

Interpretation of Equilibrium Exchange Rates for Nonelementary Reactions

In a system that is close to chemical equilibrium, the relaxation of each elementary step toward equilibrium obeys the linear laws of nonequilibrium thermodynamics. For a series reaction in which the concentration of the intermediate species are low or do not change with time, the relaxation can be characterized by one time constant, which can be associated with an overall equilibrium exchange rate for the overall reaction. The relationship between the overall equilibrium exchange rate and the equilibrium exchange rates of the individual steps is analogous to that between the overall conductance and the individual conductances of a network of electrical resistors in series. A numerical example is presented to show the range of validity of this relationship. Finally, a condition for the determinability of exchange rates is presented. Exchange rates are independently determinable if and only if the determinant of the matrix, whose elements are made up of squares of the inner products of the vectors that are made up of the stoichiometric coefficients of the species in the reactions, is non-zero.

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SCOPE

A postulate in nonequilibrium thermodynamics states that the net flux of a chemical reaction near equilibrium is linearly proportional to the Gibbs free energy difference of the reaction (Prigogine, 1967). The proportionality factor is termed the equilibrium exchange rate which, for an elementary reaction is the rate of the forward or the reverse direction at equilibrium. The magnitude of the equilibrium exchange rate determines the rate of relaxation of the reaction system toward equilibrium. For parallel competing reactions, the exchange rates measure the relative rates of each reaction.

However, for complex reactions, such as a series reaction, it

is sometimes convenient to measure only the relaxation and the equilibrium exchange rate of the overall reaction. It becomes important to understand the physical meaning of such an overall equilibrium exchange rate, and the relationship between this overall exchange rate and the exchange rates of the elementary steps. For practical purposes, it is also desirable to have a criterion that determines if different exchange rates can be independently measured. These questions are being addressed in this paper.

CONCLUSIONS AND SIGNIFICANCE

The relaxation of a series reaction $A_1 \rightleftharpoons A_2 \rightleftharpoons \dots \rightleftharpoons A_{n+1}$ toward equilibrium can be meaningfully described by one time constant if the concentrations of the intermediate species are small. Under such a condition, the equilibrium exchange rate, X_o , for the overall reaction, $A_1 \rightleftharpoons A_{n+1}$, is related to the exchange rates of the individual steps by:

$$\frac{1}{X_o} = \frac{1}{X_1} + \frac{1}{X_2} + \dots + \frac{1}{X_n}$$

Thus the overall exchange rate is always smaller than the exchange rates of the individual steps. It would approach that of the slowest or rate limiting step if one is present. By performing a numerical example on the reaction $A_1 \rightleftharpoons A_2 \rightleftharpoons A_3$, it is shown that the above relationship is accurate to within five percent if the concentration of the intermediate A_2 is less than 10% that of the other species. The above relationship also suggests an

electrical analog of the reaction scheme. Indeed, as long as the pseudo-steady state approximation can be applied to all intermediate species, the relationship between an overall exchange rate and the individual exchange rates for any reaction stoichiometry is analogous to that between an overall conductance and the individual conductances of an equivalent electrical circuit.

Modifying the argument of Feinberg (1977) for mass action kinetics, a criterion for the determinability of independent exchange rates is derived. For n reactions, the n equilibrium exchange rates can be independently determined if the determinant of the $n \times n$ matrix whose elements are $(g_i \cdot g_j)^2$, for $i, j = 1, \dots, n$, is nonzero. The vector g_i consists of the stoichiometric coefficients of the species in reaction i , and $g_i \cdot g_j$ is the inner product of these two vectors.

INTRODUCTION

Relaxation towards chemical equilibrium was first used by Eigen (1954) as a method to measure the kinetics of a chemical reaction.

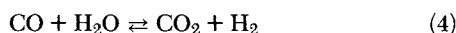
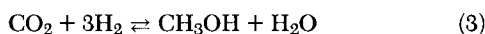
The usefulness of this method relies on the fact that, according to the postulates of nonequilibrium thermodynamics (Prigogine, 1967; Glandsdorff and Prigogine, 1971), the net flux of a reaction, J , near chemical equilibrium is linearly proportional to the Gibbs free energy difference of the reaction, $\Delta G = \sum_{i=1}^n v_i \mu_i$, where v_i = stoichiometric coefficient, and μ_i = chemical potential of species i ,

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$$J = X(-\Delta G/RT) \quad (1)$$

R is the gas constant, and T is the temperature. The proportionality constant X is known as the equilibrium exchange rate. It has been shown by Prigogine (1967) that for an elementary step, X equals the forward rate (which equals the reverse rate) of the reaction at equilibrium. Since the early work by Eigen (1954), the relaxation method has been used rather widely primarily to measure the rate constants for very fast reactions (Czerlinski, 1966). More recently, the method was used to study adsorption and desorption on solid catalysts. An example for the latter is by Kubsh and Dumesic (1982) who used the equilibrium exchange rates of the oxidation/reduction reaction of a catalyst by CO_2/CO , and by $\text{H}_2\text{O}/\text{H}_2$ to study the mechanism of the water-gas shift reaction.

There are two advantages in measuring kinetics by measuring X . First, because of Eq. 1, X can be determined without knowledge of the detailed reaction mechanism or the rate expression. It can easily be shown that ΔG can be written as a linear function of concentrations close to equilibrium. This leads to the second advantage that the exchange rates can be measured for reaction systems that contain a larger number of mechanistically independent reactions than independent chemical species. Thus, the absolute rate of each reaction can be measured in a relaxation experiment but not in an ordinary flow reactor experiment without a mechanism. An example of this is the catalyzed methanol synthesis reaction using a CO , CO_2 , and H_2 mixture. Three reactions are potentially important:

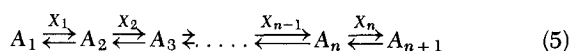


These three are mechanistically independent reactions. However, of the five chemical species, only two are independent because they are related by three mass conservation equations: conservation of carbon, hydrogen, and oxygen. Thus the rates of these three reactions cannot be uniquely determined by measuring the rates of disappearance or appearance of the reactants or products. The use of Eq. 1 in the near-equilibrium relaxation technique essentially provides a rate expression for each of these reactions, thereby enabling their rates to be measured.

To better understand and utilize the near-equilibrium relaxation method, several questions need to be answered. Often in a complex reaction, such as a heterogeneous catalytic reaction, only the exchange rate of the overall reaction can be conveniently measured, but not the exchange rates of the individual elementary steps, which may contain unstable intermediates and/or species at very low concentrations. The exchange rate of an elementary step measures how rapidly the reactants and products of that step interconvert. However, what is the physical meaning of the exchange rate of the overall reaction? Also, how is the overall exchange rate related to the exchange rates of the individual elementary steps? In addition, from the practical point of view, it is important to know how many exchange rates of mechanistically independent reactions can be determined theoretically. It is the purpose of this paper to address these questions. The relaxation towards chemical equilibrium of a batch reaction system is analyzed. From the analysis, an expression relating the exchange rate of the overall reaction to those of the individual steps, the electrical circuit analog of this relationship, and a criterion that determines the measurability of exchange rates of proposed reaction steps are obtained.

Overall Equilibrium Exchange Rates

The relationship between the overall equilibrium exchange rate and the exchange rates of the elementary steps can be derived for a series reaction:



The relaxation towards equilibrium is followed by measuring the concentrations of the appropriate species as a function of time in a batch reactor. The deviation from equilibrium can be introduced by a perturbation in concentration, temperature or pressure. Corresponding to each elementary step $\text{A}_i \rightleftharpoons \text{A}_{i+1}$, there is an equilibrium exchange rate X_i which is related to the net flux J_i by an expression analogous to equation (1):

$$J_i = X_i(-\Delta G_i/RT) \quad (6)$$

In other words, it is assumed that for every elementary step, the deviation from equilibrium is small such that the postulates of nonequilibrium thermodynamics apply. For many reasons, it may be convenient to measure only the original reactant A_1 and the final product A_{n+1} such that reaction 5 may be expressed as an overall reaction:



This may be the case for a heterogeneously catalyzed reaction in which species $\text{A}_2, \text{A}_3, \dots, \text{A}_n$ are adsorbed species that are not conveniently measurable, while only the gas phase reactant A_1 and the desorbed product A_{n+1} can be determined conveniently. The exchange rate X_o for reaction 7 is defined by Eq. 1. Clearly, $\Delta G = \sum_{i=1}^n \Delta G_i$.

The term ΔG_i in Eq. 6 measures the degree of deviation from equilibrium for the i th step. It can be expressed in terms of the chemical potentials of the appropriate species:

$$\Delta G_i = \mu_{i+1} - \mu_i \quad (8)$$

If we choose equilibrium as the standard state for the chemical potential, and assume that the deviation from equilibrium is small such that the activity coefficient of every species remains constant throughout the relaxation, Eq. 8 can be written as:

$$\Delta G_i = RT[\ln(C_{i+1}/C_{i+1}^*) - \ln(C_i/C_i^*)] \quad (9)$$

or

$$\begin{aligned} \frac{\Delta G_i}{RT} &= [(C_{i+1} - C_{i+1}^*)/C_{i+1}^* - (C_i - C_i^*)/C_i^*] \\ &\equiv \Delta_{i+1} - \Delta_i \end{aligned} \quad (10)$$

The quantity C_i^* is the concentration of species A_i at equilibrium. Equation 10 is obtained from Eq. 9 by expanding the logarithm terms in a series and keeping only the linear terms. It also defines Δ which is a measure of the deviation of the concentrations from equilibrium. Substituting Eq. 10 into Eq. 6, we obtain the following for the rate of appearance of each of the species:

$$\begin{aligned} \frac{dC_1}{dt} &= X_1(\Delta_2 - \Delta_1) \\ \frac{dC_2}{dt} &= X_1(\Delta_1 - \Delta_2) + X_2(\Delta_3 - \Delta_2) \\ &\vdots \\ \frac{dC_i}{dt} &= X_{i-1}(\Delta_{i-1} - \Delta_i) + X_i(\Delta_{i+1} - \Delta_i) \\ &\vdots \\ \frac{dC_{n+1}}{dt} &= X_n(\Delta_n - \Delta_{n+1}) \end{aligned} \quad (11)$$

Since dC_i/dt equals $C_i^*(d\Delta_i/dt)$, this set of equations can be written in the matrix form as:

$$\begin{aligned}
|D| &= \det \begin{bmatrix} -(X_1 + X_2) & X_2 & 0 & \dots & 0 \\ X_2 & -(X_2 + X_3) & X_3 & 0 & \\ 0 & & & & \\ \vdots & & & & \\ \vdots & & & & \\ \vdots & & & & \end{bmatrix} \\
|D_1| &= \det \begin{bmatrix} -(X_2 + X_3) & X_3 & 0 & \dots & \\ X_3 & -(X_3 + X_4) & X_4 & & \\ 0 & & & & \\ \vdots & & & & \\ \vdots & & & & \\ \vdots & & & & \end{bmatrix} \\
|D_n| &= \det \begin{bmatrix} -(X_1 + X_2) & X_2 & 0 & \dots & \\ X_2 & -(X_2 + X_3) & X_3 & 0 & \dots \\ 0 & & & & \\ \vdots & & & & \\ \vdots & & & & \\ \vdots & & & & \end{bmatrix}
\end{aligned}$$

Each of these three determinants can in turn be evaluated by using an LU decomposition (Strang, 1976). The results are:

$$|D| = (-1)^{n-1} P(n)$$

$$|D_1| = (-1)^{n-2} P_1(n)$$

and

$$|D_n| = (-1)^{n-2} P_n(n)$$

where $P(n) = X_1 \cdot X_2 \cdot \dots \cdot X_n$ ($\sum_{i=1}^n 1/X_i$) is the sum of all distinct products of $n-1$ exchange rates.

$$\begin{aligned}
P_1(n) &= X_2 \cdot X_3 \cdot \dots \cdot X_n \left(\sum_{i=2}^n \frac{1}{X_i} \right) \\
P_n(n) &= X_1 \cdot X_2 \cdot \dots \cdot X_{n-1} \left(\sum_{i=1}^{n-1} \frac{1}{X_i} \right)
\end{aligned}$$

Substituting these into Eq. 16, and realizing that $X_1|D| + X_1^2|D_1| = X_n|D| + X_n^2|D_n| = X_1X_2 \cdot \dots \cdot X_n$, we obtain the solution:

$$\lambda_o = \frac{\left(\frac{1}{C_1^*} + \frac{1}{C_{n+1}^*} \right) X_1 X_2 \cdot \dots \cdot X_n}{P(n)}$$

or

$$\frac{1}{\lambda_o} = \frac{1}{\frac{1}{C_1^*} + \frac{1}{C_{n+1}^*}} \left(\frac{1}{X_1} + \frac{1}{X_2} + \dots + \frac{1}{X_n} \right) \quad (17)$$

The above analysis indicates that within the assumption of negligibly small amounts of intermediate products, there is only one nonzero eigenvalue of the order of magnitude one for the system. Perlmuter-Hayman (1975) suggests that this corresponds to only one observable mode of relaxation. That is, relaxation of the intermediate steps have small amplitudes and proceed too rapidly to be observable in an experiment.

Therefore, only the relaxation of the overall reaction $A_1 \rightleftharpoons A_{n+1}$ is observed, and an overall exchange rate X_o can be defined as in Eq. 6. Following the above analysis, the matrix equation (Eq. 12) becomes:

$$\begin{bmatrix} \frac{d\Delta_1}{dt} \\ \frac{d\Delta_{n+1}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{-X_o}{C_1^*} & \frac{X_o}{C_1^*} \\ \frac{X_o}{C_{n+1}^*} & \frac{-X_o}{C_{n+1}^*} \end{bmatrix} \begin{bmatrix} \Delta_1 \\ \Delta_{n+1} \end{bmatrix} \quad (18)$$

This has the nonzero eigenvalue:

$$\lambda = X_o \left(\frac{1}{C_1^*} + \frac{1}{C_{n+1}^*} \right) \quad (19)$$

The eigenvalues of Eqs. 19 and 17 must be identical because they describe the same dynamic response. Thus, equating these two equations yields the relationship between the overall and the individual exchange rates:

$$\frac{1}{X_o} = \frac{1}{X_1} + \frac{1}{X_2} + \dots + \frac{1}{X_n} \quad (20)$$

In principle, the exactness of this relationship can be judged by solving for the next terms in the asymptotic series expansion of λ , Eq. 14. Evaluation of these terms requires a knowledge of C_i^* and X_i which are generally unavailable. However, the validity of this relationship may be examined experimentally by trying to fit the experimental data with two exponential terms. The relation is valid if the second exponential term has a time constant much smaller than the first and is of the order of magnitude of the time constant for the experimental noise.

There is an alternate method for deriving Eq. 20 due to Prigogine (1967) if we assume a strict adherence to the pseudo-steady state assumption, that is, assuming that the concentrations of all the intermediate species A_2, A_3, \dots, A_n are constant during relaxation. The derivation is as follows. The flux of each reaction step in Eq. 5 is assumed to follow the linear relationship of Eq. 6. Then at pseudo-steady state, the flux J_o of the overall reaction, $A_1 \rightleftharpoons A_{n+1}$ must be equal to the flux of each of the individual steps, and we have:

$$J_o = J_1 = J_2 = \dots = J_n \quad (21)$$

The overall Gibbs free energy change ΔG_o is the sum of the ΔG_i 's,

$$\Delta G_o = \sum_{i=1}^n \Delta G_i \quad (22)$$

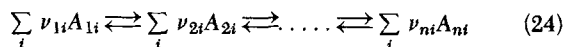
Expressing the ΔG 's in terms of J_i and X_i as in Eq. 6, we obtain:

$$\frac{J_o}{X_o} = \frac{J_1}{X_1} + \frac{J_2}{X_2} + \dots + \frac{J_n}{X_n} \quad (23)$$

which, when coupled with Eq. 21 yields:

$$\frac{1}{X_o} = \frac{1}{X_1} + \frac{1}{X_2} + \dots + \frac{1}{X_n}$$

which is Eq. 20. Equation 20 is also valid for a reaction mechanism of general stoichiometry:



The latter derivation can be extended to this case without modifications as long as the pseudosteady-state assumption applies. The former derivation may also be extended, but must be worked out for each case with the appropriate stoichiometry. However, the structure of this problem is similar to the unimolecular case in that each step in the mechanism typically has one species which is unique to that step. The matrix problem can then be written down most easily in terms of these species, and the result is valid if these species are sufficiently unstable.

While the two derivations arrive at the same result, they have subtle differences. The first method applies to relaxation in a batch reaction system in which all the species relax toward equilibrium simultaneously. None of the time rates of change of the species are exactly zero. An approximate solution can be obtained when the concentrations of the intermediates are small. The error in this approximation can be evaluated in principle by including higher order terms in Eq. 14. Although the relaxation of such a system can be characterized by one time constant, it does not imply that any individual step relaxes with the same time constant.

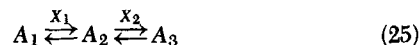
The second method of derivation starts with the assumption of a steady state such that the fluxes of all steps are equal. As long as this is true, the final result of Eq. 20 is obtained. Thus the derivation applies strictly to a flow system at steady state and not a batch system undergoing relaxation. An example of such a steady state flow system (Prigogine, 1967) is a biological system bound by semipermeable membranes. Only A_1 and A_{n+1} can enter and leave the system, while all the intermediate species are trapped inside. Then, as long as the linear dependence of J_i on ΔG_i is valid, which usually requires that the system is not far from equilibrium, the relationship between X_o and the X_i 's obtained is also valid. The assumption that the amounts of intermediates are small is not needed in this case.

The relationship between the overall exchange rate, X_o , and the individual exchange rates, X_i , Eq. 20, shows that X_o must be smaller than any of the individual exchange rates. In the limit that one of the steps is rate limiting such that its exchange rate is much smaller than the others, X_o becomes equal to this smallest exchange rate. That X_o is always smaller than the X_i 's is physically reasonable. A molecule, say A_1 , reacts to form A_2 at a rate of X_1 . However, once it becomes A_2 , it can either react to form A_3 at a rate of X_2 , or it can reform A_1 . Because of this possibility of the reverse reaction, the average rate at which a molecule goes through the whole sequence of reactions is smaller than its rate in any one step. Another consequence is that, since the time constant of relaxation is inversely related to the exchange rate, the time constant for the overall reaction is longer than the time constant for the individual steps occurring in isolation.

Equation 20 has the form identical to one which states that the overall resistance to electricity flow of a number of resistors in series is the sum of the individual resistors. This analogy follows from the postulates of linear nonequilibrium thermodynamics which result in Eq. 6. The analog in electric flow of J is the current, I , and $\Delta G/RT$ is the potential drop ΔV . The proportionality between I and ΔV , analogous to X , is the conductance, which is the inverse of the resistance. In fact, it can be easily shown that the overall exchange rate of any reaction scheme is related to the exchange rates of the individual reaction steps by an equation analogous to one that relates an overall resistance to the individual resistance of the network, provided that linear kinetics of Eq. 6 hold for every step, and that the pseudo-steady state approximation can be applied to all the intermediate species.

Range of Validity for Overall Exchange Rate: Numerical Example

The error induced by modelling a mechanism by a single overall reaction can be qualitatively examined by numerically analyzing the following simple example:



The overall exchange rate, X_o , for the overall reaction $A_1 \rightleftharpoons A_3$ is related to X_1 and X_2 by Eq. 20 for $n + 1 = 3$:

$$X_o = (X_1 X_2) / (X_1 + X_2) \quad (26)$$

The analysis in the last section suggests that the relaxation of this reaction system should be accurately approximated by a single time constant if A_2 is sufficiently unstable. Therefore, the range of validity for using X_o can be determined by varying C_2^* for various values of the other parameters.

In the specific case treated, C_1^* was set to unity, while C_3^* , X_1 , and X_2 took on various values. From these final equilibrium concentrations and an assumption of an initial perturbation of a 5% concentration jump in A_1 , the initial values of Δ_1 , Δ_2 and Δ_3 can be calculated. The resulting 3×3 system of differential Eqs. 12 can then be solved analytically. In general, the solution for Δ_1 has two exponential terms with time constants $1/\lambda_1$ and $1/\lambda_2$. Δ_2 and Δ_3 have similar solutions with identical time constants.

This exact true response was then approximated by a single-exponential decay curve found by using a continuous least squares interpolation on either Δ_1 or Δ_3 . The validity of this approximation was judged from the magnitudes of the residual. These magnitudes are plotted in Figures 1a-c. It can be seen that the residual is smaller for larger differences between X_1 and X_2 . This is expected because if one of the X 's is much smaller than the other, the step with the smaller X is the rate limiting step and its relaxation characteristic dominates the relaxation of the system. The region of validity for using an overall reaction and overall exchange rate was then judged by the percent error between the exchange rate calculated by the single exponential fit, X_{regress} , and Eq. 26. This error is summarized in Figures 2a-c, which show that for the range of parameters investigated, the error is less than 5% when the equilibrium concentration of A_2 is less than 10% that of the other species. Therefore, an overall exchange rate may be used for many reactions since the concentrations of unstable intermediates are often much less than this. It is interesting to note that this error can become zero even when C_2^* is rather large. Furthermore, the error is generally smaller in a reaction scheme with a rate determining step, which is typical of many reactions.

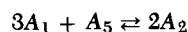
Condition That Governs Determinability of Exchange Rates

Apart from limitations imposed by uncertainties in experimental data, there is a theoretical constraint that governs the determinability of independent exchange rates in a relaxation experiment. The condition that must be satisfied by the stoichiometry for the determinability of exchange rates is derived here. The derivation follows almost identically that of Feinberg (1977) for mass action kinetics. Instead of restricting the discussion to a particular reaction scheme such as reaction 5, consider a general system containing S chemically distinct species which can interconvert via n reactions.

For a general reaction scheme, the set of rate equations that corresponds to Eq. 11 can be expressed in the matrix notation as:

$$\frac{dC}{dt} = \sum_{i=1}^n -(X_i \Delta \cdot g_i) g_i \quad (27)$$

Here C is the concentration vector $(C_1, C_2, \dots, C_S)^T$, Δ is the perturbation vector $(\Delta_1, \Delta_2, \dots, \Delta_S)^T$ in which Δ_i is defined by Eq. 10. X_i is the exchange rate for reaction i , and g_i is the vector made up of the stoichiometric coefficients of the species in reaction i . For example, if the i th reaction is:



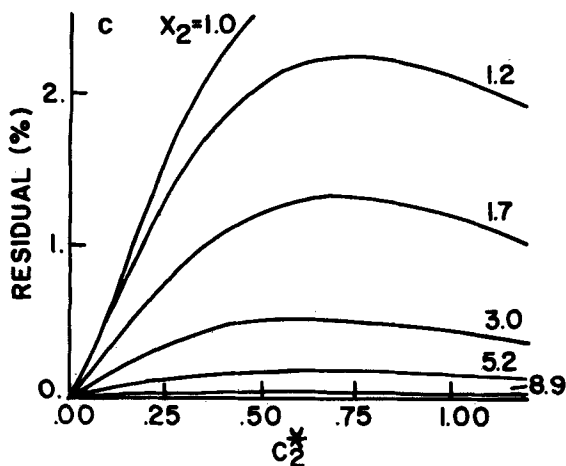
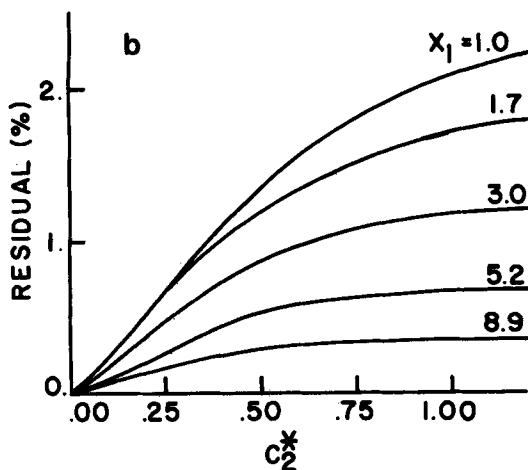
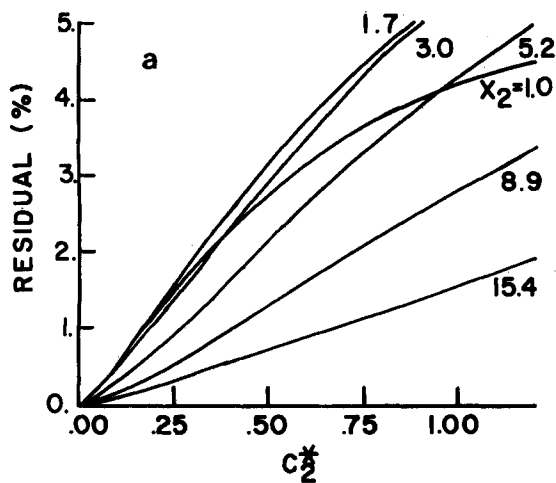


Figure 1. A plot of the residual error as a function of C_2^* . Residual error is defined as $[\int_0^1 [F(t) - Y(t)]^2 dt / \int_0^1 F(t) dt]^{1/2}$, where $F(t)$ is the single-exponential approximation curve, and $Y(t)$ is the analytical solution. Values of the other parameters used are: curve (a), $C_1^* = 1$, $C_3^* = 5$, $X_1 = 1$, X_2 as indicated, regression was on Δ_3 ; (b), $C_1^* = 1$, $C_3^* = 5$, $X_2 = 1$, X_1 as indicated, regression was on Δ_3 ; (c), $C_1^* = 1$, $C_3^* = 1$, $X_1 = 1$, X_2 as indicated, regression was on Δ_1 .

then the vector g_i is:

$$g_i = (-3, 2, 0, 0, -1, 0, 0, \dots, 0)^T$$

It can be readily seen that the term $-X_i \Delta \cdot g_i$ is the net flux of the i th reaction. Equation 27 can be rewritten as:

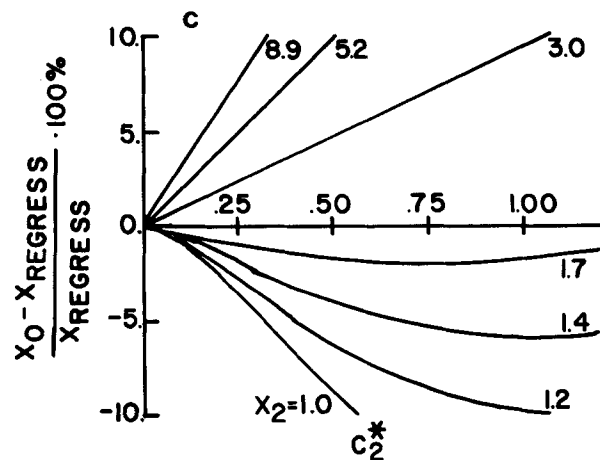
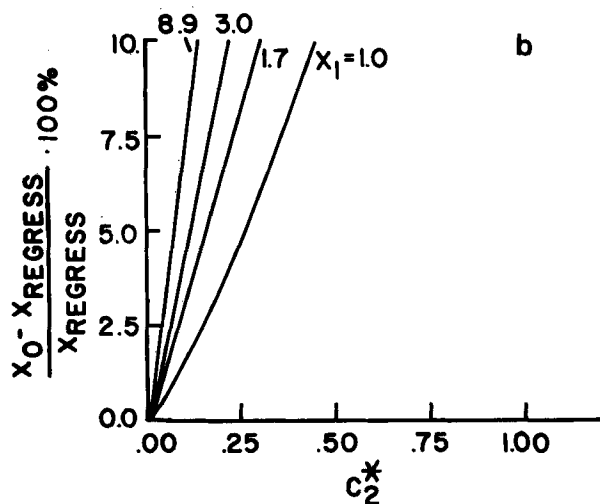
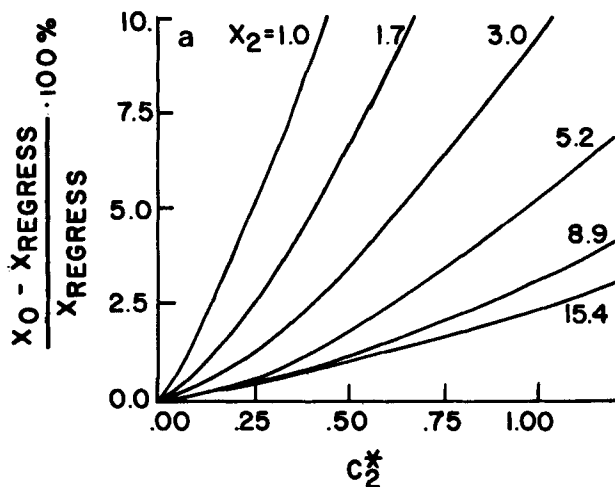


Figure 2. Percent error in the exchange rate predicted as a function of C_2^* . Values of the parameters used are the same as in Figure 1.

$$\frac{dC}{dt} = \sum_{i=1}^n -X_i (g_i g_i) \cdot \Delta \quad (28)$$

where $(g_i g_i)$ denotes the tensor dyad corresponding to the vector g_i .

The matrix $\Sigma_{i=1}^n -X_i (g_i g_i)$ is measured in a relaxation experiment. It can be used to solve for the individual exchange rates if and only if the dyads $(g_i g_i)$ are linearly independent.

The linear independence of these dyads can be determined by Gaussian elimination (Strang, 1976). Alternatively, this can be determined by making use of the Gram determinant theorem

(Davis, 1975). This theorem states that the vectors v_1, v_2, \dots, v_n are linearly independent if and only if:

$$\det \begin{bmatrix} v_1 \cdot v_1 & v_1 \cdot v_2 & \dots & v_1 \cdot v_n \\ v_2 \cdot v_1 & & & \\ \vdots & & \ddots & \\ v_n \cdot v_1 & \dots & \dots & v_n \cdot v_n \end{bmatrix} > 0 \quad (29)$$

where $v_i \cdot v_j$ denotes the inner product for the vector space. The vectors are linearly dependent if the determinant is zero. As is shown in the appendix, for a tensor

$$G^i = g_i g_i \text{ such that } G_{jk}^i = g_{ij} g_{ik}, \quad (30)$$

$$(G^i, G^j) = (g_i \cdot g_j)^2$$

where (G^i, G^j) denotes the inner product in the vector space of dyads, and $g_i \cdot g_j$ denotes the inner product of vectors. It follows that the exchange rates are all independently determinable if and only if the determinant of the $n \times n$ matrix whose elements are $(g_i \cdot g_j)^2$ is nonzero.

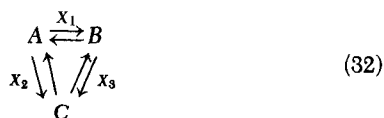
As an example, consider a reaction scheme:



In this, $g_1 = (-1, 1)$, and $g_2 = (-2, 2)$, thus

$$\det \begin{bmatrix} (g_1 \cdot g_1)^2 & (g_1 \cdot g_2)^2 \\ (g_2 \cdot g_1)^2 & (g_2 \cdot g_2)^2 \end{bmatrix} = 0$$

Therefore, X_1 and X_2 cannot be independently determined from a relaxation experiment. However, for the scheme:



$g_1 = (-1, 1, 0)$, $g_2 = (0, -1, 1)$, and $g_3 = (1, 0, -1)$. Thus

$$\det \begin{bmatrix} (g_1 \cdot g_1)^2 & (g_1 \cdot g_2)^2 & (g_1 \cdot g_3)^2 \\ (g_2 \cdot g_1)^2 & (g_2 \cdot g_2)^2 & (g_2 \cdot g_3)^2 \\ (g_3 \cdot g_1)^2 & (g_3 \cdot g_2)^2 & (g_3 \cdot g_3)^2 \end{bmatrix} = 54$$

Therefore, X_1 , X_2 and X_3 can be determined. Furthermore, Feinberg (1977) states that reaction schemes for which this determinant is zero are rare.

ACKNOWLEDGMENT

This work is supported by the Basic Energy Sciences Div., Department of Energy. We also acknowledge support by Department of Energy through the Energy Traineeship.

NOTATION

A_i	= chemical species i
C_i^*	= concentration of species A_i at equilibrium
C_i	= instantaneous concentration of species A_i
C	= vector whose components are concentrations of species, $(C_1, C_2, \dots, C_S)^T$
$ D $, $ D_1 $, $ D_n $	= determinants of matrices as defined in text
g_i	= vector whose components are stoichiometric coefficients of species in reaction i
G_i	= tensor dyad, $g_i g_i$
ΔG	= Gibbs free energy difference of a reaction
ΔG_i	= Gibbs free energy difference of reaction i
J	= net flux of a chemical reaction
J_i	= net flux of reaction i

n	= number of elementary reactions in a series
$P(n)$	= sum of all distinct products of $n - 1$ of the first n exchange rates
$P_1(n)$	= a summation of products of exchange rates as defined in text
$P_n(n)$	= a summation of products of exchange rates as defined in text
R	= gas constant
t	= time
T	= absolute temperature
v_i	= a general vector i
X	= equilibrium exchange rate
X_o	= equilibrium exchange rate of an overall reaction
X_i	= equilibrium exchange rate of an elementary reaction i

Greek Letters

Δ_i	= $(C_i - C_i^*)/C_i^*$
Δ	= a vector composed of Δ_i 's, $(\Delta_1, \Delta_2, \dots, \Delta_S)^T$
λ	= reciprocal decay time constant, an eigenvalue
$\lambda^0, \lambda_1^1, \lambda_{ij}^2$	= the zeroth order, first order, and second order terms in a series expansion of λ
μ_i	= chemical potential of species A_i

APPENDIX

The inner product for a vector space of tensors can be defined as:

$$(A, B) = \text{Tr}(A \cdot B^T) \quad (A1)$$

where A and B are tensors, B^T is the transpose of B , and Tr denotes the trace of the tensor. As written, (A, B) represents the scalar product, while $A \cdot B$ represents the tensor product.

Let $G^i = g_i g_i$, so that $G_{jk}^i = g_{ij} g_{ik}$, then:

$$(G^i \cdot G^j)_{kl} = \sum_n G_{kn}^i G_{nl}^j$$

$$= \sum_n g_{ik} g_{in} g_{jn} g_{jl}$$

$$= g_{ik} g_{jl} \sum_n g_{in} g_{jn}$$

$$= g_{ik} g_{jl} (g_i \cdot g_j) \quad (A2)$$

Therefore,

$$(G^i, G^j) \equiv \text{Tr}(G^i \cdot G^j T)$$

$$= \text{Tr}(G^i \cdot G^j)$$

$$= \sum_k [g_{ik} g_{jk} (g_i \cdot g_j)]$$

$$= (g_i \cdot g_j) (g_i \cdot g_j)$$

$$= (g_i \cdot g_j)^2$$

which is Eq. 30.

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Manuscript received February 16, 1983; revision received and accepted July 21, 1983.

High-Pressure Phase Equilibria for the Water/Methane System

A semitheoretical method has been established for superimposing the residual thermodynamic properties of pure methane and of pure water over wide ranges of pressure (0.01 to 1,000 MPa) and temperature (triple point to twice the critical temperature). Using reasonable mixing rules with two binary parameters, this superposition also gives mixture properties, including high-pressure vapor-liquid equilibria.

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SCOPE

Since natural-gas aquifers may become significant sources of energy, there exists a need towards a quantitative description of vapor-liquid equilibria pertinent to aquifers. This work presents a method to correlate, at high densities, thermodynamic properties for mixtures of water and methane, the two most abundant fluids in natural-gas aquifers.

The experimental residual thermodynamic properties for pure methane are superimposed upon those for pure water, using an extended form of corresponding states theory with molecular shape factors. Residual properties are thermodynamic properties of the real fluid minus those that an ideal gas would have at the same temperature, density, and composition.

A semitheoretical equation of state is established to represent

the superimposed residual properties. This equation of state is separated into three terms: the first arises from repulsive forces; the second, from attractive contributions to the second virial coefficient; and the third, from attractive contributions to dense-fluid properties. This separation allows different mixing rules for each term in the equation of state.

The equation of state is extended to mixtures with mixing rules that include two adjustable binary parameters that are functions of temperature, but not of density or composition. This extension produces thermodynamic properties for mixtures of water and methane, including vapor-liquid equilibria in the region 300 to 630 K and to 150 MPa.

CONCLUSIONS AND SIGNIFICANCE

The residual thermodynamic properties for pure water and for pure methane are superimposed with good accuracy over wide ranges of temperature and density. Superposition is achieved through extended (Prigogine, 1957) corresponding states, coupled with molecular shape factors (Leach et al., 1968). The resulting equation of state correlates well the PVT behavior and vapor-liquid equilibria for pure water and for pure methane for the pressure range 0.01 to 1,000 MPa and for the temperature range triple point to twice the critical temperature. For methane, all molecular shape parameters are constants. For water,

one parameter is a constant, one is a weak function of temperature, and one is a weak function of temperature and density.

For water/methane mixtures, the equation of state gives correct second virial coefficients and good agreement with experimental high-pressure vapor-liquid equilibria and with experimental gas-phase excess enthalpies.

The method presented here may serve as an initial basis for description of vapor-liquid equilibria for natural-gas aquifers.

INTRODUCTION

Natural gas has been a major source of energy for the United States, second only to petroleum. In 1974, 30.4% of the energy in

the U.S. came from natural gas (Campbell, 1977). Since our current sources of natural gas are finite, we seek new sources. Natural-gas aquifers (geopressed natural-gas deposits) may offer a new source of natural gas not yet utilized. Aquifers are high-pressure reservoirs containing natural gas (mostly methane) and water (or brine). Estimates of recoverable natural gas from aquifers range from a

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