contribution. The energy contributed by the atoms to reaction is admissible if the total energy contribution of all the atoms in a molecule to that molecule does not exceed Gibb's free energy of the molecule. Of all the admissible energies, those which maximize the total energy contribution from each of the constituent atoms in the mixture correspond to Gibb's free energy of the mixture.

Therefore the equilibrium values of the species can be obtained either by minimizing Gibb's function subject to mass constraints or maximizing the energy contribution function subject to energy constraints. The theory is sound as Dorn (1960) developed. For proofs see references (Brinkley, 1947; Clasen, 1963 and 1965; Dorn, 1960, and; Hardy, et al., 1959). Thus a dual program can be formulated for the problem of chemical equilibrium.

CONVEX DUAL PROGRAM

We would now like to formulate the chemical equilibrium problem under specified conditions as a dual convex program. It may be formulated as a dual geometric program, too, as Duffin, Peterson, and Zener (1967) developed.

Let F be Gibb's free energy, u be the energy contributed by constituent atoms, D be free energy column matrix, and E be the transpose of matrix A, then it is clearly that a general convex dual program may be formulated for n components made of m different atoms as follows:

A. Dual Program Maximizes the energy contribution function

$$f(u) = \sum b_i u_i \qquad (5)$$

subject to

$$EU \leqq D \qquad (6)$$

and

all $b_i \geqq O$, $i = 1, 2, \ldots, m$

here u_i is the energy contributed by atom b_i.

By virtue of the duality theory of convex program we have the following equivalent procedure for determining the composition of the equilibrium state.

B. Primal Program Minimizes Gibb's free energy function

$$f(x) = \sum d_j x_j \qquad (7)$$

subject to the mass constraints

$$AX \geqq B \qquad (8)$$

and

all $x_j \leqq O$, $j = 1, 2, \ldots, n$

here d_j is Gibb's free energy of jth component and

$$D = \begin{vmatrix} d_1 \\ d_2 \\ \cdot \\ \cdot \\ d_n \end{vmatrix} \qquad B = \begin{vmatrix} b_1 \\ b_2 \\ \cdot \\ \cdot \\ b_m \end{vmatrix}$$

When the system is at equilibrium state

$$f(u) = f(x) . \qquad (9)$$

This equation shows that the constrained maximum of the dual function f(u) is equal to the minimum of the primal function f(x). The constraints of the primal function are active, whereas the constraints of the dual function are inactive. Hence the dual function is essentially without constraints, an important property from computational point of view. Thus the dual problem can easily be solved by standard numerical techniques with the help of a computer.

Each value of the dual function provides a lower bound on the minimum value of the primal function. Because the minimum value of the primal function is equal to the maximum value of the dual function, this common optimal property reduces the number of calculation iterations and can be approximated by any given arbitrary accuracy (Calsen, 1965).

The problem of chemical equilibrium has a long history. However, not until 1960 has much attention been paid (Calsen 1965). White, Johnson, and Dantzig (1958) observed that minimization of Gibb's free energy is a convex program and they compared two numerical techniques for carrying out the minimization, one of which was suggested by the work of Charnes (1961) and Duffin (1967). However, Dantzig's work is not as dual program.

Related theoretical work is given in the papers by Clasen (1963 and 1965), Shapiro (1964), and Shapiro and Shapley (1964) of Rand Corporation. These theorems can easily be translated into properties of the dual program.

AN EXAMPLE

As an example of the application of the duality theorem to the determination of chemical equilibrium composition consider the reaction between methane and steam, CH_4 and $5H_2O$, at atm and 1,000°K. The reaction mixture possibly contains

species: $CO_2(x_1)$, $CO(x_2)$, $H_2(x_3)$, $O_2(x_4)$, $C_2H_6(x_5)$, $H_2O(x_6)$, $CH_4(x_8)$ and the atoms of the molecules are $H(b_1)$, $O(b_2)$, $C(b_3)$. Therefore, the atom-constituent matrix equation is

$$\begin{bmatrix} 0 & 0 & 2 & 0 & 6 & 4 & 2 & 4 \\ 2 & 1 & 0 & 2 & 0 & 0 & 1 & 0 \\ 1 & 1 & 0 & 0 & 2 & 2 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_8 \end{bmatrix} = \begin{bmatrix} 14 \\ 5 \\ 1 \end{bmatrix} \qquad (10)$$

It is obvious that the coefficient matrix is 3x8 and the rank of this matrix is 3 so that we shall have three mass balance constraints for the primal function with 5 possible reactions. The number of independent components is 3, the matrix rank in specifying the mixture composition.

To have an explicit form for the primal function f(x) we assume that the pressure P is sufficiently low so that the component gases can be regarded as obeying the perfect gas law $PV = RT$. Gibb's free energy for a simple substance satisfies the relation

$$dF = VdP - SdT \qquad (11)$$

where S is entropy. In particular, for one mole of a perfect gas

$$\left[\frac{aF}{aP} \right]_T = V = \frac{RT}{P} \qquad (12)$$

Integration of this differential equation gives

$$F = RTLnP + F° \qquad (13)$$

where F° is Gibb's free energy per mole at temperature T and 1 atm.

To evaluate F for the mixture, appeal is made to Dalton's law of partial pressure. Thus, if P is the total pressure and P_j are the partial pressures of the species, respectively, then

$$P_j = \frac{x_j}{x} P \qquad , j = 1, 2, \ldots, 8$$

Thus the total free energy of the mixture in dimensionless form is

$$f(x) = \frac{F}{RT} = \sum x_j (LnP_j + \frac{F_j°}{RT}) \qquad (14)$$

or equivalently,

$$\frac{F}{RT} = \sum x_j (C_j + Lnx_j) - xLnx \qquad (15)$$

where

$$C_j = \frac{F_j°}{RT} + LnP$$

and

$$x = x_1 + x_2 + \cdots + x_8 .$$

Then the system of equations is

$$\sum a_{ij} x_j = b_i \text{ for all } x_j \geqq O .$$

The free energy at equilibrium is

$$F = - RTLn \frac{x_j}{x} \text{ when derivative of } f(x) = O.$$

The energy contributed by the ith atom to the reaction is designated by u_i and is admissible. In mathematical form it is

$$f(u_i) = b_i u_i \qquad (16)$$

But the total energy contribution of all atoms in a molecule can not exceed Gibb's free energy of the molecule and is expressed as

$$f(u) = \sum b_i u_i \leqq f(x) \qquad (17)$$

and

all $b_i \geqq O$ for i = 1, 2, 3.

Also the total energy contribution at equilibrium is

$$F = RTf(u) \text{ when derivative of } f(u) = O.$$

We are now in the position to formulate the chemical equilibrium problem as a convex dual program. Consider the dual function that consists of maximizing

$$f(u) = 14u_1 + 5u_2 + u_3$$

subject to the energy constraints

$2u_2 + u_3 = d_1$	$6u_1 + 2u_3 = d_5$
$u_1 + u_3 = d_2$	$4u_1 + 2u_3 = d_6$
$2u_1 = d_3$	$2u_1 + u_2 = d_7$
$2u_2 = d_4$	$4u_1 + u_3 = d_8$

It is of interest to write the primal program corresponding to this dual program. Clearly, the primal program is to minimize the free energy function

$$f(x) = d_1 x_1 + d_2 x_2 + \cdots + d_8 x_8$$

subject to the mass constraints

$$2x_3 + 6x_5 + 4x_6 + 2x_7 + 4x_8 = 14$$
$$2x_1 + x_3 + 2x_4 + x_7 = 5$$
$$x_1 + x_3 + 2x_5 + 2x_6 + x_8 = 1$$

and $x_1, x_2, \ldots, x_8 \geqq O$, $d_j = C_j + Ln(x_j/x)$, and $x = x_1 + x_2 + \cdots + x_8$.

According to Gibb's variational principle, the equilibrium values of x_j are obtained at minimizing f(x) subject to constraints. But, because the energy contribution can not exceed Gibb's free energy, it follows clearly that the equilibrium values of x_j may be obtained equally well by solving the dual program at maximizing f(u) subject to energy constraints. For numerical solution to the chemical equilibrium problem, the convex dual program was coded on a computer. This computer code contains the following parts:

1. Possible feasible solutions of x_j are obtained by free energy calculation with assumed positive values of x_j to initiate the program. Under mass constraints, all x_j must be nonnegative. If any x_j is negative, reassume a set of x_j and compute the energy function again.

2. The energy contribution u_i is constructed at its lowest value when $Ln(x_j/x) = 1$ from the selected principal components in which all different atoms in the mixture are included according to the energy constraints.

3. The main code of both primal and dual programs. Average values of previous calculations of x_j are used as the values of x_j for next calculation. Set an arbitrary numerical accuracy, say 0.01, as near zero for $f(x) - f(u) = O$. When the primal function shows no appreciable difference with the dual function or vice versa, the values of x_j from the last calculation are the optimal feasible solutions.

The results of the first trial are listed in Table 3. It can be seen from the table that species 4, 5, 6 are present at negligible amounts and that x_2 is negative. Thus it is necessary to re-assign a set of x_j for calculation iteration. The possible species in the mixture then becomes $CO_2(x_1)$, $CO(x_2)$, $H_2(x_3)$, $H_2O(x_4)$, $CH_4(x_5)$. The rank of the atom-constituent matrix remains 3 but the minimum number of the possible independent reactions is 2. The re-assumed non-negative x_j are shown in Table 1. The species 1, 3, and 4 are chosen as the principal components of the mixture for constructing u_1, u_2, u_3. Optimization is pursued.

It is interesting to note that a significant difference between the energy contributed by all constituent atoms and Gibb's free energy exists. Thus the procedures are repeated until the energy function f(x) shows no appreciable further improvement. The results are presented in Tables 2 and 3. The values of f(u) and f(x) from the 11th calculation are nearly identical; hence the values of x_j from this calculation are considered to be the optimal feasible solutions.

RESULTS AND CONCLUSIONS

The solution of this problem is based on the assumption that equilibrium is attained. In actual operations that do not reach equilibrium, quit different results may be obtained, depending on the rates of various reactions. It is common for equilibrium to be approached with respect to one or more reactions while many other re-

actions which are not thermodynamically possible do not occur to any appreciable extent. The minimum number of the independent reactions in this example is found to be 2 by the rank of the constituent atom matrix. These reactions involve all possible resultant compositions at equilibrium and may be used to compute the equilibrium composition if the equilibrium constants are known. The reactions are

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
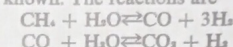
From the calculation of Gibb's free energy, the chemical species in the reaction mixture are found to be CO_2, CO, H_2, H_2O, CH_4 and the amounts of O_2, C_2H_4, C_2H_6 are present at negligible extent. The results of this work are comparable with those by Dodge (1944) and Hougen (1954).

In the chemical equilibrium problem, the molecular products must be pre-determined for the equilibrium composition if equilibrium constant method is used. However, if dual method is used, the calculation of free energy and the measurement of a compound can predict all possible products from which a constituent-matrix can be formed to determine the minimum number of possible independent chemical reactions involved. Therefore, no assumption is needed to neglect some of the species in the mixture. As the free enrgy at equilibrium is minimum and the admissible energy contributed by the atoms is maximum, with mass constraints and energy constraints to relate the energy functions, the existence of a solution to the problem can be assured and a quick convergence can be expected by duality theorem.

The duality theory takes minimization of free energy and maximization of admissible energy contributed by the atoms to approach equilibrium, while Dantzig's (1953) work takes only minimization of free energy compared with two numerical techniques but his work is not a dual program. Furthermore, the dual method is easily adapted to either by hand or by computer and only basic mathematics is required to do the computation. It takes only one initial trial value of x_j/x for construction of atom-energy contribution and less calculation iterations for optimal solutions. This implies faster convergence to the optimal solutions. No simultaneous equations need be solved by trial and error procedures with this dual method in contrast to the steepest descent or equilibrium constant method. A computer code is developed for solutions to a general convex dual program.

TABLE 3:

Possible Components on the Reaction Mixture

No.	Species	y_j	$f(x_j)$	H	O	C	x_j
1	CO_2	0.425	—9.3901	—	0.85	0.425	6.8651
2	CO	0.360	—32.0882	—	0.36	0.360	—2.4593
3	H_2	3.120	—53.6672	6.10	—	—	1.8969
4	O_2	0.120	—3.5128	—	0.24	—	3.99×10^{-30}
5	C_2H_6	0.010	—0.4528	0.06	—	0.020	1.48×10^{-8}
6	C_2H_4	0.010	—0.2773	0.04	—	0.020	4.90×10^{-7}
7	H_2O	3.600	—39.1288	7.10	3.55	—	1.7289
8	CH_4	0.175	—1.1122	0.70	—	0.175	0.1871
total		7.830		14.00	5.00	1.000	