

equivalent to adding  $(n(n-1) - l(l+1))/2r^2$  to the Hamiltonian in eq A2. A more drastic approximation can be made by replacing the  $z_N/r_{1N}$  in eq A2 by  $2\alpha^2 r^2 - l(l+1)/2r^2$ . The resulting Gaussian functions  $e^{-\alpha r^2} Y_{lm}$  constitute an inferior basis set and are only used because the multicenter, two-electron integrals become easier to evaluate. In any case, the point of this discussion is that if a perturbation which is a sum of one-electron operators is included, in eq A1, we can proceed in the same way as before and no new approximations need to be introduced.

In the presence of a perturbation, eq A1 becomes

$$\mathcal{H}(\lambda) = -1/2 \sum_i \nabla^2(i) - \sum_{iN} z_N/r_{iN} + \sum_{i < j} \frac{1}{r_{ij}} + \lambda \sum_i h(i)$$

The one-electron perturbation introduces no new correlation effects so that we drop the  $\sum_{i < j} 1/r_{ij}$  term as before. The total problem then separates into one-electron problems involving an electron moving in the

field of all the nuclei plus the perturbation. In the vicinity of the nucleus  $N$  the Hamiltonian is approximately

$$H^N(\lambda) = -1/2 \nabla^2(1) - \frac{z_N}{r_{1N}} + \lambda h(1) \quad (\text{A3})$$

Again a  $z_N(\text{eff})$  can be introduced. It might be argued that  $z_N(\text{eff})$  should depend on  $\lambda$ . This would be equivalent to optimizing exponents for the perturbed problem. Obviously this refinement would have little meaning unless exponents for the unperturbed problem were already optimized. Should this become desirable, optimization could be done in a manner similar to a method recently suggested for the unperturbed problem.<sup>28</sup> If we wish to use Slater orbitals we add  $[n(n-1) - l(l+1)]/2r^2$  to eq A3. For Gaussian orbitals we replace  $z_N/r_{1N}$  by  $2\alpha^2 r^2 - l(l+1)/2r^2$  as before. This procedure can be used to define the perturbed, local Hamiltonians discussed earlier. Since we are only interested in the first-order solution, we proceed by conventional perturbation theory.

## Geometric Programming and the Darwin-Fowler

### Method in Statistical Mechanics<sup>1a</sup>

by R. J. Duffin and C. Zener

Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213 (Received December 11, 1969)

This paper concerns the classical problem of chemical equilibrium as formulated in the language of geometric programming. Thus the equilibrium state at constant temperature and volume is characterized by the duality principle, minimum  $F$  = maximum  $F^*$ . Here  $F$  is the Helmholtz function for free energy and  $F^*$  is a new function termed the anti-Helmholtz function. The minimization of  $F$  is constrained by the mass balance equations. However the maximization of  $F^*$  is unconstrained. Hence this gives a simplified practical procedure for calculating equilibrium concentration. The chemical equilibrium can also be analyzed by statistical mechanics. Comparing the two methods brings to light an intimate relationship between geometric programming and Darwin-Fowler<sup>2</sup> statistics.

### Introduction

Geometric programming is a systematic analysis to aid engineers in designing for minimum cost.<sup>3</sup> The design problem so formulated is termed the *primal program*. The objective of the primal program is to minimize the cost function. Moreover, there is a related problem termed the *dual program*. The objective of the dual program is to maximize the "anticost function." These programs are termed dual because of the following basic theorem: minimum cost =

maximum anticost. This dual formulation has proven to be a great aid both in understanding and solving optimum design problems.

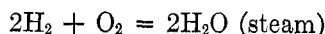
The chemical equilibrium problem, as formulated by

(1) (a) Prepared under Research Grant DA-AROD-31-124-G680 Army Research Office, Durham, N. C.

(2) C. C. Darwin and R. H. Fowler, *Proc. Cambridge Phil. Soc.*, **21**, 730 (1922).

(3) R. J. Duffin, E. Peterson, and C. Zener, "Geometric Programming," John Wiley and Sons, New York, N. Y., 1967.

Gibbs, is to minimize  $G$ , the free energy. The temperature and pressure are to be held constant. This program is feasible to carry out for reactions in which the reactants are gases obeying the laws of Boyle and Charles. For example, consider, the reaction



Then the Gibbs free energy function  $G$  is given by a known formula  $G = G(N_1, N_2, N_3)$  where  $N_1$  is the number of moles of  $\text{H}_2$ ,  $N_2$  is the number of moles of  $\text{O}_2$ , and  $N_3$  is the number of moles of steam.<sup>4</sup> It is a rather strange coincidence of science that such gaseous equilibrium problems can be expressed as geometric programs. The history of this coincidence can be found in Appendix C of ref 3.

The formulation of the chemical equilibrium problem by the geometric programming scheme leads to the dual relation, minimum  $G(N) = \text{maximum } G^*(\nu)$ . The minimization problem posed on the left is the classical Gibbs approach. The maximization problem posed on the right is a new approach. We term the function  $G^*(\nu)$  the *anti-Gibbs function*. Recently Passy and Wilde<sup>5</sup> have treated the hydrazine equilibrium problem by use of the anti-Gibbs function. They point out an advantage of this new approach in that  $\nu$  has only three components while  $N$  has ten components in the hydrazine problem.

The initial purpose of this note is to give a further simplification of the chemical equilibrium problem by using the Helmholtz free energy function  $F$  instead of the Gibbs function  $G$ .  $F$  and  $G$  are related by  $F = G - PV$  where  $P$  is the pressure and  $V$  is the volume. Thus the equilibrium state is characterized by minimizing the Helmholtz function, the volume being held constant. We first show that this Helmholtz problem leads to a geometric program of extended type and that the duality theorem applies. For example, in the steam equilibrium problem,  $\min F(N_1, N_2, N_3) = \max F^*(\nu_H, \nu_O)$ . The minimization problem on the left is the classical Helmholtz approach. Of course the composition vector  $N$  is not arbitrary but must satisfy the mass balance equations

$$2N_1 + 2N_3 = E_H$$

$$2N_2 + N_3 = E_O$$

where  $E_H$  is the total number of moles of H atoms and  $E_O$  is the total number of moles of O atoms in the reaction chamber.

We term  $F^*$  the *anti-Helmholtz function*. Maximizing  $F^*(\nu_H, \nu_O)$  gives a new approach to the chemical equilibrium problem. This approach is simpler for two reasons. (1) There is no constraint whatsoever on the dual variables  $\nu_H$  and  $\nu_O$ . (This is not true for the anti-Gibbs method.) (2) There are only two variables  $\nu_H$  and  $\nu_O$  even when other molecular species such as  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  are considered.

The dual program applied to the chemical equilibrium problem was presented in Appendix C of ref 3 merely as a mathematical aid. Here we desire to give a physical interpretation of the functions and variables. Thus it results that  $\nu_H$  may be interpreted as the chemical potential of atomic hydrogen. In other words,  $\nu_H = \partial F / \partial E_H$ . Then the anti-Helmholtz function may be defined as

$$F^*(\nu_H', \nu_O') = \nu_H' E_H + \nu_O' E_O - P'V$$

Here  $\nu_H'$  and  $\nu_O'$  are the chemical potentials and  $P'$  is the pressure when  $E_H = E_H'$  and  $E_O = E_O'$ .

The chemical equilibrium problems just described have been interpreted in the light of classical thermodynamics. In this connection geometric programming is simply a rigorous mathematical structure which quantitatively corresponds to the phenomena of gaseous equilibrium.

However, there is another way of viewing chemical equilibrium. It may be interpreted in the light of statistical mechanics. In particular, Darwin and Fowler developed a beautiful statistical method based on complex function theory. Their method is especially suited to treat chemical equilibrium problems.

Of course properties derived by the thermodynamic approach must also be obtained by the statistical approach. Nevertheless this correspondence is remarkable because at heart the two approaches have no apparent similarity. With this thought in mind, we examined the treatment of the gaseous equilibrium problem given by Darwin and Fowler<sup>2</sup> to see if there was a correspondence with the geometric programming structure. Indeed, we found that their mathematical development does imply the existence of the anti-Helmholtz function. However, they did not bring this implication to the surface. Our analysis exposes a very interesting relationship between geometric programming and Darwin-Fowler statistics.

### Gaseous Equilibrium Treated by Geometric Programming

The chemical potential for a perfect gas is

$$\mu = RT \log P + \mu^0 \quad (1)$$

where  $R$  is the gas constant,  $T$  is the absolute tempera-

(4) The authors have been faced by two notational problems. Firstly, intrinsic to their analysis are two sets of mole numbers. One set refers to molecular species and is consequently dependent upon equilibrium conditions. The other set refers to atomic species and is dependent only on the overall composition. Associated with these two sets of mole numbers are the corresponding two sets of chemical potentials. Secondly, geometric programming developed outside the field of physical chemistry and has developed its own connotation for  $n, m, i, j$ . In order to help emphasize the applicability of geometric programming to physical chemistry, these symbols are here used in precisely the same way as in geometric programming. For mole numbers referred to molecular and to atomic species, we use  $N_1, \dots, N_n, \dots, N_m$ , and  $E_1, \dots, E_i, \dots, E_m$ , respectively, and for the corresponding chemical potentials we use  $\mu_1, \dots, \mu_i, \dots, \mu_n$ , and  $\nu_1, \dots, \nu_j, \dots, \nu_m$ .

(5) U. Passy and D. J. Wilde, *SIAM J. Appl. Math.*, **16**, 363 (1968).

ture,  $P$  is the pressure, and  $\mu^0$  is the chemical potential at one atmosphere pressure. Then the Gibbs free energy for  $N$  moles of this gas is

$$G = NRT \log P + N\mu^0$$

The Helmholtz free energy is  $F = G - PV$  where  $V$  is the volume. Thus

$$F = NRT \log P + N\mu^0 - PV$$

Using the perfect gas law  $PV = NRT$  we eliminate  $P$  to obtain

$$F = NRT \log (N/eb)$$

where

$$b = (V/RT) \exp(-\mu^0/RT)$$

Next consider a homogeneous mixture of  $n$  perfect gases in a chamber of volume  $V$ . Each of these gases is to be composed of a single molecular species. If none of these  $n$  species are alike then the total free energy  $F$  is a sum

$$F = RT \sum_{i=1}^n N_i \log (N_i/eb_i) \quad (2)$$

Here  $N_i$  denotes the number of moles of the molecular species  $i$ . We term  $F(N)$  the *Helmholtz function*.

Suppose that there are  $m$  different chemical elements which compose the molecules of the  $n$  different gases. Then the following *mass balance equations* must hold

$$\sum_{i=1}^n N_i a_{ij} = E_j \quad j = 1, 2, \dots, m$$

Here  $a_{ij}$  is the number of atoms of the  $j$ th chemical element in a molecule of the species  $i$ . Thus  $E_j$  is the total number of moles of the  $j$ th chemical element present in the chamber. (As is well known, it is often convenient to let  $E_j$  also denote stable groups of atoms.)

There are many different states  $N_i$  which satisfy the mass balance equation. However, the equilibrium state is the one that minimizes the Helmholtz function at constant temperature.

The chemical equilibrium problem just described may be put in the format of a geometric program as follows.

*Equilibrium Program I.* Seek the minimum of the Helmholtz function

$$F(N) = RT \log \left[ \prod_{i=1}^n (N_i/eb_i)^{N_i} \right]$$

The variables  $N_i$  are subject to the linear constraints

$$N_1 > 0, N_2 > 0, \dots, N_n > 0$$

$$\sum_{i=1}^n N_i a_{ij} = E_j \quad j = 1, 2, \dots, m$$

Program I comes under the category "extended geometric programming" and is discussed on page 100 and

page 209 of ref 3. The analysis given there shows that program I has the following dual program.

*Equilibrium Program II.* Seek the maximum of the anti-Helmholtz function

$$F^*(\nu) = \sum_{j=1}^m \nu_j E_j - RT \sum_{i=1}^n b_i \exp \left( \sum_{j=1}^m a_{ij} \nu_j / RT \right)$$

The correspondence between program I and program II is indicated by the following theorem.

*Theorem 1.* Let  $N$  satisfy the constraints of program I and let  $\nu$  be arbitrary; then

$$F(N) \geq F^*(\nu)$$

Moreover this inequality becomes an equality if and only if

$$N_i = b_i \exp \left( \sum_{j=1}^m a_{ij} \nu_j / RT \right) \quad (3)$$

for  $i = 1, \dots, n$ . *Proof.* It is clear that the elementary inequality  $x \geq \log ex$  becomes an equality if and only if  $x = 1$ . Let  $x = u_i/N_i$  where  $u_i = b_i \exp(\sum_{j=1}^m a_{ij} \nu_j)$  so  $u_i \geq N_i \log (eu_i/N_i)$ . Summing gives

$$\sum_1^n u_i \geq \sum_1^n N_i \log (eu_i/N_i)$$

$$\sum_1^n u_i \geq \sum_1^n N_i \log (eb_i/N_i) + \sum_1^n N_i \sum_1^m a_{ij} \nu_j / RT$$

Using the mass balance equations gives

$$RT \sum_1^n N_i \log (N_i/eb_i) \geq \sum_1^m \nu_j E_j - RT \sum_1^n u_i \quad (\text{QED})$$

It remains to show that conditions (3) can be satisfied.

*Theorem 2.* If  $N''$  is a minimum point for program I then program II has a maximum point  $\nu''$  and  $F(N'') \equiv F^*(\nu'')$ . *Proof.* Let  $N_i = N_i'' + x_i s$  where  $s$  is a parameter. Then

$$\frac{dF}{ds} = \sum_1^n \frac{\partial F}{\partial N_i} x_i \quad (4)$$

Also note that

$$\sum_1^n N_i a_{ij} = s \sum_1^n x_i a_{ij} + E_j$$

Therefore if  $x$  is chosen to satisfy

$$\sum_1^n x_i a_{ij} = 0 \quad j = 1, \dots, m \quad (5)$$

then  $N$  satisfies the mass balance equation so when  $s = 0$

$$\sum_1^n \frac{\partial F}{\partial N_i} x_i = 0 \quad (6)$$

Thus relations 5 imply relation 6 so by the theory of linear dependence we know that there exist numbers  $\nu_1'', \dots, \nu_m''$  such that

$$\frac{\partial F}{\partial N_i} = \sum_{j=1}^m a_{ij} \nu_j'' \quad i = 1, \dots, n \quad (7)$$

But differentiating 2 shows that

$$\frac{\partial F}{\partial N_i} = RT \log \left( \frac{N_i}{b_i} \right) \quad (8)$$

Then (7) and (8) give

$$N_i'' = b_i \exp(\sum a_{ij} \nu_j'' / RT)$$

But this is relation 3 so it is a direct consequence of Theorem 1 that  $F(N'') = F^*(\nu'')$ . This completes the proof of Theorem 2. It is now desired to give the anti-Helmholtz function  $F^*$  and the variable  $\nu$  a direct chemical interpretation.

*Theorem 3.* The anti-Helmholtz function may be written as

$$F^*(\nu') = \sum_{j=1}^m \nu_j' E_j - P'V \quad (9)$$

where  $P'$  is the pressure as a function of  $\nu'$ . At equilibrium the following relations hold

$$\mu_i = \sum_{j=1}^m a_{ij} \nu_j \quad (10)$$

$$\sum_{i=1}^n \mu_i N_i = \sum_{j=1}^m \nu_j E_j \quad (11)$$

where  $\mu_i = \partial F / \partial N_i$  is the chemical potential of molecular species  $i$ . *Proof.* Observe that relation 10 follows from relation 7. Multiply relation 10 by  $N_i$  and sum. Then on the right we obtain  $\sum_1^n \sum_1^m a_{ij} N_i \nu_j$ . Making use of the mass balance equations then proves relation 11. The function  $F^*$  may be written as

$$F^*(\nu') = \sum_1^m \nu_j' E_j - V \sum_1^n \exp \left( \frac{\sum_1^m a_{ij} \nu_j' - \mu_i^0}{RT} \right)$$

Making use of (10) gives

$$F^*(\nu') = \sum_1^m \nu_j' E_j - V \sum_1^n \exp \left( \frac{\mu_i' - \mu_i^0}{RT} \right)$$

But if  $P_i$  is the partial pressure of the molecular species  $i$  we know by relation 1 that  $RT \log P_i' = \mu_i' - \mu_i^0$  so

$$F^*(\nu') = \sum_1^m \nu_j' E_j - V \sum_1^n P_i'$$

But by Dalton's law the partial pressures add to the total pressure so  $P' = \sum P_i'$  and this proves (9).

*Theorem 4.* If  $a_{ij}$  is of rank  $m$  then  $\nu_j$  is the chemical potential of atomic type  $j$ . That is  $\nu_j = \partial F / \partial E_j$ . *Proof.* Since  $a_{ij}$  is of rank  $m$  it is possible to solve the equations

$$\sum_1^n x_i a_{ij} = 1 \quad j = k$$

$$\sum_1^n x_i a_{ij} = 0 \quad j \neq k$$

Then relations 4 and 10 give

$$dF/ds = \sum_1^n x_i \mu_i = \sum_1^n \sum_1^m x_i a_{ij} \nu_j = \nu_k$$

This is equivalent to the statement of the theorem so the proof is complete.

We are now able to give a complete thermodynamic interpretation of the anti-Gibbs program given in ref 3. In that program the variables are denoted by  $t_1, t_2, \dots, t_m$ . The variable  $t_j$  is now seen to be the *activity* of atomic type  $j$  and is defined by the relation

$$t_j = e^{\nu_j/RT}$$

Then the objective of the program is to maximize the anti-Gibbs function

$$G^*(t) = \log (t_1^{E_{11}} t_2^{E_{21}} \dots t_m^{E_{m1}})$$

This maximization is subject to as many constraints as there are phases. By virtue of the analysis just given it is seen that the constraint on the phase  $k$  is of the form  $\sum_k P_i < P$ . Here  $P$  is the ambient pressure and  $P_i$  is the partial pressure of molecular species  $i$  in phase  $k$ . If phase  $k$  does not vanish then this becomes an equality and expresses Dalton's law for phase  $k$ .

### Darwin-Fowler Statistics

The partition function  $Z$  is defined in terms of the Helmholtz function by the formula

$$Z = e^{-F/RT}$$

Let us express the extremal property of the anti-Helmholtz function in terms of the partition function  $Z$  and activity variables  $t$ . This is seen to be

$$Z = \min \frac{\exp \left( \sum_1^n b_i \prod_1^m t_j^{a_{ij}} \right)}{\prod_1^m t_j^{E_j}} \quad (12)$$

To one familiar with the Darwin-Fowler approach to statistical mechanics relation 12 strikes a familiar chord. Our  $t_j$  is just the value along the real axis of their selector variable that ensures conservation of type  $j$  atoms. In fact (12) is embedded in their 1922 paper,<sup>1</sup> although not explicitly stated or employed. We give below a brief analysis of our problem by their method.

If  $A$  is Avogadro's number let  $n_i = AN_i$ ,  $e_j = AE_j$ , and  $R = Ak$ . Then according to Darwin and Fowler

$$e^{-F/kT} = \sum \pi_i(z_i)^{n_i} / n_i!$$

the summation is over all values of the distribution numbers  $n_i$  satisfying

$$\sum_1^n n_i a_{ij} = e_j \quad (13)$$

Here  $z_i$  is the partition function for a molecule of type  $i$ . Following Darwin and Fowler we remove the con-

straint 13 by introducing complex selector variables, one for each atomic species

$$e^{-F/kT} = \left(\frac{1}{2\pi i}\right)^m \oint \cdots \oint \sum \pi_i \frac{(z_i \pi_j t_j^{a_{ij}})}{(n_i! \pi_j t_j^{e_j})} \pi_j \left(\frac{dt_j}{t_j}\right)$$

The path of integration is once around the origin of the complex plane. The summation is over all values of  $n_i$  so  $\sum \pi_i = \pi_i \sum_{n_i=0}^{\infty}$ . Also  $\sum_0^{\infty} x^k/k! = e^x$  so (4) becomes

$$e^{-F/kT} = \left(\frac{1}{2\pi i}\right)^m \oint \cdots \oint \psi(t) \pi_j \frac{dt_j}{t_j}$$

$$\psi(t) = \exp\left(\sum_i z_i \pi_j t_j^{a_{ij}}\right) / \pi_j t_j^{e_i}$$

Since all the  $z_i$  are positive, it follows that for  $t$  confined to the positive real axis the function  $\psi(t)$  has a minimum at a point  $t'' = (t_1'', \dots, t_m'')$ . Choose contours of integration to be circles centered at the origin and of radii  $t_1'', \dots, t_m''$  and employ polar coordinates  $t_1 = t_1'' e^{i\theta_1}$  etc. Thus

$$e^{-F/kT} = (2\pi)^{-m} \oint \cdots \oint_{-\pi}^{\pi} \psi(t) \pi_j d\theta_j$$

To estimate integrals of this form Darwin and Fowler use the saddle point method. It is easy to see that  $t''$  is a saddle point for the real part of  $\psi(t)$ . Thus the integrand is small at all points of the circular contours except at  $t''$ . It results that

$$e^{-F/kT} = \psi(t'')/C$$

where  $C$  is a number whose order of magnitude is  $A^{n/2}$ . Taking the  $A$ th root gives

$$e^{-F/RT} = \exp(\sum_i b_i \pi_j t_j^{a_{ij}}) / \pi_j t_j^{E_i}, \quad t = t''$$

where  $b_i = z_i/A$ . Also we take  $C^{1/A} \cong 1$  without appreciable error. Thus we have derived the important relation 12 as a consequence of the Darwin-Fowler method in statistical mechanics.

## Equilibrium of Sulfur Molecules

The following problem gives a simple example for the anti-Helmholtz approach.

**Problem.** Two moles of atomic sulfur are in a reaction chamber at temperature  $T = 850^\circ\text{K}$  and of volume  $V = 1/RT$ . Find the partial pressures of  $S$ ,  $S_2$ ,  $S_6$ , and  $S_8$  molecules. **Solution.** Let  $N_1$ ,  $N_2$ ,  $N_6$ , and  $N_8$  denote moles of  $S$ ,  $S_2$ ,  $S_6$ , and  $S_8$  molecules. Then the mass balance equation is  $N_1 + 2N_2 + 6N_6 + 8N_8 = 2$ . Let  $x = \nu_1/RT$ ; then  $F^*$  can be written as

$$F^*/RT = 2x - (e^{x-23.7} + e^{2x} + e^{6x+0.366} + e^{8x+1.65})$$

Here the numbers  $-23.7$ ,  $0$ ,  $0.366$ , and  $1.65$  are tabulated values of  $\mu_i^0/RT$  for  $S$ ,  $S_2$ ,  $S_6$ , and  $S_8$ . It is readily found that  $F^*$  has a maximum at  $x = -0.493$ . At this value of  $x$  successive terms in the parentheses have the values  $3.10 \cdot 10^{-11}$ ,  $0.373$ ,  $0.0744$ ,  $0.1009$ . These are just the partial pressures, in atmospheres, of the  $S$ ,  $S_2$ ,  $S_6$ , and  $S_8$  molecules. The free energy is here referred to  $S_2$  as a standard state.

So far we have been supposing the reactants are perfect gases. However, the definition 9 for  $F^*$  could be extended to an arbitrary chemical system. This raised the question: is it true that the maximum of  $F^*$  is the equilibrium free energy? We answer this question in the affirmative by introducing a more basic function  $S^*$  termed the anti-entropy which applies to general thermodynamic systems. Then we find that maximum  $S = \text{minimum } S^*$ , where  $S$  is the entropy. In making this generalization we have been guided by Castigliano's principle in mechanics and by the general duality concepts given in ref 6. This analysis is developed in ref 7.

(6) R. J. Duffin, *SIAM J. Appl. Math.*, **10**, 119 (1962).

(7) R. J. Duffin and C. Zener, *Proc. Nat. Acad. Sci.*, **62**, 629 (1969).