Generalized Kinetics of Chemical Change: Some Conditions for Validity of the Steady State Approximation

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Equations based on an expansion around the equilibrium state are not particularly useful for treating chemical systems of general interest to chemists. However, equations that neglect potential reversibility when systems are far from equilibrium initially do not reduce to equilibrium conditions at long times. By classifying each chemical species as reactant, product or intermediate, generalized equations can be developed to describe the time dependent behavior of any homogeneous uniform closed chemical system. Applicability of the method is illustrated by developing necessary and sufficient conditions for validity of the steady state approximation for systems in which all intermediates are free radicals.

Introduction

Any isolated chemical system ultimately approaches an equilibrium state satisfying the principles of thermodynamics. It is natural that some efforts to treat such systems have regarded every state of interest to be a perturbation on the final equilibrium state. In the limit, properties of non-equilibrium states are regarded as linear functions of the displacement from equilibrium.

It is fully appropriate to use such treatments to discuss regression of fluctuations in an equilibrium system or to examine relaxation after a deliberate disturbance like a temperature jump. However, most systems of interest to chemists cannot be treated effectively by power series expansions of perturbations from the equilibrium state.

It is also dangerous to go to the opposite extreme and to write chemical mechanisms as consequences of completely irreversible processes. Such a procedure may very easily perpetrate a violation of microscopic reversibility. It is safer to admit initially that every chemical process in a homogeneous system is potentially reversible. Those steps that go almost entirely in only one direction can then be handled by specific approximations for the system of interest.

An urgent need exists for procedures that can handle any closed homogene-
ous system arbitrarily far removed from equilibrium but can do so in ways that make smooth transitions to the equations of irreversible thermodynamics as the equilibrium state is approached. The present manuscript is not intended as a final answer to this need, but it suggests some approaches that may be useful for approximating such procedures.

**An exactly soluble example**

The general principles proposed can be illustrated by a simple example that can be solved exactly and that can sometimes be approximated further in a very useful way,

\[ R \xrightarrow{k_1} I \xrightarrow{k_2} P. \]  

(1)

For this situation the concentrations \( R + I + P = C \) where \( C \) is a constant. Then the equilibrium state in a closed thermostated system corresponds to

\[ R_{eq} = k_{-1}k_{-2}C/p, \quad I_{eq} = k_{1}k_{-2}C/p, \quad P_{eq} = k_{1}k_{2}C/p, \]  

(2)

where

\[ p = k_{1}k_{2} + k_{1}k_{-2} + k_{-1}k_{-2}. \]  

(3)

Any state of this system can be defined by two parameters \( x \) and \( y \) describing displacements from equilibrium. Let

\[ x = R - R_{eq}, \quad y = I - I_{eq}. \]  

(4)

The differential equations describing rate of change of state are then

\[ \dot{x} = -k_{1}x + k_{-1}y, \]

\[ \dot{y} = (k_{1} - k_{-2})x - (k_{-1} + k_{1} + k_{-2})y. \]  

(5)

It is convenient to define two “normal coordinates” \( \theta \) and \( \phi \) such that

\[ \theta = x + ry = \theta_{0} \exp(-k_{4}t), \]

\[ \phi = y + sx = \phi_{0} \exp(-k_{3}t). \]  

(6)

(7)

Because \( \dot{x} + ry = -k_{4}(x + ry) \) and \( \dot{y} + sx = -k_{3}(y + sx) \) for all values of \( x \) and \( y \), we can solve for \( r, s, k_{4} \) and \( k_{3} \) in terms of the rate constants for individual steps. The solutions involve roots of quadratic equations, and we have chosen signs to give minimum absolute values of \( r \) and \( s \) for the case that \( k_{4} < k_{-1} + k_{2} + k_{-2} \). Note that \( m^{2} + 4k_{-1}(k_{1} - k_{-2}) = n^{2} - 4p, \)

\[ r = \frac{-m + \sqrt{m^{2} + 4k_{-1}(k_{1} - k_{-2})}}{2(k_{1} - k_{-2})}, \]  

(8)
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\[ s = \frac{m - \sqrt{m^2 + 4k_1(k_1 - k_2)}}{2k_1}, \]  

where

\[ m = -k_1 + k_{-1} + k_2 + k_{-2}, \]  

\[ k_8 = \frac{n - \sqrt{n^2 - 4p}}{2}, \]  

\[ k_8 = \frac{n + \sqrt{n^2 - 4p}}{2}, \]  

where

\[ n = k_1 + k_{-1} + k_3 + k_{-2}. \]

These somewhat cumbersome solutions assume a particularly convenient form for the special condition

\[ k_{-1} + k_2 \gg k_1 + k_2. \]  

Then

\[ \theta \approx x + \frac{k_{-1}}{k_{-1} + k_2} y \approx x, \]  

\[ \phi \approx y - \frac{k_{-1} + k_2}{k_{-1} + k_2} x \approx y - y_{ss}, \]  

\[ k_9 \approx \frac{k_1 k_2 + k_{-1} k_{-2}}{k_{-1} + k_2}, \]  

\[ k_9 \approx \frac{k_{-1} + k_2}. \]

Note that \( k_9 \gg k_9 \). The system very rapidly relaxes to a steady state such that \( y_{ss} = (k_1 - k_{-2}) x / (k_{-1} + k_2) \). The subsequent approach to equilibrium involves a much longer time constant, the steady state being maintained during that approach. Prigogine has shown that for a system derived from this one the steady state during the final approach to equilibrium does indeed correspond to the minimum rate of entropy production. However, because entropy is a logarithmic rather than a linear function of concentration, the steady state far from equilibrium is not simply related to rate of entropy production even for this simple first order mechanism.

**A generalized model for chemical mechanisms**

The above example does little except to illustrate the well-known fact that a set of simultaneous linear differential equations is soluble in closed form.
It has been presented because the form of the approximate solution is similar to approximate solutions for nonlinear differential equations of a type often encountered in chemical mechanisms.

Any such mechanism is the consequence of a number of elementary processes, each of which takes place in a single step and involves no more than two or at most three molecules and perhaps some surrounding solvent. Rates of elementary processes obey the kinetics predicted by their molecularity, and net directions of change are determined strictly by the thermodynamic parameters of the species consumed and produced.

In any reacting chemical system, it is useful to classify species as reactants, products and intermediates depending upon their behavior under the conditions of interest. The classification may be further modified by the adjectives conditional and unequivocal.

The concentration of a conditional reactant (product) decreases (increases) monotonically during all times of interest. Such a species is an unequivocal reactant (product) if its concentration decreases (increases) at all times for each process in which it takes part. Net rates of different elementary processes may be such that a species is a conditional but not an unequivocal reactant.

A conditional intermediate is produced in some elementary processes and consumed in others. It is an unequivocal intermediate if its concentration goes through a local extremum (usually a maximum) during the time of interest. (Note that a species may be both a conditional reactant and a conditional intermediate. There may be an arbitrariness as to which it is called during the analysis of the system.)

A catalyst is a form of intermediate in terms of this analysis. The concentration of a conditional catalyst is virtually the same at the beginning and the end of a reaction. It is an unequivocal catalyst if its concentration remains constant throughout all time of interest.

Let \( R \), \( P \) and \( I \) denote the total concentrations of all specific species designated reactants, products and intermediates, respectively,

\[
R = R_a + R_b + R_c + R_d + \cdots, \quad (19)
\]

\[
P = P_e + P_f + P_g + P_h + \cdots, \quad (20)
\]

\[
I = I_1 + I_2 + I_3 + I_4 + I_5 + I_6 + \cdots. \quad (21)
\]

Let us consider a system in which \( R \) and \( P \) designations are restricted to unequivocal reactants and products and in which all elementary processes are unimolecular or bimolecular in each direction. For such a system, every conceivable elementary process can be assigned to one of five general classes designated (a) to (e) in Table I. The classification is based on change in the number of intermediate molecules. Thus intermediate molecules are created de
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 novo in \((\alpha)\) processes and consumed entirely in \((\beta)\) processes. The number of intermediate molecules does not change in \((\gamma)\) processes. In \((\delta)\) processes, the number of intermediate molecules increases autocatalytically from one to two, and the number is reduced from two to one in \((\varepsilon)\) processes.

<table>
<thead>
<tr>
<th>process</th>
<th>(dI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\alpha))</td>
<td>(R \rightleftharpoons I)</td>
</tr>
<tr>
<td>((\beta))</td>
<td>(I \rightleftharpoons P)</td>
</tr>
<tr>
<td>((\gamma))</td>
<td>(R+I \rightleftharpoons P+I)</td>
</tr>
<tr>
<td>((\delta))</td>
<td>(R+I \rightleftharpoons 2I)</td>
</tr>
<tr>
<td>((\varepsilon))</td>
<td>(2I \rightleftharpoons P+I)</td>
</tr>
</tbody>
</table>

These five general classes of elementary processes can be further divided into twenty-five specific types enumerated in Appendix A. Although such a classification is cumbersome, it is pursued as a potentially useful procedure for examining the consequences of all conceivable chemical mechanisms.

Extension to termolecular elementary processes

The classification of Table I and Appendix A assumes that all elementary processes are unimolecular or bimolecular. Some concerted termolecular elementary processes indubitably exist also. Let \((\alpha)\) be such a process,

\[
A + B + C \rightleftharpoons P + Q.
\]

(a)

This process can be handled within the framework of Appendix A by postulating the dummy intermediate \(I_x\). Process \((\alpha)\) is then the consequence of elementary bimolecular processes \((b)\) and \((c)\),

\[
A + B \rightleftharpoons I_x,
\]

(b)

\[
I_x + C \rightleftharpoons P + Q.
\]

(c)

If \(k_{-x} \gg k_x C\), then \(k_x = K_b k_{-x}\), and it is possible to model the experimental facts with no process having a higher order than two. This treatment adds another intermediate, which Clarke\(^9\) designates a flow-through reactant. By this procedure, all conceivable chemical mechanisms in homogeneous uniform closed systems can be handled within the classification scheme developed here.

Generalized kinetic equations

The model as developed can be used to obtain three general kinetic equations. In these equations, the \(f\)'s are generalized first order rate constants
having dimensions time\(^{-1}\) and defined by expressions presented in Appendix
B,
\[
\dot{R} = - f^aR + f^aP - f^\rho P + f^\nu P - f^\omega P + f^\gamma I,
\]
\[
\dot{I} = f^aR - f^\nu I - f^\omega P + f^\rho P + f^\omega I - f^\gamma I - f^\nu I + f^\nu I,
\]
\[
\dot{P} = f^aR - f^\nu P + f^\omega I - f^\gamma P + f^\nu P + f^\nu I - f^\omega P.
\]

Of course these equations are too complex to permit closed form solutions for all possible chemical mechanisms. However, they provide a basis that can be simplified in various ways for important reaction types and can then be applied usefully as approximations. Such an application is illustrated in the next section.

**Steady states during radical reactions**

A very large class of chemical reactions involve reactant and product molecules having even numbers of electrons, while intermediates are free radicals having odd numbers of electrons. Because of the rules for combination of even and odd numbers, elementary processes of forms \(A1, A3, A5, A6, B1, B2, B5, B6, D1, D2, E1\) and \(E2\) are forbidden in such a system. Elimination of these reaction types also eliminates all terms in \(f^\nu, f^\omega, f^\gamma\) from Eqs. (22~24). These eliminations greatly simplify the permissible kinetic expressions.

Radical species in such a system are formed by bond breaking or by ionization and often have such large energies of formation that they never attain concentrations of significance compared to those of species with even numbers of electrons. Net chemical change in the system can then be approximated very well by an equation of the form of (25) which involves reactants and products only,

\[
\nu_aR_a + \nu_bR_b + \cdots \Rightarrow \nu_cP_c + \nu_dP_d + \cdots.
\]

The \(\nu\)'s in such an equation need not be integers or even rational numbers, but the overall equation must balance stoichiometrically for each chemical element.

No generality is lost if reactant and product species are designated so that

\[
R_a/\nu_a \leq R_b/\nu_b \leq R_c/\nu_c, \quad P_c/\nu_c \leq P_d/\nu_d \leq P_e/\nu_e.
\]

Then the distance of the system from equilibrium can be defined by a parameter \(\theta\) such that
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\[ \theta = \left( R_a - R_a(\text{eq}) \right) / \nu_a. \]  

(27)

If Eq. (25) is indeed a valid approximation to describe chemical change in the system, then

\[ I \ll \theta \]  

(28)

at all times except perhaps for the final approach to equilibrium.

For systems in which Eq. (28) is satisfied, it is often proposed that concentrations of intermediates can be described by a steady state approximation. Such an approximation is often written as \( \dot{I} = 0 \), but a better formalism is

\[ |\dot{I}| \ll |\dot{\theta}| \]  

(29)

over any period of sufficient duration for a significant fractional change in \( \theta \). The steady state concentration, \( I_{ss} \), is a function of \( R \) and \( P \) only, and application of Eq. (23) to this system generates

\[ I_{ss} \approx \frac{f_a R + f_{-\beta} P}{f_a' + f_{\beta}}. \]  

(30*)

The asterisk (*) after the number indicates that this equation has invoked a special approximation considered in the Discussion. For any state of the system, a parameter \( \phi \) can be defined by

\[ \phi = I - I_{ss}. \]  

(31*)

The parameters \( \theta \) and \( \phi \) both approach zero as the system approaches equilibrium. It is possible to define two effective relaxation rate constants such that

\[ f_\theta = -\frac{d \ln \theta}{dt} \]  

(32)

\[ f_\phi = -\frac{d \ln |\phi|}{dt} \]  

(33*)

These \( f \)'s are not necessarily true rate constants except near the equilibrium state, but they can be defined for any other state of the system.

Two conditions must both be satisfied if the steady state approximation is to be valid throughout all times of significant net chemical change. Equation (29) is one of those conditions. The other is

\[ f_\phi \gg f_\theta. \]  

(34)

Equation (29) cannot be valid over extended times unless Eq. (28) is also valid. Then Eq. (30) requires that

\[ f_a' + f_\phi \gg f_a' + f_{-\beta}. \]  

(35*)
Thus this inequality is necessary if the steady state approximation is to be valid. It resembles Eq. (14) obtained for the simple example considered at the start of this manuscript. That equation generated (17) and (18) which satisfy the equivalent of Eq. (34). Therefore, in the simple example Eq. (14) was both necessary and sufficient to justify application of a steady state approximation.

For the more complicated generalized radical reaction, application to Eqs. (22~24) generates the approximations

\[ f'_a \approx f'_{a-} + f'_\beta, \]  
\[ f'_g \approx g'_a f'_g/\nu_a + g'_{-g} f'_{-a}/\nu_e + g'_e/\nu_a + g'_e/\nu_e. \]

In Eq. (37), \( g'_a R_a \) is the contribution of \( R_a \) terms only to the summation defining \( f'_a R \) in Appendix B. Thus all of the \( g \) terms are smaller than the corresponding \( f \) terms would be.

Because of the terms for \( \gamma \) steps in Eq. (37), Eq. (34) need not be satisfied. Therefore, Eq. (35) is necessary but is not sufficient to insure validity of the steady state approximation. As Edelson has pointed out, this lack of sufficiency is not always recognized.

**Discussion**

The development has been rather formal, and it may be useful to consider some applications to real systems:

The classification in the Appendices is complete only when the symbols \( R_a \) and \( P_a \) are reserved for unequivocal reactants and products, respectively. Conditional reactants and products are treated as intermediates. Often the kinetic treatment of a real system will be facilitated if a conditional reactant or product whose concentration changes monotonically is designated by an \( R \) or \( P \) type of symbol. Thus the mechanism of the Belousov-Zhabotinsky reaction includes the almost irreversible step

\[ 2\text{HBrO}_3 \rightarrow \text{BrO}_4^- + \text{HOB} + H^+. \]

Bromate ion, \( \text{BrO}_4^- \), is the strong oxidant whose chemical potential drives the reaction, and it should be treated as a reactant even though step (d) is of the form \( 2I_2 \rightarrow R_a + P_e \) which does not exist in Appendix A.

The above discussion of steady states was restricted to situations in which the only intermediates were free radicals with odd numbers of electrons. Steps of classes (\( \delta \)) and (\( \varepsilon \)) are impossible in such systems. However, combustion reactions generate oxygen atom intermediates having an even number of electrons. Steps like \( O + H_2 \rightarrow OH + H \) and \( H + O_2 \rightarrow OH + O \) are (\( D_2 \) ex-
amples of class (δ). Because they increase the concentrations of reactive intermediates, they contribute to the explosive potential in such systems.

Several equations have been marked with an asterisk (*). Derivation of those equations assumed equalities of the form \( f_x = (f_y I)/I \). An examination of Eqs. (19-21) and Appendix B reveals that such equalities are not strictly valid. However, we believe the expressions marked * are reasonable approximations, especially for testing whether or not Eqs. (34) and (35) are indeed gross inequalities.

We have attempted here to treat systems far from equilibrium by general procedures that evolve smoothly as equilibrium is approached. Many of the expressions obtained are only approximations, and some of the methods of derivation are not mathematically rigorous. We do not claim complete success for the procedures presented here, but we are encouraged to think they have some potential utility. We hope they will suggest still more rigorous general procedures for handling the complications associated with chemical mechanisms.

Acknowledgement

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Appendix A

---Specific Classification of Elementary Processes---

Table I indicates five general classes (α~ε) to which all unimolecular and bimolecular elementary processes belong. The specific classification presented here lists the 25 specific reaction steps that are possible if no effort is made to distinguish whether pairs like \( R_a \) and \( R_b \) or \( P_e \) and \( P_f \) are or are not chemically identical.

\[ \begin{align*}
\alpha \text{ Steps} \\
R_a \rightleftharpoons I_t, & \quad (A \cdot 1) \\
R_a \rightleftharpoons I_t + I_f, & \quad (A \cdot 2) \\
R_a + R_a \rightleftharpoons I_t, & \quad (A \cdot 3) \\
R_a + R_a \rightleftharpoons I_t + I_f, & \quad (A \cdot 4) \\
R_a \rightleftharpoons P_e + I_t, & \quad (A \cdot 5) \\
R_a + R_a \rightleftharpoons P_e + I_t, & \quad (A \cdot 6) \\
\beta \text{ Steps} \\
I_t \rightleftharpoons P_e, & \quad (B \cdot 1)
\end{align*} \]
Appendix B

---Generalized First Order Rates---

\[ f_a R = \sum_a [k_{A1} + k_{A2} + k_{A3} + 2 \sum_b (k_{A3} + k_{A4} + k_{A5}) R_b] R_a , \]

\[ f_{-a} I = \sum_c [k_{-A1} + 2k_{-A3} + \sum_f (k_{-A3} + 2k_{-A4}) I_f + \sum_e (k_{-A3} + 2k_{-A5}) P_e] I_t , \]

\[ f_a' R = \sum_a [k_{A1} + 2k_{A2} + k_{A5} + \sum_b (k_{A3} + 2k_{A4} + k_{A5}) R_b] R_a , \]

\[ f_{-a}' I = \sum_c [k_{-A1} + k_{-A3} + 2\sum_f (k_{-A3} + k_{-A4}) I_f + \sum_e (k_{-A3} + k_{-A5}) P_e] I_t , \]

\[ f_a'' R = \sum_a (k_{A5} + \sum_b k_{A6} R_b) R_a , \]
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\[ f''_\alpha P = \sum_{\epsilon} \sum_{i} (k_{\beta \epsilon} + k_{\alpha \epsilon}) I_i P_{\epsilon}, \]
\[ f_\delta I = \sum_{\tau} [k_{\beta \tau} + k_{\alpha \tau} + \sum_{a} (k_{\beta a} + k_{\alpha a}) R_a + 2 \sum_{f} (k_{\beta f} + k_{\alpha f}) I_f] I_i, \]
\[ f_{-\beta} P = \sum_{\epsilon} [k_{-\beta \epsilon} + 2k_{-\beta \epsilon} + k_{-\alpha \epsilon} + \sum_{f} (k_{-\beta f} + 2k_{-\beta f} + k_{-\alpha f}) P_f] P_{\epsilon}, \]
\[ f'_{\beta} I = \sum_{\epsilon} [k_{\beta \epsilon} + 2k_{\beta \epsilon} + \sum_{a} (k_{\beta a} + 2k_{\beta a}) R_a + \sum_{f} (k_{\beta f} + 2k_{\beta f}) I_f] I_i, \]
\[ f'_{-\beta} P = \sum_{\epsilon} [k_{-\beta \epsilon} + 2k_{-\beta \epsilon} + k_{-\alpha \epsilon} + 2 \sum_{f} (k_{-\beta f} + k_{-\beta f} + k_{-\alpha f}) P_f] P_{\epsilon}, \]
\[ f_{\beta''} R = \sum_{a} \sum_{i} (k_{\beta a} + k_{\alpha a}) I_i R_a, \]
\[ f''_{\beta} P = \sum_{\epsilon} (k_{-\beta \epsilon} + \sum_{f} k_{-\beta f} P_f) P_{\epsilon}, \]
\[ f_{\alpha} R = \sum_{a} [k_{\alpha a} + k_{\alpha a} + 2 \sum_{b} (k_{\alpha b} + k_{\alpha b}) R_a + \sum_{i} (k_{\alpha i} + k_{\alpha i}) I_i] R_a, \]
\[ f_{-\alpha} P = \sum_{\tau} [k_{-\alpha \tau} + 2k_{-\alpha \tau} + \sum_{f} k_{-\alpha f} I_f + \sum_{\epsilon} (k_{-\alpha \epsilon} + 2k_{-\alpha \epsilon}) P_f] P_{\epsilon} + \sum_{\epsilon} k_{-\alpha \epsilon} I_f, \]
\[ f'_{\alpha} R = \sum_{a} [k_{\alpha a} + 2k_{\alpha a} + \sum_{f} k_{\alpha f} I_f + \sum_{\epsilon} (k_{\alpha \epsilon} + 2k_{\alpha \epsilon}) R_a] R_a + \sum_{i} k_{\alpha i} I_i, \]
\[ f'_{-\alpha} P = \sum_{\epsilon} [k_{\alpha \epsilon} + k_{\alpha \epsilon} + \sum_{f} (k_{-\alpha f} + k_{-\alpha f}) I_f + 2 \sum_{\epsilon} (k_{\alpha \epsilon} + k_{-\alpha \epsilon}) P_f] P_{\epsilon}, \]
\[ f_{\beta} I = \sum_{\epsilon} [k_{\beta \epsilon} + \sum_{f} k_{\beta f} R_a] I_i, \]
\[ f'_{-\beta} I = \sum_{f} \sum_{\epsilon} (k_{-\beta \epsilon} + k_{-\beta \epsilon}) I_i I_f, \]
\[ f_{\alpha} I = \sum_{f} \sum_{\epsilon} k_{\alpha f} R_a I_i, \]
\[ f'_{-\epsilon} I = \sum_{f} \sum_{\epsilon} (k_{\beta f} + k_{\alpha f}) I_i I_f, \]
\[ f_{-\epsilon} I = \sum_{f} (k_{\beta \epsilon} + \sum_{\epsilon} k_{\beta \epsilon} P_f) I_k, \]
\[ f'_{\epsilon} I = \sum_{f} \sum_{\epsilon} k_{\beta f} I_i I_f, \]
\[ f'_{-\epsilon} P = \sum_{\epsilon} k_{-\beta} I_k P_{\epsilon}. \]

References

2) B. L. Clarke, J. Chem. Phys. 64 (1976), 4165.
Discussion

N. G. van Kampen: Suppose I have a reaction involving a number of intermediaries, which, are eaten up rapidly, in such a way that an overall rate equation of third or higher order emerges. Is it possible to still see the effect of the intermediaries on the fluctuations, or would that effect tend to zero when the reaction rates for the disappearance of intermediaries become infinite? In fact it might also be very big since there are so few intermediary molecules.

R. M. Noyes: As reactivities of intermediates increase, their absolute concentrations become smaller. Reactions of intermediates are stochastic rather than strictly deterministic processes. I would expect that effects of statistical fluctuations would be relatively more important in a system with very small concentrations of very reactive intermediates.

D. Ruelle: Take a chemical reaction consisting of elementary steps as you describe, with coefficients satisfying reasonable restrictions, but not necessarily being the coefficients for a real system. You believe that no chaotic or turbulent behavior will then appear. I believe the contrary, but this obviously has to be proved. I think that is a good problem.

R. M. Noyes: Any satisfactory model of a chemical system should satisfy the following five restrictions:

1. All chemical change is the sum of the effects of reversible elementary processes involving one, two or three molecules in each direction.

2. The rate of an elementary process in any direction is proportional to the product of the concentrations of appropriate molecules raised to appropriate integral powers.

3. All rate coefficients and all concentrations are real and positive.

4. The model must predict that a closed system will eventually approach an equilibrium state such that the forward and reverse rates of each elementary process are equal to each other.

5. If the model is applied to an open system, molecules are introduced at rates independent of time or of concentration in the system, and molecules are removed from the system at rates proportional to their concentrations (the restriction of time independence need not apply to all systems, but chaotic behavior might be possible if this restriction were removed).

These are powerful restrictions. My personal prejudice is that it will be impossible to satisfy them with a model generating chaotic behavior. If Professor Ruelle can prove me wrong, I shall have served my purpose as a devil’s advocate.