

Thermodynamic Constraints on Multicomponent Catalytic Systems

II. Limits to Pseudo-Mass-Action Kinetics¹

M. S. SPENCER

Imperial Chemical Industries, PLC, Agricultural Division, P.O. Box No. 1, Billingham, Cleveland TS23 1LB, England

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Similar expressions to those derived before for both exact and approximate limits to first-order kinetics are shown to apply to systems which follow pseudomonomolecular kinetics. A more rigorous derivation of the approximate limits is given. The treatment is extended to some multicomponent systems displaying pseudo-mass-action kinetics. In all cases the approximate constraints on rate constants are those which would be derived if the Principle of Microscopic Reversibility could be applied in regions away from equilibrium. Previous work on three catalysed reactions (sulphur dioxide oxidation, water-gas shift, and methanol synthesis), in which the catalyst is not a constant entity across the composition space, is shown to be in accord with theory. © 1985 Academic Press, Inc.

INTRODUCTION

The constraints imposed by thermodynamics on expressions for reaction rates have been much discussed (e.g., Refs. (1-6)) in various formal ways for systems both close to and far from equilibrium. These analyses apply to catalysed, heterogeneous reactions as well as homogeneous reactions when the catalyst is a constant entity across the full range of composition of the system. While this is sometimes valid, many real catalysts vary with reactant and product composition, e.g., changes in the concentration and nature of active sites, or in bulk composition of the catalyst. In Part I (7) both exact and approximate thermodynamic constraints were deduced for systems with variable catalysts and following first-order kinetics. It was also shown that the properties required in a useful catalyst, i.e., high activity combined with catalyst stability, lead to the approximate constraints which would have been obtained if the Principle of Microscopic Reversibility (PMR) could be applied away from equilibrium.

The treatment is extended here first to systems following pseudomonomolecular

kinetics, as used by Wei and Prater (6), and then to some systems described by pseudo-mass-action kinetics.

NOMENCLATURE

a_i	Activity of component A_i
a_i'	Activity of component A_i at equilibrium
A_i	i th component in multicomponent system
b_{ij}	Activity of component B_{ij}
B_{ij}	Component reacting with A_i to give A_j in some multicomponent systems
C	Constant for given systems
G	Gibbs free energy of system
ΔG_c	Gibbs free energy change for catalyst reaction
ΔG_{ij}	Gibbs free energy change for reaction $A_i \rightleftharpoons A_j$
i	Number of component in system
j	Number of component in system
k_c	Initial rate of catalyst change
k_{ij}	Pseudo-first-order rate constant of reaction $A_i \rightarrow A_j$ in the neighbourhood of P
k'_{ij}	Pseudo-first-order rate constant

¹ For Part I, see Ref. (7).

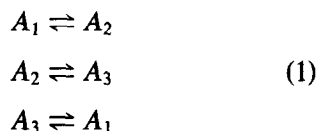
	of reaction $A_i \rightarrow A_j$ in the neighbourhood of P'
k_1	Forward rate constant of multi-component, single-reaction system in the neighbourhood of P
k_{-1}	Reverse rate constant of multi-component, single-reaction system in the neighbourhood of P
K_{ij}	Equilibrium constant of reaction $A_i \rightleftharpoons A_j$
1	Number of component in system
m	Total number of components B_i in system
n	Total number of components A_i in system
P	Point in composition space of system
P'	Equilibrium point in composition space of system
Q	Point in composition space of system near to P'
t	Time
T	Absolute temperature
$\mu(A_i), \mu_i$	Chemical potential of component A_i in system
$\mu(B_i)$	Chemical potential of component B_i in system
$\mu(B_{ij})$	Chemical potential of component B_{ij} in system
μ_i^0	Standard chemical potential of component A_i
μ_i'	Chemical potential of component A_i in system at equilibrium
ν	Stoichiometric number of multi-component reaction
ρ_i	Stoichiometric coefficient of A_i in multicomponent reaction
ρ_{ij}	Stoichiometric coefficient of B_{ij} in multicomponent reaction
σ_i	Stoichiometric coefficient of B_i in multicomponent reaction
ϕ	Unspecified function of time and the amounts of the various species of the system

TREATMENT

Pseudomonomolecular Systems

The reduction of some nonlinear reaction

systems to pseudomonomolecular systems was used by Wei and Prater (6) for ease of analysis. These systems are reaction systems in which the rates of change of the various species are given by first-order mass action terms, each multiplied by the *same* function of composition and time. Thus, for a system consisting of three components, $A_1, A_2,$ and $A_3,$ which react by the equations



the pseudomonomolecular rate equations are

$$\frac{da_1}{dt} = \phi(-(k_{12} + k_{13})a_1 + k_{21}a_2 + k_{31}a_3)$$

$$\frac{da_2}{dt} = \phi(k_{12}a_1 - (k_{21} + k_{23})a_2 + k_{32}a_3) \quad (2)$$

$$\frac{da_3}{dt} = \phi(k_{13}a_1 + k_{23}a_2 - (k_{31} + k_{32})a_3),$$

where k_{ij} is the pseudo-first-order rate constant for the reaction from A_i to $A_j,$ and ϕ is some unspecified function of the amounts of the various species and time, and must be positive for real systems.

In the general case of n components, the rate equation for component A_i is given by

$$-\frac{da_i}{dt} = \phi \sum_{j=1}^n (k_{ij}a_i - k_{ji}a_j), \quad (3)$$

where values for $i = j$ are omitted.

*Exact Constraints for**Pseudomonomolecular Systems*

Suppose the system undergoes a catalysed, adiabatic change at constant pressure from the point P in the composition space of the system.

Then, from a similar analysis to that used before (7), the constraint imposed by the second law of thermodynamics is

$$0 < \sum_{i=1}^n \left[\mu_i \sum_{j=1}^n (k_{ij}a_i - k_{ji}a_j) \right] \quad (4)$$

This is the same form as the exact constraint deduced for first-order systems, but with the difference that k_{ij} and k_{ji} are now the pseudo-first-order rate constants. It follows that, as before (7), thermodynamics imposes no constraints on the relative values of the pair of pseudo-first-order rate constants, k_{ij} and k_{ji} , except as part of Eq. (4).

Closer constraints can be deduced for various special cases as for linear systems (7).

The equation, $k_{21}/k_{12} = K_{21}$, which would be derived by the use of PMR if it could be applied at P in a two-component system, fits Eq. (4) but only as a further special case.

Approximate Constraints for a Pseudomonomolecular System

In the previous paper (7) the rate constants of both two-component and multi-component systems which followed linear kinetics were shown to be related as if the PMR could be applied approximately away from equilibrium, i.e., $k_{ij}/k_{ji} \approx K_{ij}$ for all i, j (as above, all terms with $i = j$ are omitted). A more rigorous derivation of the same conclusion is given in the Appendix for a two-component pseudomonomolecular system. For all the real cases considered, the approximate constraint is

$$k_{12}/k_{21} \approx K_{12}. \quad (5)$$

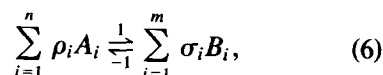
This is identical with the equation which would have been derived by the use of PMR at P . The applicability of PMR in various nonequilibrium systems has been discussed by Astarita (8), but in this case the form of Eq. (5) arises from the properties of a practical catalyst.

Extension to the multicomponent system considered before is straightforward and follows the previous analysis (7).

Pseudo-Mass-Action Systems

The concept of pseudomonomolecular kinetics can be extended further to pseudo-mass-action systems. These were defined

by Wei and Prater (6) as "systems in which all rates of change of the various species are given by mass action terms of *various* integral order each multiplied by the same function of composition and time." Two types of pseudo-mass-action systems will be considered in this section. The first is one in which the reactions in the system can be represented by a single, multicomponent reaction:



where ρ_i and σ_i are the stoichiometric coefficients. The rate equation, following pseudo-mass-action kinetics, is

$$\begin{aligned} -\frac{1}{\rho_1} \cdot \frac{da_1}{dt} &= -\frac{1}{\rho_i} \cdot \frac{da_i}{dt} = \frac{1}{\sigma_i} \cdot \frac{db_i}{dt} \\ &= \phi \left[k_1 \prod_{j=1}^n a_j^{\rho_j} - k_{-1} \prod_{j=1}^m b_j^{\sigma_j} \right]. \quad (7) \end{aligned}$$

Although this is a multicomponent system the restriction of fixed stoichiometry in a single reaction makes it formally equivalent to the simple, two-component reaction



considered as a special case previously (7). With appropriate transformations, the composition space becomes one dimensional, with any composition falling to the left or right (as defined by Eq. (6)) of the equilibrium point. For the left-hand side arbitrarily in excess of equilibrium, i.e.,

$$\prod_{j=1}^n a_j^{\rho_j} / \prod_{j=1}^m b_j^{\sigma_j} > (K_1)^{-1/\nu}, \quad (9)$$

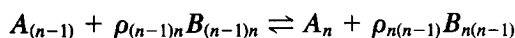
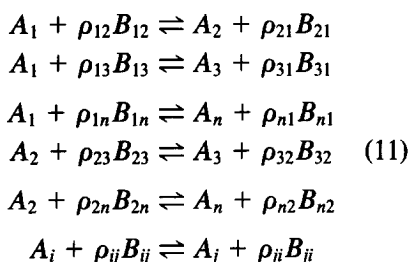
where ν is the stoichiometric number of the reaction, the constraint is

$$k_1 \prod_{j=1}^n a_j^{\rho_j} > k_{-1} \prod_{j=1}^m b_j^{\sigma_j}. \quad (10)$$

The relation $k_1/k_{-1} = (K_1)^{1/\nu}$, which would be derived by the additional use of the PMR or other equilibrium properties (5) fits the above relations (9) and (10) but only as a special case. Even in this special case there

is no direct or necessary relationship between k_1 , k_{-1} , and the values of any rate constants in the region near equilibrium.

The second pseudo-mass-action system consists of a set of n components, $A_1 \dots A_i \dots A_n$ each of which reacts with components from a second set, $B_{12}, B_{21} \dots B_{ij} \dots B_{(n-1)n}, B_{n(n-1)}$. This is expressed in a set of $n(n-1)/2$ reactions, each first order in one component, A_i :



The rate equation for component A_i is given by

$$-\frac{da_i}{dt} = \phi \sum_{j=1}^n (k_{ij}a_i b_{ij}^{\rho_{ij}} - k_{ji}a_j b_{ji}^{\rho_{ji}}) \quad (12)$$

for $i \neq j$.

Similarly, for component B_{ij} :

$$-\frac{1}{\rho_{ij}} \cdot \frac{db_{ij}}{dt} = \phi (k_{ij}a_i b_{ij}^{\rho_{ij}} - k_{ji}a_j b_{ji}^{\rho_{ji}}) \quad (13)$$

The free energy of the system at P is G , where

$$G = \left[\sum_{i=1}^n a_i \mu(A_i) + \sum_{i=1}^n \sum_{j=1}^n b_{ij} \cdot \mu(B_{ij}) \right] \quad (14)$$

again for all $i \neq j$.

The constraint on the rate constants is then derived from Eqs. (12), (13), and (14) as before:

$$\begin{aligned} 0 < \left[\sum_{i=1}^n \mu(A_i) \sum_{j=1}^n (k_{ij}a_i b_{ij}^{\rho_{ij}} - k_{ji}a_j b_{ji}^{\rho_{ji}}) \right. \\ &+ \sum_{i=1}^n \sum_{j=1}^n \rho_{ij} (k_{ij}a_i b_{ij}^{\rho_{ij}} \\ &\left. - k_{ji}a_j b_{ji}^{\rho_{ji}})(\mu(B_{ij}) + RT) \right]. \quad (15) \end{aligned}$$

Approximate constraints for practical catalysts in both of these systems can be derived most readily by the use of the qualitative argument applied before (7) to multicomponent first-order systems. Thus, the approximate relations between the rate constants in these systems are those which would apply if PMR were valid away from equilibrium.

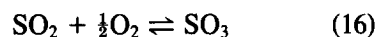
COMPARISON WITH EXPERIMENTAL RESULTS

Most monomolecular systems which have been studied experimentally have contained catalysts which can be regarded as constant entities across the full range of composition space, e.g., butene isomerisation over alumina (6). More far-reaching chemical changes in the reactions between the components of a system are customarily needed to bring about changes in catalysts. Some of these follow, at least approximately, pseudo-mass-action kinetics.

In each of the examples considered, sulphur dioxide oxidation, water-gas shift reaction, and methanol synthesis, there are wide variations in the forms of reaction rate equations proposed. However, allowances for the reverse reactions were made satisfactorily as if PMR were valid across the full experimental range, so confirming the validity of the approximate constraints derived above.

Sulphur Dioxide Oxidation

The reaction for sulphur dioxide oxidation



is a case of Eq. (6), with $n = 2$ and $m = 1$. Then the constraint on the rate constants [Relation (10)] becomes

$$k_1 a_{\text{SO}_2} a_{\text{O}_2}^{1/2} > k_{-1} a_{\text{SO}_3}. \quad (17)$$

The kinetics of SO_2 oxidation have been widely studied (9-11) for supported V_2O_5 catalysts. Alkali metal promoters are added and the active phase is a melt of composition which is dependent on the gas phase.

Thus, this system is an example of a catalyst with variable bulk composition.

Attempts have been made (12–15) to include the changes in composition of the active melt into the kinetics but the difficulties are formidable. The wide variety of conventional kinetic equations proposed (9–11) reflects more than the idiosyncrasies of different workers in fitting experimental data. Livbjerg and Villadsen (10) concluded that “most rate expressions are adequate only in a narrow temperature and composition range and that probably no single rate expression can be applied in the whole range of industrial operating conditions.” Thus SO₂ oxidation is a system showing the expected variability of kinetics.

The diversity of kinetic equations does nevertheless show a consistency in the allowance made for the reverse reaction (9, 11), which is always of the form

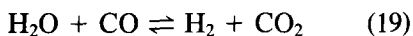
net rate = (forward rate)

$$\left[1 - \left\{ \frac{a_{\text{SO}_3}}{K \cdot a_{\text{SO}_2} a_{\text{O}_2}^{1/2}} \right\}^{1/\nu} \right], \quad (18)$$

where $\nu = 1$ or $\frac{1}{2}$. The derivation of Eq. (18) requires the application of PMR, even where this is not strictly valid. The experimental use of Eq. (18) under these conditions confirms the arguments used above for approximate constraints consistent with the application of PMR.

Water-Gas Shift Reaction

The water-gas shift reaction



is another case of Eq. (6), with $m = n = 2$. Only the catalyst for the high-temperature region, Fe₃O₄/Cr₂O₃, is considered here. From Relation (10) the constraint

$$0 < \left[1 - \frac{k_{-1}}{k_1} \left(\frac{a_{\text{H}_2} a_{\text{CO}_2}}{a_{\text{H}_2\text{O}} a_{\text{CO}}} \right)^{1/\nu} \right] \quad (20)$$

can be derived.

Various forms of kinetic equations have been reported for the water-gas shift reaction (16, 17). Unlike the V₂O₅-based cata-

lysts for SO₂ oxidation, the bulk composition of the active phase of water-gas shift catalysts stays constant as Fe₃O₄ under all normal industrial conditions. Nevertheless, the degree of surface oxidation of these catalysts is dependent on the gas composition (18) and so variable kinetics can be expected. The empirical kinetic equations are all (16, 17) of the form

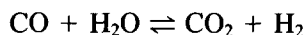
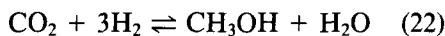
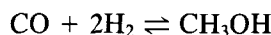
net rate = (forward rate)

$$\left[1 - \frac{a_{\text{CO}_2} a_{\text{H}_2}}{K a_{\text{CO}} a_{\text{H}_2\text{O}}} \right], \quad (21)$$

so again the performance of the system is as if PMR can be applied in regions of composition away from equilibrium.

Methanol Synthesis

The formation of methanol from synthesis gas and the concurrent water-gas shift reaction which occurs in the presence of H₂O and CO₂ is described by the set of three reactions (two only of which are independent):



This set can be described by Eq. (11), in which

$$A_1 = \text{CO}; \quad A_2 = \text{CH}_3\text{OH}; \\ A_3 = \text{CO}_2$$

$$\rho_{12} B_{12} = 2\text{H}_2; \quad \rho_{23} B_{23} = \text{H}_2\text{O}; \\ \rho_{31} B_{31} = \text{H}_2 \quad (23)$$

$$\rho_{21} B_{21} = -; \quad \rho_{32} B_{32} = 3\text{H}_2; \\ \rho_{13} B_{13} = \text{H}_2\text{O}$$

The exact constraint on the relevant rate constraints is then the inequality (15) with $n = 3$ and the substitutions (23). The approximate constraints are given by the application of PMR to each of the reactions in (22).

Various kinetic equations for methanol synthesis over zinc oxide/chromia catalysts are given by Denny and Whan (19). The

lack of consistency between different equations may be attributed in part to variation of the catalyst surface with the composition of the reacting gases. Bowker *et al.* (20) have shown that the defect state of the surface of the ZnO is of critical importance in the reaction. This defect state is a function of gas composition (21, 22), giving a variable catalyst. Allowance for methanol decomposition in the empirical kinetics is of the form

net rate = (forward rate)

$$\left[1 - \frac{a_{\text{CH}_3\text{OH}}}{K \cdot a_{\text{CO}} a_{\text{H}_2}} \right] \quad (24)$$

again giving support for the application of PMR in regions away from equilibrium.

CONCLUSIONS

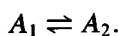
1. The exact constraints on the rate constants in multicomponent catalytic systems which follow pseudomonomolecular or pseudo-mass-action kinetics are similar expressions, involving chemical potentials as well as rate constants, to those deduced before for first-order systems.

2. Again as for first-order systems, approximate constraints for other systems with practical catalysts are those which would apply *as if* the Principle of Microscopic Reversibility could be used well away from equilibrium.

3. The empirical kinetics obtained from three multicomponent systems with practical catalysts are compared with the theoretical constraints on rate constants. The wide variability of kinetics is attributed, at least in part, to variations in the catalysts with gas composition. In accord with theory, the Principle of Microscopic Reversibility can be applied approximately, even in regions well away from equilibrium where its exact use is not valid.

APPENDIX

Consider the two-component system involving A_1 and A_2 which reacts by



The rate of reaction near P is then

$$-\frac{da_1}{dt} = \frac{da_2}{dt} = \phi(k_{12}a_1 - k_{21}a_2). \quad (25)$$

Now suppose that the catalyst, at a steady state with the reacting system in the neighbourhood of P , is transferred nearly instantaneously to an equilibrium mixture of A_1 and A_2 (at the same total pressure, volume, and temperature as the system at P) at activities a'_1 and a'_2 , respectively. If the catalyst is transferred sufficiently quickly the catalyst is initially in the system at the equilibrium point P' in the same state as it was at P . After the transfer of the catalyst the system is assumed to be adiabatic and at constant pressure. For the following argument P' may be the unique point of equilibrium or one of several possible points of equilibrium to be found in some nonideal systems (23). After the transfer, two reactions, which may (and indeed in real systems must) be coupled, need to be considered:

(i) The reactions of A_1 and A_2 on the catalyst, leading initially to a displacement from equilibrium.

(ii) Changes in the catalyst from its steady state at P to its steady state at P' . These can range from changes in adsorbed species to reactions in the bulk of the catalyst.

Suppose the action of the catalyst on the system at the equilibrium point P' causes initially a move to point Q , very close to P' , with an increase in A_1 . Then, at Q :

$$\begin{aligned} a_1 &= a'_1 + \delta a \\ a_2 &= a'_2 - \delta a. \end{aligned} \quad (26)$$

At P' the free energy of the system is given by

$$G' = (a'_1 \mu'_1 + a'_2 \mu'_2) \quad (27)$$

and at Q :

$$G = (a_1 \mu_1 + a_2 \mu_2). \quad (28)$$

Substitution from Eq. (26) gives

$$G = ((a'_1 + \delta a)(\mu_1^0 + RT \ln(a'_1 + \delta a)) + (a'_2 - \delta a)(\mu_2^0 + RT \ln(a'_2 - \delta a))). \quad (29)$$

Simplification of Eqs. (27) and (29) then gives

$$G \approx G' + \frac{RT}{2} (a_1 - a'_1)^2 \left[\frac{1}{a'_1} + \frac{1}{a'_2} \right]. \quad (30)$$

Differentiation of G with respect to time and substitution from Eq. (25) gives the rate of change in free energy (due to A_1 and A_2 only) in the system at Q .

$$\frac{dG}{dt} \approx -2\phi \frac{(G - G')}{\delta a_1} (k_{12}a_1 - k_{21}a_2). \quad (31)$$

Let the initial rate of any change of the catalyst be k_c , the units of which are moles \times (catalyst volume) $^{-1}$ (time) $^{-1}$. The initial rate of free energy change for the catalyst only is $\Delta G_c \cdot k_c$. As Q is close to P' , this rate is assumed to be constant from P' to Q . The system (catalyst + A_1 + A_2) is adiabatic, so the rate of change of free energy must be negative and the constraint at Q is

$$\Delta G_c \cdot k_c - 2\phi \frac{(G - G')}{\delta a_1} (k_{12}a_1 - k_{21}a_2) < 0. \quad (32)$$

This can be rearranged to

$$2 \left[\frac{(G - G')a_1}{\Delta G_c \cdot \delta a_1} \right] \left[\frac{\phi k_{12}}{k_c} \right] \left[1 - \frac{k_{21}a_2}{k_{12}a_1} \right] < 1. \quad (33)$$

As before (7), consideration of different types of practical catalysts shows that

$$\frac{k_{21}a_2}{k_{12}a_1} \approx 1. \quad (34)$$

Since Q is close to P' , $a_2/a_1 \approx a'_2/a'_1$, so the approximate criterion imposed by the second law is

$$k_{12}/k_{21} \approx K_{12} \quad (35)$$

and the rate equation (25) may be rewritten as

$$-\frac{da_1}{dt} \approx \phi k_{12} \left[a_1 - \frac{a_2}{K_{12}} \right]. \quad (36)$$

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