A second approach, which is the approach we have adopted, is to generalize the problem. This means that methods are developed and used which are equally applicable to any chemical system (refs. 1 to 7). In order to insure that these general methods will actually lead to a solution, attention must be given to mathematical details such as iteration techniques, convergence controls, and singularities.

So far, several examples of varying degrees of complexity have been discussed, all of which can be solved by the equilibrium constant method. Now we will look at the free energy method.

Free-Energy Minimization Method

The concept of minimum free energy as the criterion for equilibrium can be illustrated graphically as shown in figure I-1. We are again dealing with the first example selected to illustrate the use of equilibrium constants, that is, the determination of the equilibrium composition of a mixture of H2 and H at T = 3000 K and P = 1 atmosphere. Figure I-1 is a plot of the free energy of the mixture G versus the partial pressure of H2. (We could equally well have used pH as the abscissa.) The minimum value of G occurs at $p_{H_2} = 0.855$ which is exactly the value obtained by the equilibrium constant method. This graphical example illustrates how one might apply the principle of minimum free energy as the criterion for chemical equilibrium. However, as soon as the problem becomes even slightly more complicated than this simple example, the graphical method becomes impractical or, more usually, impossible to use.

Therefore, we must use equations. As is often true in minimization problems, the function to be minimized is subject to certain constraints. In this case, G is to be minimized subject to the mass balance constraints given by equation (9). Equation (1) then becomes

$$6\left[G + \sum_{1} \lambda_1 \left(\sum_{j} a_{ij} n_j - b_1^0\right)\right]_{T,P} = 0$$

where λ_1 are Lagrangian multipliers. After performing some mathematical details (ref. 7), one ends up with

$$\left(\frac{G^O}{RT}\right)_j + \ln p_j + \frac{1}{RT} \sum_i \lambda_1 a_{ij} = 0$$

Here $\nu_1 = k_1[H_2], \nu_2 = k_2[O_2], \nu_3 = k_3[H_2], \nu_4 = k_4[O_2][M]$, and $\nu_5 = k_5[CO]$. Thus the exponential growth constant λ depends on the gas composition and the rate constants of reactions I to V. This paper reports measurements on mixtures chosen to permit determinations of the rates of reactions I, II, III, and V. Mixtures were selected by analyzing equation (1).

EXPERIMENTAL ASPECTS

Growth constants were obtained by measuring the blue carbon monoxide flame band emission behind incident shocks. The intensity of this radiation is proportional to the product of carbon monoxide and oxygen atom concentrations (ref. 3), and since very little carbon monoxide is consumed, the light monitors the increase of oxygen atom concentration with time.

Gas mixtures contained varying amounts of hydrogen, carbon monoxide, oxygen and in some mixtures carbon dioxide, diluted five to tenfold with argon. Hydrogen, oxygen, and argon were high purity tank gases and were used without further purification. Carbon monoxide was condensed at liquid nitrogen temperature; about one-quarter of the condensate was pumped off and discarded. Dry ice served as a convenient source of carbon dioxide. It was purified by sub-liming three-quarters of a sample into a liquid nitrogen cooled trap. The first quarter of this trapped fraction was discarded and the middle half used for mixture preparation.

Recently we showed that boundary layer effects must be considered in analyzing data obtained behind incident shocks; the growing boundary layer causes increases in temperature, density, and residence time with increasing distance behind the shock. Conditions behind the shocks, in the region of the experimental measurements, were obtained from a computer program which integrated the equations of chemical change for a shocked gas accounting for the effects of boundary layer buildup. In general, the extent of chemical reaction was small, and changes in gas properties were brought about largely by the gas dynamics associated with boundary layer growth.

Exponential growth constants were obtained from plots of the logarithm of observed light intensity against gas time; the relation between gas and laboratory times was obtained from the computer calculations.

SELECTION OF GAS MIXTURES

Let us turn now to the rationale used to select gas mixtures by analysis of

equation (1). To begin with, under our experimental conditions ν_4 is generally small in comparison with the other ν 's and can be neglected for purposes of a qualitative discussion. Secondly, λ turns out to be a small positive root - of the order of the smaller ν values and small compared with the larger ν values. Thus, we neglect λ^3 in comparison with the other terms and rewrite equation (1):

$$[(\nu_1 + \nu_5) + \nu_2 + \nu_3] \lambda^2 + \nu_3(\nu_1 + \nu_5) \lambda \cong 2\nu_2\nu_3(\nu_1 + \nu_5)$$

If the amount of hydrogen in a mixture is large in comparison to oxygen, ν_1 and ν_3 are large and the term involving λ^2 may be neglected; in this event,

$$\lambda \cong 2\nu_2$$

On the other hand, if only a trace of hydrogen is present, ν_3 is small, the term involving λ may be neglected, and

$$\lambda^2 \simeq \frac{2\nu_2\nu_3(\nu_1 + \nu_5)}{\nu_2 + (\nu_1 + \nu_5)}$$

If we choose a mixture with a large amount of carbon monoxide, ν_5 is large and

$$\lambda \sim \sqrt{2\nu_2\nu_3}$$

Whereas if there is a large amount of oxygen, ν_2 is large and

$$\lambda \sim \sqrt{2\nu_3(\nu_1 + \nu_5)}$$
$$-\sqrt{2\nu_3\nu_1}$$
$$[H_2] > [CO]$$
$$-\sqrt{2\nu_3\nu_5}$$
$$[CO] > [H_2]$$

This, then, outlines a strategy for obtaining rates of reactions I, II, III, and V. First, a mixture rich in hydrogen is used to determine k2. Next, with k2 known, a mixture with a trace of hydrogen and rich in carbon monoxide is used to deter-mine k3. Finally, with k3 known, mixtures with excess oxygen and varying pro