The Determination of Equilibrium Exchange Rates in Catalytic Reactions: Application to Methanol Synthesis on Cu-Zn-Oxide

A method is described to obtain reaction rates of chemical reactions in a network in which there are more independent reactions than independent chemical species. The method makes use of the linear theory of nonequilibrium thermodynamics to obtain the equilibrium exchange rates of the reactions, which are calculated from the relaxation data as the system approaches chemical equilibrium. A method which follows very closely that of Wei and Prater (1962) can be used to treat the relaxation data. As an example, the method was applied to the methanol synthesis reaction from CO, CO_2, and H_2 over a Cu-Zn oxide catalyst. It was concluded that successful application of the method is limited to systems in which all the processes contributing to the observed relaxation are known, in addition to the common limitations due to noise in experimental measurements.

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SCOPE

It has been pointed out previously (Willcox and Kung, 1984) that, based on nonequilibrium thermodynamics, the relaxation of a chemical reaction system toward equilibrium can be described by a set of linear differential equations that relate the rate of change of the various species to their concentrations relative to equilibrium, the stoichiometric coefficients, and the equilibrium exchange rates. It was stated that this relationship can be used to determine the relative rates of chemical reactions in systems in which the number of reactions exceeds the number of independent species.

Using the methanol synthesis reaction in a feed of CO, CO_2, and H_2 over a Cu-Zn oxide catalyst, a method is described to determine the equilibrium exchange rates of the three reactions: $CO + 2H_2 = CH_3OH$, $CO_2 + 3H_2 = CH_3OH + H_2O$, and $CO_2 + H_2 = CO + H_20$. The method involves measuring the composition of the reaction mixture as it approaches equilibrium in a batch reactor. The data are analyzed using a technique similar to that of Wei and Prater (1962), which applies to linear kinetics.

CONCLUSIONS AND SIGNIFICANCE

The theories of nonequilibrium thermodynamics are successfully applied to describe the relaxation of the chemical reaction system of methanol synthesis over a Cu-Zn oxide catalyst, which contains a larger number of mechanistically independent reactions than independent chemical species. Equilibrium exchange rates of the three parallel reactions are determined, although uncertainties in these values are large because of noise in the present experimental data. From this study it is concluded that unambiguous conclusions can be obtained with this method only if the signal to noise ratio in the data is adequate, and if all the relaxation processes in the system are known, which may require other experimental evidence. In this study, the measured exchange rates could be influenced by other undesirable relaxation processes, such as a change in the activity of the catalyst due to inhibition by some species, deactivation, or a change in the nature of the catalyst.

The magnitudes of the measured equilibrium exchange rates are similar to the rates of these reactions as determined by isotope labeling and kinetic measurements. The agreement provides justification of the validity of this technique.

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INTRODUCTION

Many common chemical processes are networks of interrelated chemical reactions. It is often important to be able to measure the rates of each of the chemical reactions in the network. However, this is sometimes impossible to achieve by measuring the rates of appearance or disappearance of the chemical species. This happens when the number of mechanistically independent reactions exceeds the number of independent chemical species that must satisfy the mass conservation equations. For example, in the catalytic methanol synthesis reaction using a CO, CO_2, and H_2 mixture, three mechanistically independent reactions are potentially important:

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad (1)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (2)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad (3)$$

Since the five chemical species must satisfy the equations for the conservation of carbon, hydrogen, and oxygen, only two are independent. Therefore, it is not possible to measure the rates of these three reactions in a conventional flow reactor.

We have earlier noted that by measuring the relaxation of the reaction system toward chemical equilibrium, the theories of nonequilibrium thermodynamics provide an independent rate expression for each of the reactions, thereby enabling their rates to be measured (Willcox and Kung, 1984). According to the postulates of nonequilibrium thermodynamics, the net flux of a reaction, J, near chemical equilibrium is linearly proportional to the Gibbs free energy difference of the reaction, ΔG:

$$J = X(-\Delta G/RT) \qquad (4)$$

where R is the gas constant, T is the temperature, $\Delta G = \Sigma \nu_i \mu_i$, μ_i = chemical potential of i, and ν_i = stoichiometric coefficient (Prigogine, 1967). The proportionality constant X is known as the equilibrium exchange rate. We have shown previously (Willcox and Kung, 1984) that for an overall reaction consisting of a network of elementary reactions, X of the overall reaction is related to the equilibrium exchange rates X_i of the individual elementary reactions in the same way that the overall conductance of a network of electrical resistors is related to the conductances of the individual resistors. For example, for a series of elementary reactions, $A_1 \rightleftarrows A_2 \rightleftarrows \ldots \rightleftarrows A_N$, where the individual exchange rates are $X_1, X_2, \ldots, X_{N-1}$, the exchange rate X for the overall reaction, $A_1 \rightleftarrows A_N$, is related to the X_i's by:

$$\frac{1}{X} = \sum_{i=1}^{N-1} \frac{1}{X_i} \qquad (5)$$

From this relationship, it was concluded that X is approximately equal to the exchange rate of the rate limiting step, if it exists. Since the exchange rate of an elementary reaction is the forward (or reverse) rate of the reaction at equilibrium (Prigogine, 1967), the magnitude of X measures how rapidly a reaction proceeds. That is, the relative magnitudes of the X's of different reactions measure the relative rates of these reactions.

To demonstrate this method, we have applied the theories of nonequilibrium thermodynamics to determine the relative contributions of the reactions 1–3 in the methanol synthesis reaction by measuring their exchange rates as the system approaches equilibrium. We present here in detail the application of the theory to this reaction system, the experimental procedure for the relaxation experiments, and the adaptation of the method of Wei and Prater (1962) to extract the exchange rates from the data. In the next section, the equations describing the relaxation process are presented. This is followed by a description of the experimental details and a discussion of the results.

THEORY

Consider an experiment in which the five chemical species involved in methanol synthesis are present in an isothermal constant-volume reactor. The system is relaxing toward chemical equilibrium. Let C_i be the concentration of species i, and we denote CO, CO_2, H_2, CH_3OH, and H_2O as species 1,2,3,4, and 5. The chemical potential μ_i can be expressed, for small deviations from equilibrium and using chemical equilibrium as the standard state, as:

$$\mu_i = RT\ln(C_i/C_i^*) \simeq RT(C_i - C_i^*)/C_i^* = RT\Delta_i \qquad (6)$$

where the superscript * denotes equilibrium. This equation defines Δ_i, and it is linearized by expansion of the logarithm into a Taylor series, keeping only the linear term. Substituting this into Eq. 4, and recognizing that $\Delta G_j = \Sigma \nu_{ij}\mu_i$, the flux for reaction j becomes:

$$J_j = X_j\Big(-\sum_i \nu_{ij}\Delta_i\Big) \qquad (7)$$

While J_j is the desired quantity, it is not determinable, as mentioned earlier. The measurable quantities are the rates of change of the concentrations of the species, dC_i/dt, which are given by:

$$\frac{dC_i}{dt} = \sum_j \nu_{ij} J_j = -\sum_j X_j \nu_{ij} \sum_k \nu_{kj}\Delta_k \qquad (8)$$

There is one such equation for each species. Since $dC_i/dt = C_i^* d\Delta_i/dt$, the system of rate equations for the methanol synthesis reactions can be expressed in matrix form as:

$$\begin{bmatrix} C_1^* & & & & \\ & C_2^* & & 0 & \\ & & C_3^* & & \\ & & & C_4^* & \\ & 0 & & & C_5^* \end{bmatrix} \frac{d}{dt} \begin{bmatrix} \Delta_1 \\ \Delta_2 \\ \Delta_3 \\ \Delta_4 \\ \Delta_5 \end{bmatrix} = \begin{bmatrix} -X_1 - X_2 & X_2 & -2X_1 + X_2 & X_1 & -X_2 \\ X_2 & -X_2 - X_3 & -X_2 - 3X_3 & X_3 & X_2 + X_3 \\ -2X_1 + X_2 & -X_2 - 3X_3 & -4X_1 - X_2 - 9X_3 & 2X_1 + 3X_3 & X_2 + 3X_3 \\ X_1 & X_3 & 2X_1 + 3X_3 & -X_1 - X_3 & -X_3 \\ -X_2 & X_2 + X_3 & X_2 + 3X_3 & -X_3 & -X_2 - X_3 \end{bmatrix} \begin{bmatrix} \Delta_1 \\ \Delta_2 \\ \Delta_3 \\ \Delta_4 \\ \Delta_5 \end{bmatrix} \qquad (9)$$

$$\text{or} \quad C^* \frac{d\Delta}{dt} = X\Delta$$

It is readily seen that the matrix X is symmetric. It should be noted that, as mentioned earlier, only two of the five chemical species are independent. Thus the matrix X has a rank of only two.

In principle, Eq. 9 describes the rates of change of the concentrations of the various species. By measuring the concentrations as a function of time, the elements of X can be determined, from which the exchange rates can be obtained. In practice, however, because of experimental problems such as noise in the data it is difficult to accurately determine the elements of X directly. Wei and Prater have addressed this problem and derived a method suitable for such linear systems. According to their method, Eq. 9 is transformed into an eigenvalue problem. Then, instead of determining the elements of X directly, the eigenvalues, which are the relaxation time constants along a normal mode, are measured experimentally. Exchange rates are then calculated from the eigenvalues and the corresponding eigenvectors. Their method can be applied to our system after minor modifications; it will be described only briefly, since details can be found in the reference (Wei and Prater, 1962).

Conversion of Eq. 9 into an eigenvalue problem can be achieved by left-multiplying the equation by a matrix $C^{*-1/2}$, which is a diagonal matrix whose elements are $C_i^{*-1/2}$:

$$C^{*-1/2}C^* \frac{d\Delta}{dt} = \frac{d}{dt}(C^{*1/2}\Delta) = (C^{*-1/2}XC^{*-1/2})(C^{*1/2}\Delta) \qquad (10)$$

The elements of the diagonal matrix $C^{*1/2}$ are $C_i^{*1/2}$. Simple matrix algebra will show that the matrix $C^{*-1/2}XC^{*-1/2}$ is also symmetric. It follows that there are five linearly independent eigenvectors. This matrix also has a rank of zero; thus three of the eigenvalues are zero.

Briefly, the procedure to obtain the equilibrium exchange rates is to first identify the three eigenvectors of $\lambda = 0$. They can be constructed from mass conservation equations. The fourth eigenvector is determined from the relaxation data. The fifth eigenvector can, in principle, be obtained from the data, or it can be calculated from the first four eigenvectors after orthogonalization. Once the eigenvectors are obtained, the eigenvalues are determined from the relaxation data. Finally, the matrix X is obtained by:

$$X = C^{*1/2} V \Lambda C^{*1/2} \qquad (11)$$

Where V is a 5 × 5 matrix whose columns are the five eigenvectors, and Λ is the eigenvalue matrix.

EXPERIMENTAL

Experiments were carried out in a stainless steel batch reactor shown in Figure 1. It was made of three pieces. The bottom was a flange with a trough in the center where a magnetically driven fan sat. A Teflon tray that contained the catalyst also sat on this flange. The reactant feed, which was mixed in a stirred premixer, was introduced into the reactor through the openings in the middle section. The top section was a leak valve (Varian Vacuum Products) which leaked the gas in the reactor into a mass spectrometer chamber for analysis. The volume of the reactor was 63 mL. The entire reactor was housed in an oven with forced-air circulation; the temperature gradient along the reactor was less than 3°C. A pressure transducer located in the premixer served to measure the initial and the final pressure of the reactor, but the pressure during the experiment could not be measured directly.

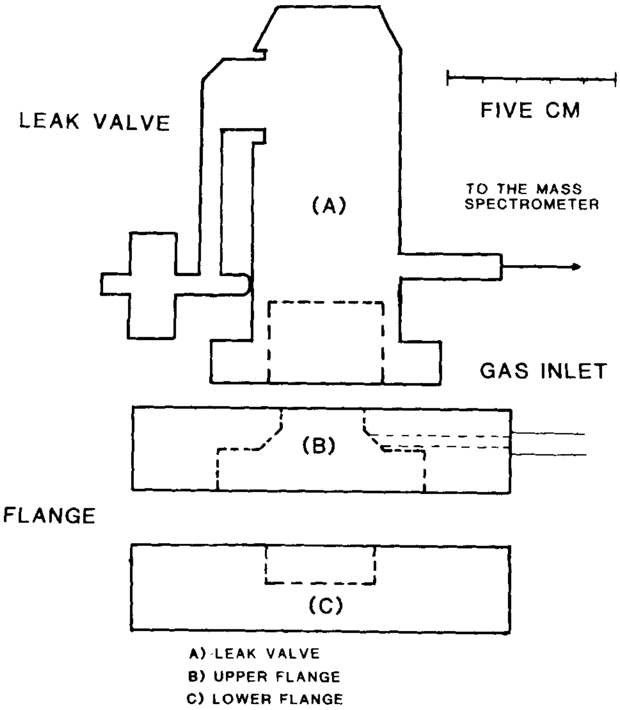

Figure 1. Reactor configuration.

A UTI 100C mass spectrometer was used. It was driven by an Apple II-plus computer that set the mass number and the sensitivity range, and collected the intensity readings. It was capable of collecting six readings of different masses per second. In these experiments, one data point was taken every 5 s.

The catalyst used has been described before (Liu et al., 1984). It was a Cu-Zn oxide catalyst prepared according to the method of Herman et al. (1979) by precipitation from a copper nitrate and zinc nitrate solution with sodium carbonate, followed by calcination. The catalyst composition was 30/70 CuO/ZnO, and had a BET area of 18 m²/g after use. As described by Liu et al., the catalyst deactivated at the beginning. The data reported are for the catalyst at the steady state activity.

In a typical experiment, known pressures of CO, CO_2, H_2, and CH_3OH were introduced into a premixer, where the gases were mixed. The mixture was then introduced into the reactor by expansion. The partial pressures in the reactor were calculated from the composition of the gas in the premixer and the measured reactor pressure. The mass spectrometer intensities of masses 44, 31, 28, 18, 17, and 2 were monitored. Extrapolation of these intensities to zero time, after correction for the cracking patterns, gave the mass spectrometer sensitivities of the various species relative to H_2. Cracking patterns measured in this apparatus were used (Liu, 1984). This calibration was repeated two or three times. Between experiments, the reactor was evacuated for 30 min. A relaxation experiment was performed by introducing a desired feed into the reactor in a similar manner. The mass spectrometer intensities of the relevant species were monitored continuously until there were no changes in the intensities above noise. Usually this took over 2h.

It was important to establish that the changes in the gas phase composition in the reactor corresponded directly to the chemical relaxation kinetics. The absence of influences due to diffusion in the catalyst bed, and the mixing in the reactor, must be established. The absence of catalyst bed diffusional influence was established when it was observed that, using a mixture of CO, CO_2, and H_2 (Liu et al., 1984), the initial rate of methanol formation was proportional to the thickness of the catalyst bed. The thickness was changed by changing the amount of catalyst used. The speed of mixing of the gas phase was tested using the reactor without any catalyst. With the reactor containing a certain gas phase mixture, a constant mass spectrometer signal was obtained. Then the composition in the reactor was changed suddenly by introducing one of the component gases. The change in the mass spectrometer signal was monitored. Some typical results are shown in Figure 2. The mass spectrometer signals attained a new steady state in about 2 min with over 60% of the changes essentially completed in less than 1 min. Since this mixing time was substantially shorter than the relaxation time measured in the experiments, the reactor was regarded as perfectly mixed in the data treatment.

Results are presented for two experiments the conditions of which are listed in Table 1. In both experiments, 0.4197 g of catalyst was used. The experiments were carried out at 225°C at an initial pressure of about 1.7 MPa.

RESULTS

Because of errors and uncertainties in the mass spectrometer intensities and sensitivities, the compositions in the reactor as deduced directly from the mass spectrometer readings were sometimes not suitable for calculating the exchange rates. In addition to discarding experiments in which the data showed erratic behavior, such as a sudden shift in the baseline, or sloping baselines, the quality of the data was also judged by comparing the mass spectrometer sensitivities calculated at the end of the experiment using the equilibrium composition calculated from thermodynamic data (Klier et al., 1982), with those determined in the calibration runs. Good agreement between sensitivities from the two

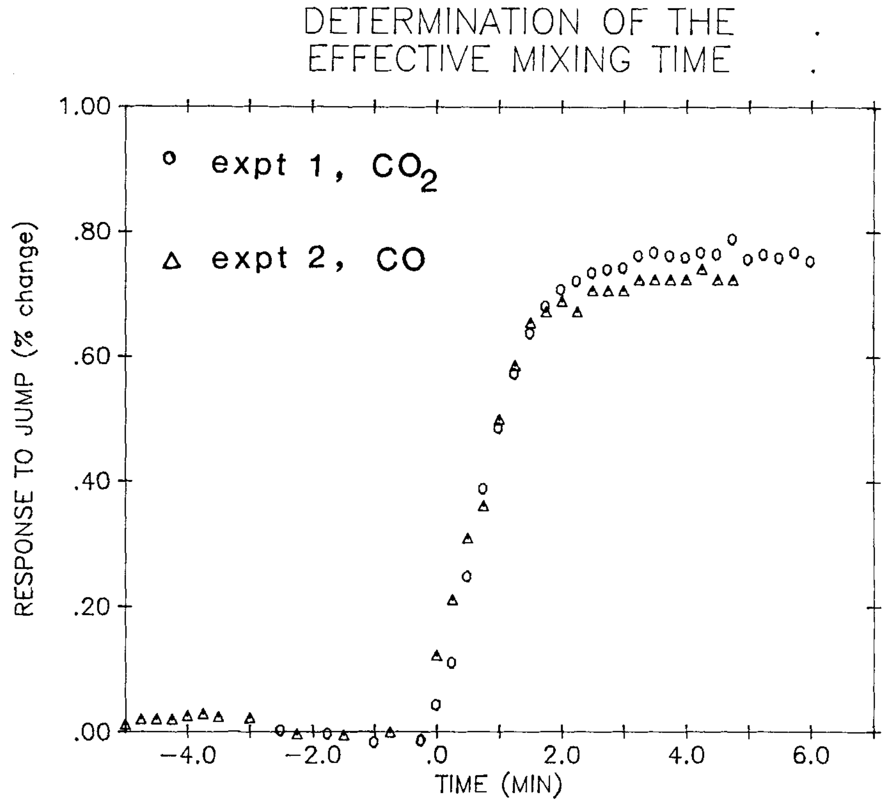

Figure 2. Response of system to a concentration jump when there was no catalyst in the reactor; 230° C.

	Exp. 1, CO_2 Jump **MPa**	**Exp. 2, CO Jump** **MPa**
Initial H_2	**1.36**	**1.36**
CO	**0**	**0.14**
CO_2	**0.16**	**0.49**
Final CO_2	**0.29**	**—**
Final CO	**—**	**0.26**

TABLE 1. SUMMARY OF DATA FOR RELAXATION EXPERIMENTS WITH 0.4197 g CATALYST AT 225 °C

	Exp. 1	Exp. 2
	Feed Conditions	
Pressure, 10^3 kPa	1.75	1.72
% Composition		
H_2	69.04	69.26
H_2O	0	0
CO	0	5.47
CH_3OH	1.58	1.88
CO_2	29.38	23.39
	Equilibrium Conditions	
Pressure, 10^3 kPa	1.73	1.66
% Composition		
H_2	64.7	66.2
H_2O	3.9	2.0
CO	3.3	5.8
CH_3OH	2.2	3.8
CO_2	25.8	22.3
	Equilibrium Exchange Rate, 10^{12} mol/cm^2•s	
X_1	2.7±0.3	1.25±0.88
X_2	0.92±0.23	0.78±0.6
X_3	1.5±0.7	−0.21±1.0
X_1/X_2	3±1	1.63±0.05
X_3/X_2	1.6±0.6	0±0.3

methods was taken as an indication that equilibrium had been reached. Using these criteria, it was found that only the data from two experiments out of about 30 were satisfactory.

The data of the acceptable experiments were then normalized according to the procedure described in the Appendix. The normalization procedure was to find a composition in the reactor that satisfied the mass conservation equations and that was as close as possible to that calculated directly from the spectrometer data. The normalization yielded the mole fractions of the species, Y_i, and the pressure of the reactor at each point in time. These were then used to calculate the exchange rates.

To use Eq. 11 to find the exchange rates, the eigenvectors and the eigenvalues must first be obtained. According to Wei and Prater (1962), the reaction system must decay along a path which could be described by a combination of the two eigenvectors of nonzero eigenvalues.

Figure 3 shows the relaxation pathways of two experiments. The composition of the reaction mixture was described by the partial pressures of two components, water and methanol. Alternatively, it could be described equally satisfactorily by the extents of two independent reactions (see the Appendix for the definition of the extent of reaction). As expected, the reaction mixture followed a curved path initially. As it approached equilibrium ($\epsilon_1 = \epsilon_2 = 0$), the path approached a straight line that is the projection onto these components of the eigenvector with the smaller but nonzero eigenvalue. From the slope of this line and the mass

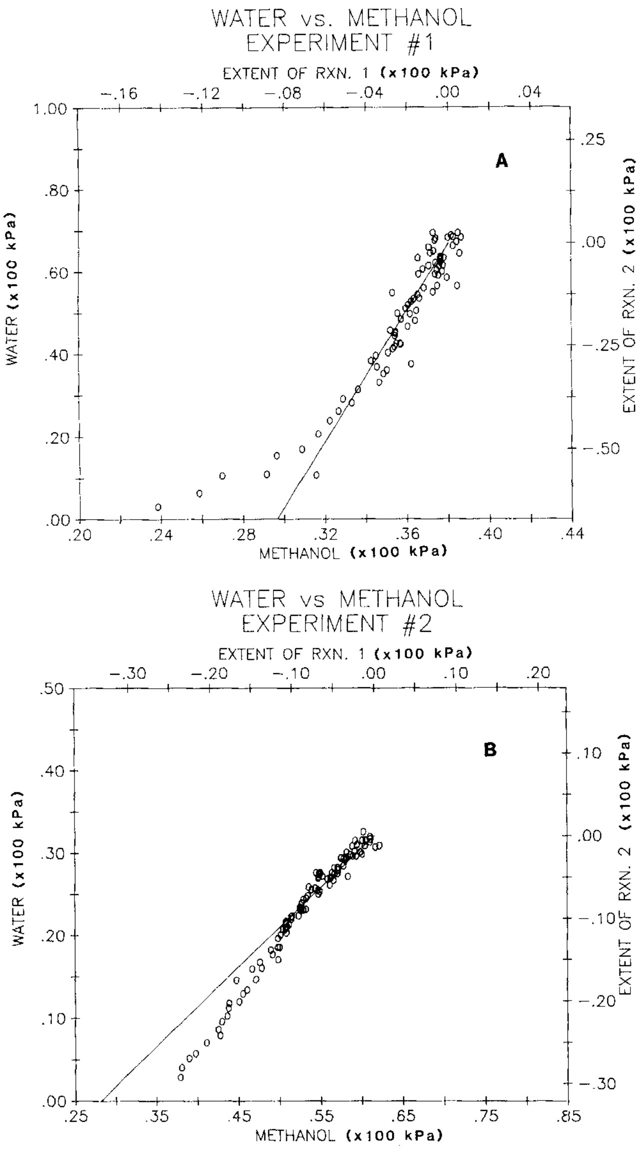

Figure 3. Partial pressures of water and methanol as reaction system approached equilibrium ($\epsilon_1 = \epsilon_2 = 0$).

See Table 1 for experimental conditions. Straight lines are the projection of the principal eigenvector onto the plane of the diagram.

conservation equations, the principal eigenvector was found.

To find the eigenvector of the second nonzero eigenvalue, the orthogonality relationship among eigenvectors of distinct eigenvalues was employed. Three eigenvectors of $\lambda = 0$ (but not orthogonal) can readily be written based on the stoichiometric coefficients in the mass conservation equations. Listing the five components in the order CO, CO_2, H_2, CH_3OH, and H_2O, the three eigenvectors in theΔ system were (1, 1, 0, 1, 0), (1, 2, 0, 1, 1), and (0, 0, 2, 4, 2), which corresponded to the carbon, oxygen, and hydrogen balance equations, respectively. These three eigenvectors are orthogonal to the principal eigenvector because the mass balance equations were used in obtaining the principal eigenvector. From these four eigenvectors, the fifth eigenvector can be calculated by the Gram Schmidt orthogonalization procedure. The eigenvectors of $\lambda = 0$ were simultaneously orthoganolized.

Once the two eigenvectors of $\lambda = 0$ were found, the experimental data, represented by the vector λ, were transformed from the delta coordinate system into the normal coordinates by $\lambda = V Z$. Here V is a matrix made up of the orthogonal eigenvectors, and the elements in Z are the normal coordinates. Figure 4 shows the normal coordinates of the data of the two experiments shown in Figure 3. Each normal coordinate decayed toward equilibrium with a certain exponential λ. The λ that best fit the data were obtained using linear regression. The exponential decay corresponding to the acceptable maximum and minimum values of λ are shown in Figure 4 as the dotted (or dashed) and the solid (or dash-dot) lines, respectively. The average of the maximum and minimum was used in further calculations, and the range was used as the uncertainty. Furthermore, by eliminating time from the two normal modes, the ratio of λ_2/λ_1 could be obtained by a linear regression from the slope in the plot of $\ln Z_2$ versus $\ln Z_1$, according to the equation: $\ln Z_2 = (\lambda_2/\lambda_1) \ln Z_1 +$ constant. The ratio λ_2/λ_1 thus obtained was less uncertain than the λ_2/λ_1 calculated from the individual λ's. This ratio was then used to calculate the ratios of the exchange rates.

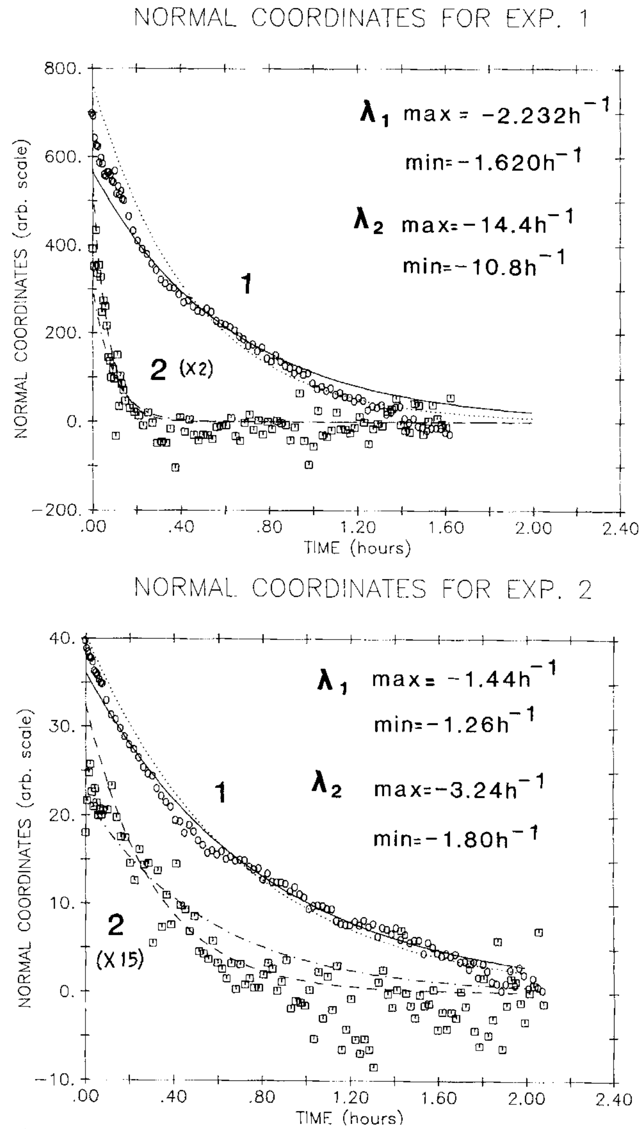

Figure 4. Relaxation of system along the two normal modes. The two lines drawn through the data points for each normal mode correspond to the maximum and the minimum that can reasonably fit the data.

Finally, the exchange rates were found using Eq. 11. Their values for these two experiments are shown in Table 1. It can be seen that the uncertainties in the ratios of the exchange rates were much smaller than the uncertainties in the individual exchange rates. This was due to the fact that calculated exchange rates all tended to increase or decrease simultaneously as λ_2/λ_1 was changed.

DISCUSSION

In the preceding sections a method was presented in which nonequilibrium thermodynamic theories were used to make possible the determination of the kinetics of a set of simultaneous chemical reactions. From the description of the method, the experimental details, and the data, the usefulness and the limitations of the method became apparent. As discussed in the Introduction, the theories of nonequilibrium thermodynamics provide independent rate expressions for the reactions. This is very powerful because the rate expressions can be written down entirely from the stoichiometric coefficients of the reaction. There is absolutely no need to know the reaction mechanism, or to know the order of the reaction in any of the reactants. The latter point distinguishes this method from other perturbation methods about a steady state. Furthermore, kinetic parameters reported in the literature are often limited by the kinetic model used. Such a limitation is not present with this technique because the stoichiometric coefficients are always known. This method is, in principle, applicable to all systems, subject to a maximum number of determinable exchange rates for a given system (Willcox and Kung, 1984).

In practice, however, the application of the method is often limited by experimental constraints. The most serious constraint is the fact that the linear regime of the nonequilibrium thermodynamic theory is exact only when the system is very close to equilibrium. Thus the method is only practical for systems where small percentage changes in the concentrations of the chemical species can be measured accurately when all species are close to equilibrium. This limits the method to systems in which all species are present in easily measurable concentrations at equilibrium. Our experiments in fact did not achieve the ideal condition. In our experiments, the closeness of the system to equilibrium can be seen in Figure 3. Water, which is the component of the lowest concentration at equilibrium, was relatively far from equilibrium in the data shown, while methanol was within 20% of equilibrium. The noise in the data excluded the possibility of obtaining useful relaxation data closer to equilibrium. In our data analysis, the deviation of the data from the straight line drawn (Figure 3) was assumed to be related to the second normal mode. However, because the system was far enough from equilibrium, the deviation could also be due to the breakdown of the linear approximation of the theory. We excluded this possibility because the relative rates of the three reactions as deduced from these exchange rates were in general agreement with the rates deduced from isotope labeling experiments (Liu et al., 1985) and kinetic experiments (Liu et al., 1984), which show that the rates of reactions 1 and 2 were comparable when the water pressure is low.

The exchange rates obtained are the exchange rates of reactions 1–3 only if they are the only relaxation processes. Other transient processes, if present, would contribute to the relaxation and they must be recognized before meaningful interpretation of the data can be made. In a catalytic reaction, a particular concern would be the change of the activity of the catalyst. Such a change can be due to the change in the nature of the catalyst with the change in the gaseous composition, or inhibition by products, or other mechanisms of poisoning.

The exchange rate of an overall reaction does not necessarily contain mechanistic information, although it has a physical meaning of being equal to the exchange rate of the rate-limiting step. To emphasize this point, it can be noted that if the reaction $2CO + H_2 + H_2O = CH_3OH + CO_2$ was used to replace one of the reactions 1 to 3, its equilibrium exchange rate could be determined similarly. Thus the equilibrium exchange rates measure the relative rates of the reactions as written, which could involve any number of steps. The ability to determine the exchange rates does not imply uniqueness of the chemical reactions.

On the other hand, if the primary (that is, mechanistically significant) reactions are identified, the net rates of these reactions can be calculated from their equilibrium exchange rates and degree of deviation from equilibrium. If the equilibrium exchange rates are measured for a variety of pressures, a rate expression can be derived. Such an application has been demonstrated in the catalytic water-gas shift reaction (Kubsh and Dumesic, 1982).

We turn now to discuss briefly the values of the exchange rates obtained. First, it should be mentioned that the various experimental difficulties described above contributed to the large uncertainties of the results. This is not an inherent problem of the method. Better mass spectrometers or other methods of detection that have lower noise levels can bring improvements easily. The negative X_3 in the second experiment is due to the uncertainties in the measurements. In theory, the exchange rate would not be negative. Since the compositions of the two experiments were similar, we expect that the exchange rates are similar, as were observed. Furthermore, we found that the magnitudes of these exchange rates were of the order of the initial rates of methanol production measured under similar conditions (Liu et al., 1984), which provide a further justification of this method.

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NOTATION

C^* = a diagonal matrix whose nonzero elements are C_i^*'s
C_i, C_i^* = concentration and equilibrium concentration of species i
ΔG = Gibbs free energy change of a chemical reaction
I_i = measured mass spectrometer intensity of species i
ΔI_i = uncertainty in I_i
J_j = net flux of reaction j
J = net flux of a reaction
R = gas constant
T = absolute temperature
V = a matrix whose columns are eigenvectors
W_i = weighting factor for species i
X, X_i = equilibrium exchange rate of a reaction, of reaction i
X = a matrix of equilibrium exchange rates
Y_i = normalized mole fraction of species i
Z_i = measured mole fraction of species i
ΔZ_i = uncertainty in Z_i
Z = vector of normal coordinates
Z_1, Z_2 = normal coordinates

Greek Letters

Δ_i = $(C_i - C_i^*)/C_i^*$
Δ = a vector of Δ_i's
λ = eigenvalue
Λ = eigenvalue matrix
ϵ_i = extent of reaction i

μ_i = chemical potential of species i

ν_i = stoichiometric coefficient of species i

ν_{ij} = stoichiometric coefficient of species i in reaction j

APPENDIX: REDUCTION OF DATA

The conversion of the mass spectrometer intensities into the equilibrium exchange rates involved first converting the intensities into concentrations of the species in the reactor. From the manner in which the concentrations approached equilibrium concentrations, the orthogonal eigenvectors and their eigenvalues were determined. Equation 11 was then used to calculate the exchange rates.

Converting the mass spectrometer intensities into concentrations involved first subtracting the background intensities from the measured intensities. The background intensities were taken as those before the introduction of feed. The resulting intensities were first corrected for cracking patterns of each mass, and then for the relative sensitivities to yield the measured mole fractions Z_i in the reactor. Because of errors in the relative sensitivities and in the mass intensities, the mole fractions at this point did not necessarily satisfy the mass balance equations. The relative sensitivities were calculated by comparing the mass spectrometer intensities at the end of the experiment with the equilibrium composition calculated from thermodynamic data (Klier et al., 1982). Only experiments in which the relative sensitivities calculated this way agreed well with those obtained in the calibration runs (see Experimental section) were accepted. This agreement established that equilibrium had been attained. The sensitivities determined using the equilibrium data were used because the method involved analysis of the data near equilibrium. These sensitivities made the analysis more self-consistent.

The data were then normalized so that the mass balances for carbon, oxygen, and hydrogen were exactly satisfied. This was done to improve the accuracy of the data by removing errors due to systematic and random fluctuations in the mass spectrometer or the apparatus that affected all masses simultaneously, and to put the data on an absolute basis in order to calculate the decrease in the reactor pressure due to reaction. The normalization was done by using a weighted nonlinear least-squares estimation to find the composition that satisfied the mass balances and was as close as possible to the measured composition. That is, the normalized mole fractions Y_i were obtained by minimizing the function: $\min F = \min \Sigma_i W_i (Y_i - Z_i)^2$. W_i are the weighting factors.

Minimization was performed with respect to two parameters, ϵ_1 and ϵ_2, which were chosen as the extents from equilibrium of reactions 1 and 2, respectively. Since only two of the three reactions are independent, only two parameters were needed. The partial pressures of each component could be written using these extents (in units of pressure) as follows.

$$\begin{aligned} P_{H2} &= P_{H2}{}^{*} - 2\epsilon_1 - \epsilon_2 \\ P_{H_2O} &= P_{H_2O} + \epsilon_2 \qquad {}^{*} \\ P_{CO} &= P_{CO}{}^{*} - \epsilon_1 + \epsilon_2 \\ P_{CH_3OH} &= P^{*}_{CH_3OH} + \epsilon_1 \\ P_{CO_2} &= P_{CO_2}{}^{*} - \epsilon_2 \end{aligned}$$

The weighting factors W_i were taken as the inverse of the uncertainties in the measured mole fractions Z_i such that the larger weights were given to the components with the smaller absolute uncertainties in the mole fraction. These were usually the components with the smaller mole fraction which would otherwise have been neglected without the use of the weights. The uncertainties in the mole fractions, ΔZ_i, were estimated from the random noise in the raw data. They were: $\Delta Z_i = W_i^{-1} = [(1 - Z_i)\, \Delta I_i + Z_i \sum_{j \neq i} \Delta I_j] / \Sigma\, I_j$. The terms I_i andΔI_i are the measured mass spectrometer intensity for component i after correction for the sensitivity and the cracking patterns, and the uncertainty in this value, respectively.

The function F was minimized by setting the partial derivatives with respect to ϵ_1 and ϵ_2 to zero, and explicitly solving the resulting quadratic equation. The two roots were discriminated by using the second derivative to insure that the minimum was chosen. In this manner, the set of normalized mole fractions Y_i was obtained. From the set of Y_i, the corresponding ϵ_1, ϵ_2, and total pressure of the reaction mixture were calculated.

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