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Thermodynamic Constraints on Multicomponent Catalytic Systems

I. Limits to First-Order Kinetics

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The steady state of a catalyst is often dependent on the composition of the reacting system, so the kinetics observed in systems far from equilibrium can be very different from equilibrium kinetics. Exact constraints on first-order kinetics are derived: limits to individual rate constants are found in two component systems only. However, most practical catalysts are shown to perform as if the principle of microscopic reversibility could be applied approximately at points away from equilibrium.

INTRODUCTION

The effects of thermodynamic and other axiomatic constraints on the kinetics of multicomponent systems have been analysed in detail by Wei and Prater (*1*). They took the reactions in the systems to be first order for much of their analysis, although more complex kinetics were also considered. In both their treatment and other, less rigorous, accounts the catalyst is assumed to be a constant entity across the full range of composition of the system. This is indeed probably true in those catalytic systems to which Wei and Prater's analysis has been applied, e.g., butene isomerisation over alumina (*1*, *2*), because the chemical differences between the components are relatively small. However, catalysts cannot be assumed to be constant in many systems of practical interest. In this paper the limits imposed by thermodynamics on the kinetics of systems which follow first-order kinetics are derived. Nonlinear systems will be analysed in a subsequent paper.

State of Catalyst

An equilibrium catalyst can exist only in contact with a system of fluid reagents and products which is itself at equilibrium. A catalyst in contact with a mixture of fluids not at equilibrium may be in a state of quasi equilibrium with one or more components of the mixture, but it cannot then be at equilibrium with all the other components. Real catalysts, even after prolonged exposure to equilibrium mixtures, are rarely at equilibrium, if only in the sense that the solid catalyst must have excess surface to possess useful activity.

Thus a catalyst in contact with a nonequilibrium mixture of fluids can at best be in a steady state which is essentially constant for a certain region of composition of reactants and products. In the general case this steady state is different for different regions of the system. The changes occurring in the catalyst can be physical or chemical. Physical changes can be alterations in the crystal faces exposed, sintering of the active phase, etc. Chemical changes can vary from changes in chemisorbed layers to surface reconstructions, bulk phase changes or bulk composition changes.

Bulk changes may lead to discontinuities in catalyst performance with variations in reactant and product composition. A plot of initial rate of reaction over the steady-state catalyst against initial reactant composition will show ideally a discontinuity at a change of solid state, but the formation of defect or

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nonstoichiometric phases will allow a continuous change. Clearly, the rate of change in an isolated system must also vary continuously over all possible changes in the catalyst because none of these changes can occur instantaneously. Nevertheless, some doubt remains about the general validity of an axiom invoked in some treatments of reaction systems (*3*): "The rate of change of the mass of each species is a continuous function of all the masses."

The complete kinetic equation for the reaction system with a given catalyst should include, implicitly or explicitly, all the consequences of the changes of the catalyst steady state. The resulting complexity would be formidable, so in this treatment it is assumed that a simpler, conventional rate equation can be used over a limited region of the composition space. The rate equations for different regions of the same system, including catalyst, are not assumed to be necessarily of the same form or to involve the same constants.

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
C	Constant for given system
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 components in system
j	Number of components in system
k_c	Initial rate of catalyst reaction
k_{ij}	First-order rate constant of reaction $A_i \rightarrow A_j$ in the neighbourhood of P
k'_{ij}	First-order rate constant of reaction $A_i \rightarrow A_j$ in the neighbourhood of P'
K_{ij}	Equilibrium constant of reaction $A_i \rightleftharpoons A_j$
P	Point in composition space of system
P'	Equilibrium point in composition space of system
Q	Point in composition space of system
t	Time
T	Absolute temperature
V	Liapounov function for system
μ_i	Chemical potential of component A_i in system
μ_i^0	Standard chemical potential of component A_i
θ	Unknown function of system

TREATMENT AND DISCUSSION

General Constraints

The existence of general constraints on the kinetics of a multicomponent system as a result of the second law of thermodynamics can be demonstrated without reference to the equilibrium state. A direct argument is the following. Consider an adiabatic system of n components, $A_1, A_2, \ldots, A_n$, which react by the following series of reactions:

$$A_i \rightleftharpoons A_j \quad \text{where } i, j = 1, 2, \ldots, n \text{ and } i \neq j.$$

Suppose that, for the system at a point P and in the neighbourhood of P, a class of selective catalysts exists such that catalyst (i, j) catalyses reaction $A_i \rightarrow A_j$ only; catalyst (j, i), reaction $A_j \rightarrow A_i$ only, etc., for all the values of i and j. It would then be possible to change the composition of the reaction system for the point P to any neighbouring point Q in the composition space by the appropriate use, either conjointly or consecutively, of various members of this class of catalysts in an adiabatic process. But this is in immediate violation of Caratheodory's formulation of the second law, viz., "It is impossible to reach *all* states in the neighbourhood of any arbitrary initial state by an adiabatic process" (*4*). Therefore the proposed class of selective catalysts cannot exist.

In the more general, and realistic, case of a catalyst which promotes, at various rates, some (or possibly all) of the reactions in the system, a similar argument shows that there must be bounds to the rates of the catalysed reactions so as to make some states in the neighbourhood of P inaccessible by any adiabatic, catalysed process. These conclusions are, of course, not dependent in any way upon either the position of equilibrium in the reaction system or the kinetics of the reaction systems at equilibrium.

Exact Constraints in Systems with First-Order Kinetics

It is necessary to define the equilibrium points of the reaction system (either explicitly, or implicitly by the use of the entropy of systems) in order to extend the results of the previous section. Let all the reactions in the multicomponent system $A_1, A_2, \ldots, A_n$ follow first-order kinetics only in the region of composition space to be considered. No necessary description of the kinetics in any other region is implied. The rate of reaction (*1*, *2*) is given by

$$-\frac{da_1}{dt} = k_{12}a_1 - k_{21}a_2$$

and the rate equation for component A_i is given by

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

where values for $i = j$ are omitted. Suppose the system undergoes a catalysed, adiabatic change at constant pressure from the point P. The free energy of the system at P is G, where

$$\begin{aligned} G &= C \sum_{i=1}^{n} a_i\mu_i \\ &= C \sum_{i=1}^{n} a_i(\mu_i^0 + RT \ln a_i). \end{aligned} \tag{2}$$

The rate of change of free energy is therefore

$$\begin{aligned} \frac{dG}{dt} &= C \sum_{i=1}^{n} \left(\frac{da_i}{dt} (\mu_i^0 + RT(1 + \ln a_i))\right) \\ &= -C \sum_{i=1}^{n} \left((\mu_i^0 + RT(1 + \ln a_i)) \sum_{j=1}^{n} (k_{ij}a_i - k_{ji}a_j)\right) \\ &= -C \sum_{i=1}^{n}\left(\mu_i \sum_{j=1}^{n} (k_{ij}a_i - k_{ji}a_j)\right). \end{aligned} \tag{3}$$

The second law constraint for irreversible reaction is

$$\frac{dG}{dt} < 0.$$

Therefore the constraint on the system is

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

as the constant C is positive.

Although (4) is a single constraint on all the values of k_{ij}, it must hold for all values of all a_i in the region around P in which the rate equations (1) apply. Thus constraint (4) is more severe than it first appears to be. Moreover the rate constants must be valid for changes at constant volume as well as changes at constant pressure, or indeed for changes with any other equivalent prescribed physical restriction. Each of these leads to constraints similar to (4) by the use of different thermodynamic functions. Wei (*3*) has proposed an axiomatic constraint on reaction systems, that an appropriate Liapounov function exists. A Liapounov function is a function $V(a_1, a_2, \ldots, a_n)$ of fixed sign that is everywhere positive (or negative) and its time derivative,

$$\frac{dV}{dt} = \sum_{i=1}^{n} \frac{\delta V}{\delta a_i} \frac{da_i}{dt},$$

is everywhere negative (or positive). The Gibbs free energy, for example, is a Liapounov function. Wei has shown that the axiom is a sufficient condition for convergence to equilibrium but as it seems likely that not all Liapounov functions correspond to real systems, the axiom may be unnecessarily constrictive.

The constraints from the principle of microscopic reversibility (or the Onsager reciprocal relationships) cannot be used here as they apply only close to equilibrium (5). Thus thermodynamics imposes no constraints on the relative values of the pair of rate constants, k_{ij} and k_{ji}, except as part of relationship (4). In particular, when A_i is in excess of equilibrium and A_j is in deficit, $k_{ij}a_i$ is not necessarily greater than $k_{ji}a_j$.

Closer constraints can be deduced for various special cases of the multicomponent, first-order system. If A_1 is in excess of equilibrium and $A_2, A_3, \ldots, A_n$ are all in equilibrium ratio, then,

all $a_1/a_i > K_{i1}$ for $i = 2, 3, \ldots, n$,
all $a_j/a_i = K_{ij}$ for $i = 2, 3, \ldots, n$ and i $\neq j$, $j = 2, 3, \ldots, n$,
$\mu_1 > \mu_i$ for $i = 2, 3, \ldots, n$,
$\mu_i = \mu_j$ for $i = 2, 3, \ldots, n$, $j = 2, 3, \ldots, n$.

Substitution in relationship (4) gives

$$0 > \theta_1 \sum_{j=2}^{n} (k_1 a_1 - k_{j1} a_j) + \sum_{i=2}^{n} \mu_i \Big(k_{i1} a_i - k_{1i} a_1 + \sum_{j=2}^{n} (k_{ij} a_i - k_{ji} a_j) \Big),$$

which simplifies to

$$0 < (\mu_1 - \mu_2) \sum_{j=2}^{n} (k_{1j} a_1 - k_{j1} a_j)$$

and, since $(\mu_1 - \mu_2)$ is positive, the constraint is

$$0 < \sum_{j=2}^{n} (k_{1j} a - k_{j1} a_j). \qquad (5)$$

Thus for this special case constraint (5) involves the rate constants and concentrations only, in contrast to (4), but again without any special relationship between k_{ij} and k_{ji}. This is found only in a two-component system, i.e., relationship (4) when $n = 2$:

$$0 < (\mu_1 - \mu_2)(k_{12} a_1 - k_{21} a_2). \qquad (6)$$

If A_1 is in excess of equilibrium, then $\mu_1 > \mu_2$ and so:

$$k_{12} a_1 > k_{21} a_2, \qquad (7)$$

$$a_1/a_2 > K_{21}. \qquad (8)$$

The relation, $k_{21}/k_{12} = K_{21}$, which would be derived by the additional use of the principle of microscopic reversibility, fits relationships (7) and (8) but only as a further special case. Even in this special case there is no direct relationship between k_{21}, k_{12}, and the values of any rate constants in the region near equilibrium.

Approximate Constraints in Systems with First-Order Kinetics

The results of the previous section show that the exact constraints allow wide variations in the relative values of rate constants. A consideration of the behaviour of systems with practical catalysts, however, indicates that the constraints are much closer in most real systems.

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

$$A_1 \rightleftharpoons A_2.$$

The rate of reaction near P is then,

$$-\frac{da_1}{dt} = \frac{da_2}{dt} = k_{12} a_1 - k_{21} a_2. \qquad (9)$$

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 those at P) at concentrations 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. Then two reactions, which may be coupled, need to be considered:

(i) The reactions of A_1 and A_2 on the catalyst, leading initially to 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 layers to bulk reactions.

Let the initial rate of any change of the catalyst be k_c, the units of which are moles times (catalyst volume)$^{-1}$ (time)$^{-1}$. If the free energy change for the reaction is ΔG_c, then the initial rate of free energy change is $\Delta G_c \cdot k_c$. If the variations in kinetics in different regions of the system are due primarily to changes in the catalyst (rather than intrinsic limitations in the kinetic equation), then Eq. (9) can be applied, at least approximately, to the initial state of the transferred catalyst at P':

$$-\left(\frac{da_1}{dt}\right)_{t=0} \approx k_{12}a_1' - k_{21}a_2'. \qquad (10)$$

Suppose a displacement of equilibrium takes place, leading to a loss of A_1. Let the free energy change of reaction (1, 2) at P' be ΔG_{12}; then the initial rate of free energy change due to reaction (1, 2) at P' is given by

$$\left(\frac{dG}{dt}\right)_{t=0} \approx \Delta G_{12}(k_{12}a_1' - k_{21}a_2'). \qquad (11)$$

As the system is adiabatic, the initial rate of change of free energy must be negative, the constraint on the hypothetical experiment is

$$\Delta G_c \cdot k_c + \Delta G_{12}(k_{12}a_1' - k_{21}a_2') \lesssim 0. \qquad (12)$$

Now k_c and $(k_{12}a_1' - k_{21}a_2')$ are both either positive or zero; ΔG_{12} is positive since the system was at equilibrium. Thus if ΔG_c is also positive, these approximations hold:

$$k_c \approx 0,$$
$$(k_{12}a_1' - k_{21}a_2') \approx 0. \qquad (13)$$

The first indicates that changes in the catalyst are negligibly slow, the second that the rate constants are related approximately to the equilibrium constant, i.e.,

$$\frac{k_{12}}{k_{21}} \approx \frac{a_2'}{a_1'} = K_{12}. \qquad (14)$$

Change in the catalyst provides the only driving force for displacing A_1 and A_2 from equilibrium. The value of ΔG_c must be negative for this to take place. Relationship (12) can then be rewritten as

$$\left(\frac{\Delta G_{12}}{-\Delta G_c}\right)\left(\frac{k_{12}a_1' - k_{21}a_2'}{k_c}\right) \lesssim 1 \qquad (15)$$

with each of the terms in parentheses in (15) being positive. Put

$$(1 - \theta)\frac{k_{12}}{k_{21}} = K_{12} = \frac{a_2'}{a_1'},$$

where θ is an unknown function of variables of the system. Then,

$$(k_{12}a_1' - k_{21}a_2') = \theta k_{12}a_1'$$

and (15) becomes

$$\theta \left(\frac{\Delta G_{12}}{-\Delta G_c}\right)\left(\frac{k_{12}a_1'}{k_c}\right) < 1. \qquad (16)$$

Now consider two extreme types of change in the catalyst:

(i) A change in the adsorbed layer on the catalyst surface as a result of the move from P to P'. In this case the mass involved, per unit volume of catalyst, is very small, so $\Delta G_{12}/(-\Delta G_c) \gg 1$. The rate of change of A_1 over the catalyst may be much faster than the catalyst change, but if it is a useful catalyst it is unlikely to be much slower, so $k_{12}a_1'/k_c \not\ll 1$. Thus for this type of change, $\theta \ll 1$.

(ii) A bulk change in this catalyst, either a phase change or composition change. The free energy change associated with this change would be expected to be of the same order of magnitude as ΔG_{12}, so $\Delta G_{12}/(-\Delta G_c)$ is roughly of the order of unity. Real catalysts are required to be both active and stable, i.e., for a substantial catalyst change, $k_{12}a_1'/k_c \gg 1$. Hence, as for (i), $\theta \ll 1$.

Similar considerations also apply to changes of an intermediate type, e.g., sintering. Thus, for all likely changes in practical catalysts, $\theta \ll 1$. It is implicit in the argument above that system volume and catalyst volume are of the same order, as in a packed catalyst reactor, but it is readily shown that if the catalyst volume is much less than the system volume the inequality $\theta \ll 1$ still applies. The reverse case, catalyst volume $>$ system volume, is unreal. Thus, for all the real cases considered,

$$k_{12}/k_{12} \approx K_{12}. \tag{17}$$

Extension to the multicomponent system considered before is straightforward. Suppose, again, the transfer of the catalyst leads to a loss in A_i; then the initial rate is given by

$$-\left(\frac{da_i}{dt}\right)_{t=0} \approx \sum_{j=1}^{n} (k_{ij}a_i' - k_{ji}a_j'). \tag{18}$$

The thermodynamic constraint is now

$$\Delta G_c k_c + \sum_{j=1}^{n} \Delta G_{ij}\,(k_{ij}a_i' - k_{ji}a_j') \lesssim 0. \tag{19}$$

If θ_j is defined by

$$(1 - \theta_j)(k_{ij}/k_{ji}) = K_{ij}$$

then (19) becomes

$$\frac{\sum_{j=1}^{n} (\Delta G_{ij} \cdot \theta_j \cdot k_{ij}a_i')}{(-\Delta G_c \cdot k_c)} \gtrsim 1. \tag{20}$$

The arguments used above for the two-component system can be modified to show that $\theta_j \ll 1$ for all j is a sufficient condition for (20) to be satisfied, but it is not a necessary condition. However, an alternative argument is the following: the initial rate of change of free energy in the catalyst is unlikely to be large enough to displace the system very far from equilibrium (for the reasons considered above), particularly when the number of reactions to be driven is large. Thus the Principle of Microscopic Reversibility can be applied, with Eq. (18), in the standard way (e.g., (*6*)) to give

$$k_{ij}/k_{ji} \approx K_{ij} \qquad \text{for all } i, j. \tag{21}$$

It is of some interest that for real catalyst systems the rate constants for any point P away from equilibrium are thus related approximately to the equilibrium constant *as if* the Principle of Microscopic Reversibility were valid at P. It suggests that the Onsager reciprocal relations may have wider applications in practical catalytic systems than has been assumed before. However, it should be emphasised that the derivation of Eq. (21) does not necessarily imply the identity of the kinetics at P and P' as indeed they may well be widely different.

CONCLUSIONS

The arguments developed above lead to the following conclusions:

1. Even when the steady state of a catalyst in a reacting system is different from that in contact with the system at equilibrium, the possible values of rate constants are constrained by thermodynamics.
2. The exact constraint on an adiabatic system is that it must move towards equilibrium, e.g., for a change at constant pressure, the free energy of the system must decrease. Within this restriction, no specific constraints exist on individual rate constants except for those in two-component systems.
3. The properties requires in a useful catalyst, i.e., high activity combined with catalyst stability, lead to the approximate constraints which would be obtained if the Principle of Microscopic Reversibility (PMR) applied away from equilibrium, i.e., $k_{ij}/k_{ji} \approx K_{ij}$. Thus the rate constants ob-

tained for practical catalytic systems should normally be expected to follow the PMR.

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