A Thermodynamic-Probabilistic Analysis of Diverse Homogeneous Stoichiometric Chemical Reactions

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Research into the nature of atom-migration dynamics has demonstrated a linear relationship between the driving force for these processes and the probability for forward as opposed to reverse reaction. An assumption that this observation would prove to be just as valid for stoichiometric chemical reactions would allow a thermodynamic-probabilistic model to be developed. Using this linear approach, the resulting probabilistic reaction path developed was correlated with empirical kinetic data. The exceedingly high correlation between the probabilistic path and the empirical data over the entire range of experimental observations constitutes definitive evidence that stoichiometric chemical reactions are themselves purely stochastic processes and, moreover, that the linear assumption is in fact valid.

Introduction

The analytical description of the reaction path transversed by a chemical process proceeding from initiation to equilibrium should be a rather straightforward affair, but this has been not the case. In fact there is a surfeit of such descriptions, often mutually exclusive. There is the mechanistic approach and the thermodynamic approach, and these can be either deterministic or probabilistic as shown below.

| Mechanistic | Mechanistic |
| Deterministic | Probabilistic |
| Thermodynamic | Thermodynamic |
| Deterministic | Probabilistic |

The mechanistic and thermodynamic approaches are easily distinguished: one investigates the interactions between reacting particles and the other the energy exchange between reaction states, respectively. Either approach can be deterministic or probabilistic.

According to the deterministic approach, the properties of the system immediately prior to the present state determine the properties of the present state and the properties of the present state determine the properties of the state immediately following the present state. Because of the assumed predetermination, an analytical expression can describe the progression of states.

In contrast, according to the probabilistic approach, the properties of the system immediately prior to the present state do not determine the properties of the present state and the present state does not determine the properties of the state immediately following the present state. Because there is no assumed predetermination, no analytical expression can describe the progression of states. The reaction can go off in any direction it desires. The only relevant consideration is that certain paths are highly probable and others are not. While it is expected that the reaction will follow the most probable path, this is not necessarily so.

The actual formalism chosen depending on the proclivity of the investigator and each approach has its proponents. Although the proponents of the Deterministic and Probabilistic approaches have found some common ground when the most probable path is the deterministic path, this is not the situation for the proponents of the Mechanistic versus the Thermodynamic approach. They are fundamentally antagonistic and rarely, if ever, share the same podium, much in the same manner as the old dispute between the corpuscular and waveform proponents in optics.

To better understand these differences, consider the homogeneous stoichiometric chemical reaction

\[ \Sigma[v_m M_m]_{T,V} = 0 \]  

proceeding in a closed system at fixed temperature \( T \) and volume \( V \) from reaction initiation to reaction equilibrium, where \( v_m \) is the stoichiometric coefficient and \( M_m \) is the molecular weight of reacting component \( m \), with \( v_m < 0 \) for reactants. The process proceeds in accordance with reaction stoichiometry.

Fundamentally, chemical kinetics as a formal study began with the Empirical Rate Equations some century and a half ago. This formalism constitutes the classical Mechanistic-Deterministic description of reaction 1 from reaction initiation to reaction equilibrium and is based on mass action. According to the classical Kinetic Mass Action Law, the reaction rate or velocity \( v \) for reaction 1 is the transformation rate for each chemical species expressed as concentrations, with this rate dependent on the concentration of each particular species in the reaction volume:

\[ v = k_f \Pi[R_m]^{v_m} - k_r \Pi[P_m]^{v_m} \]  

where \( k_f \) and \( k_r \) are the forward and reverse reaction rate constants, respectively, and \( [R_m] \) and \( [P_m] \) designate the concentration of each reactant and product, respectively. Evidently, the reverse reaction rate is zero at reaction initiation because no products are present in the reaction volume. This approach is purely deterministic in that the values of the constants and variables of eq 2 determine the future values of...
Homogeneous Stoichiometric Chemical Reactions

Objective

The objective of this study is to simulate actual chemical reaction paths for chemical reactions between reaction initiation and equilibrium using a probabilistic analysis. Essentially any transformation between a reaction state \( i \) and a subsequent reaction state \( i \pm 1 \) can either be in the forward direction toward equilibrium \( i \rightarrow i + 1 \) or in the reverse direction backward toward reaction initiation \( i - 1 \leftarrow i \). Once the transformation probability for each state is delineated, the succession of states, each described by its \( \mathcal{A}_i \), can be compared to the \( \mathcal{A}_i \) calculated from empirical chemical reaction data.

In this regard, the probabilistic reaction path and the empirical chemical data will be compared for several chemical processes whose reaction kinetics has been reported in the literature. If the probabilistic paths do coincide with the experimental data, this coincidence will constitute \textit{prima facie} evidence that chemical reactions are themselves purely stochastic processes amenable to a probabilistic analysis despite the inherent mechanistic complexities that distinguish one reaction from another.
State Variables

This probabilistic analysis requires that certain essentially self-evident assumptions be made that fully agree with the ordinary conditions under which chemical reaction are observed:

(1) The isothermal, isochoric reacting system is homogeneous in that all reacting species are uniformly distributed in a single fluid phase.

(2) The reacting system is closed in that there is no mass transfer between the reacting system and its surroundings.

(3) Transformation of one state to another involves transformations between reactants and products in a fixed stoichiometric ratio.

Although irreversible thermodynamics teaches that the progress of a chemical reaction can be fully described in terms of the intensive variables \( T \), \( P \), \( V \), and \( \omega \), the difficulty with these intensive variables is that they are classically defined only for states at equilibrium. It is immediately evident that \( V \) as a physical constant can describe a nonequilibrium system as easily as an equilibrium system. The principal difficulties arise with \( T \) and \( P \), for they are not necessarily uniform across a reacting system at any temporal state, as required to define a unique \( \omega \) for any state \( i \) in a succession of states \( i \to i + 1 \) between reaction initiation \( i_0 \) and equilibrium \( i_{eq} \). This obstacle can be overcome, however, by modifying the postulate of local equilibrium derived from Landsberg’s so-called Fourth Law of Thermodynamics.

Local equilibrium is essentially a spatial postulate for open systems, as it is concerned with contiguous time-invariant equilibrium cells. That is, the cells are temporally coincident but spatially distinct: the steady-state scenario. An example is an open flow-tube reaction with reactants uniformly entering at one end with reactants and products uniformly exiting the other end. The tube can be divided into adjacent imaginary cells with each of the invariant cells examined at stations along the tube. These cells exist simultaneously but are distinct spatially.

What is required for the homogeneous closed system, however, the conditions pertinent to this study, is a postulate of temporal equilibrium that teaches that an irreversible process can comprise a succession of homogeneous equilibrium cells of short duration, with each occupying the entire system. In this case the cells are temporally distinct but spatially coincident: a reaction in a closed reaction chamber of fixed volume.

In theory, the minimum period \( \tau_{\phi} \) required for the homogeneous equilibrium cells to occupy the entire system is simply

\[
\tau_{\phi} \propto V^{1/3}t_{\phi}^{1/3},
\]

where \( V \) is the volume of the reacting cell and \( v_{\phi} = \phi V^{1/3} \), for which \( \phi \) is the diffusion coefficient. However, reactions do not continually initiate at each state and then proceed from a single point in the reaction cell across to the cell walls a distance \( V^{1/3} \) to equilibrate the cell but rather from many points scattered throughout the cell. Ostensibly, a sufficient period is thereby available to regain uniformity across the reaction cell at each reaction state \( i \): essentially temporal equilibrium. This is generally accepted by kineticists, as it is required for absolute rate theory. Happily, this position is strongly supported by Garcia-Colin and Bhalekar who demonstrated that the nonequilibrium contributions to absolute \( T \) and \( P \) cancel. There is no such thing as nonequilibrium temperature (the adjective applies to systems, not to state parameters).

In practice, temporal equilibrium can be sufficiently approached that both temperature and pressure differences across the reacting cell essentially vanish: \( \delta T_{i} \to 0 \) and \( \delta P_{i} \to 0 \). Hence, for practical purposes both \( T_{i} \) and \( P_{i} \) have unique instantaneous values at any state \( i \), permitting \( \omega_{i} \) to be as fully definable as in a simple equilibrium system. Accordingly, the path followed by a chemical reaction in a closed homogeneous system from reaction initiation to equilibrium can be described unambiguously by determining the value of \( \omega_{i} \) at each state \( i \) of the system.

Reaction Parameters

To describe the progress of a chemical reaction as a system of transformations between states, it is necessary to first identify each state uniquely in terms of the reacting particles present. Although many such state identifiers are possible, such as simply the fraction of reactant particles present relative to the initial number or perhaps the mole fraction, instead a scheme consistent with the formalism of chemical thermodynamics will be chosen in which the identifiers for both the initial and equilibrium states each have values that can be directly related to thermodynamic functions.

Although a chemical reaction physically proceeds stepwise in terms of the change in the number of reacting particles \( n_{m} \to n_{m,eq} \), where \( i \) indicates the temporal state of the system, the influence of each component on the reacting system is represented by its thermodynamic activity \( a_{m} \). The activity is a measure of the chemical reactivity of component \( n_{m} \). Hence at any state \( i \) of the system each component \( m \) has a specific activity \( a_{m} \). Moreover, the products of the activities of the reacting components at state \( i \) can be used to describe state \( i \) by the relationship

\[
Q_{i} = \Pi(a_{m})^{y_{m}}
\]

where \( Q_{i} \) is identified as the activity ratio at state \( i \).

To represent \( Q_{i} \) at any state \( i \) in terms of the number of particles present requires that several relationships be established, first between the number of particles \( n_{m} \) and the concentration \( c_{m} \) of component \( m \) at state \( i \), and thence between \( c_{m} \) and \( a_{m} \).

The first step is straightforward with \( n_{m} = c_{m}VN \), where \( N \) is Avogadro’s number. Although \( c_{m} \) and \( a_{m} \) are related by \( c_{m} = a_{m}y_{m} \) at state \( i \) where \( y_{m} \) is the activity coefficient of component \( m \), unfortunately \( y_{m} \) is a complex function of component concentration \( c_{m} \).

Fortunately, homogeneous stoichiometric chemical reactions are generally investigated by kineticists under conditions of sufficient dilution that \( y_{m} \to 1 \) and therefore \( c_{m} \to a_{m} \), permitting \( Q_{i} \) to be approximated by the instantaneous number of each of the reacting particles at state \( i \).

\[
Q_{i} = \Pi[(n_{m})^{y_{m}}(VN)^{y_{m}}]
\]

However, as defined, \( Q_{i} \) requires that the instantaneous number of all reacting particles \( n_{m} \) be known at state \( i \). This complication can be remedied, however, by resorting to the reaction advancement term \( \xi_{i} \) conveniently defined as

\[
\xi_{i} = (n_{m} - n_{m0})(v_{m})
\]

where \( n_{m0} \) is the number of particles \( m \) present at reaction initiation. Substituting for \( n_{m0} \) in eq 5 yields

\[
Q_{i} = \Pi[(n_{m} + \xi_{i})^{y_{m}}(VN)^{y_{m}}]
\]
relating the system variable \( Q_i \) to a single concentration term \( \xi_{0,i} \).

As defined, \( Q_i \) has a unique state value of \( Q_i = Q_{eq} \) at reaction initiation and \( Q_i = Q_{eq} \) at reaction equilibrium. By definition \( Q_0 = 0 \) and \( Q_{eq} = K \), respectively, with \( K \) the thermodynamic equilibrium constant defined from eq 7c as

\[
K = \Pi \left( n_m + n_{eq} \right)^{-n(VN)^{n-1}} \tag{8}
\]

Taking the ratio of eqs 7c to 8 permits a thermodynamic extent-of-reaction term \( \xi_{0,i} \) to be defined as

\[
\xi_{0,i} = Q_i/K \tag{9}
\]

Accordingly, reaction initiation and reaction equilibrium are the uniquely defined states \( \xi_{0,i} = 0 \) and \( \xi_{0,eq} = 1 \), respectively.\(^{26}\)

**Probabilistic Modeling**

Although chemical reaction 1 is perceived macroscopically to proceed unidirectionally, this is a continuum perception that does not exclude both forward and reverse state transformations occurring on a particulate level, prohibiting only time-reversal symmetry. However, the number of forward steps must clearly outweigh the number of reverse steps overall because the reaction is perceived to progress away from its specific initiation state \( \xi_{0,i} = 0 \) toward a specific equilibrium state \( \xi_{0,eq} = 1 \). Consequently, the probability of any state transformation toward equilibrium must be greater than the probability of any state transformation away from equilibrium.

Clearly, if the reaction state \( i \) immediately following reaction initiation is specified by the thermodynamic extent-of-reaction \( \xi_{0,i} \), then a transformation toward equilibrium can be defined as the forward reaction \( \xi_{0,i} \rightarrow \xi_{0,eq} \), and a transformation away from equilibrium can be defined as the reverse reaction \( \xi_{0,eq} \rightarrow \xi_{0,eq} \).

According to this probabilistic analysis \( p_{i,j} \) is defined as the probability of reaction transformation from state \( \xi_{0,i} \) forward to state \( \xi_{0,j} \), and \( p_{j,i} \) is the probability of transformation from state \( \xi_{0,j} \) backward to state \( \xi_{0,i} \). Because any state \( \xi_{0,i} \) prior to the initiation state \( \xi_{0,i} \) by definition cannot occur, any reverse transformation from \( \xi_{0,i} \) is precluded, and therefore \( p_{0,0} = 0 \), which indicates that the transformation probability \( p_{i,j} \) clearly depends on the state of the system \( \xi_{0,i} \). Accordingly, the forward or reverse reaction probability is dependent on the state of the system \( i \).

Research into the nature of atom-migration dynamics has demonstrated a probable linear relationship between \( p_{i,j} \) and \( \xi_{0,i} \) under various circumstances.\(^{27}\) Using this simple but rather tenuous support, a verifiable assumption of linearity will be made. It must be understood, however, that this assumed linear relationship between probabilities and reaction state is totally divorced from the linear expression (4) assumed in irreversible thermodynamics between the Mass Action velocity \( v_i \) and the chemical affinity \( \xi_{0,i} \).\(^{28}\) Accordingly,

\[
p_{i,j} \propto \xi_{0,i} \tag{10}
\]

This linear proportionality is the crucial relationship of this stochastic analysis, and its veracity is essential to the validity of this probabilistic approach.

Because the reaction can only proceed in single steps (transforming from one defined state to only the previous or successive state), only transformations \( i - 1 \leftarrow i \) or \( i \rightarrow i + 1 \) from state \( i \) are allowed. Hence, for the reverse reaction

\[
p_{i,j-1} = \frac{1}{2}
\]

and for the forward reaction

\[
p_{i,j+1} = \frac{1}{2}
\]

According to this stochastic model, following reaction initiation the probability of transformation in the direction shown
between initiation $\zeta_{Q_0}$ (no products present) and completion $\zeta_{Q_f}$ (no reactants present) is always toward equilibrium. Beyond equilibrium the probability for reverse reaction becomes progressively greater than for forward reaction and consequently the probability of ever attaining completion becomes essentially nil. Note, however, from Figure 1 that according to this probabilistic approach the equilibrium state is always within a range rather than a discrete value. From the values of $P_{i+1}$ and $\zeta_{Q_i}$ identified at reaction initiation (eq 14b) and at reaction equilibrium (eqs 16a and 16b) the following equalities follow.

For the backward reaction

$$p_{i,i-1} = \frac{1}{2} \zeta_{Q_i}$$

and consequently from eq 13

$$p_{i,i+1} = 1 - \frac{1}{2} \zeta_{Q_i}$$

for the forward reaction. Equations 18a and 18b describe the progress of chemical reaction 1 from reaction initiation $\zeta_{Q_0}$ to reaction equilibrium $\zeta_{Q_{eq}}$ in terms of this stochastic model, the implications of which are addressed in detail in the following section.

**Statistical Analysis**

For stoichiometric chemical reactions to be amenable to this probabilistic analysis requires that the reaction path followed conform to certain conditions.

1. The process must be discontinuous in that it proceeds in discrete steps $d_i$ that can be identified with specific states $\zeta_{Q_i}$.
2. The process must be periodic in that the number of reaction steps $\Delta t_{i,n}$ between steps $d_i$ and $d_{i+n}$ required to return to any state $\zeta_{Q_i}$ from any other state $\zeta_{Q_{eq}}$ is a multiple of some positive integer.
3. The process must be irreducible in that the probabilities $p_{i+1}$ associated with the transformation of any present state $\zeta_{Q_i}$ to any future state $\zeta_{Q_{eq}}$ must be independent of any past state $\zeta_{Q_{eq}}$ or $\zeta_{Q_{eq}}$.

Several chemical reactions will be described in terms of an array of probabilistic $(\zeta_i, d_i)$ coordinates and these will then be compared to empirical $(\zeta_i, t_i)$ data taken from the literature. Fortunately, the chemical affinity $\zeta_i$ can be equated to the thermodynamic extent-of-reaction term $\zeta_i$ by the classical Gibbs relationship

$$\zeta_i = -RT \ln(\zeta_i)$$

allowing the rate of probabilistic affinity decay to be charted over the range of observations. Because the stochastic model depends on a procedure rather than on an analytical equation, the required analysis must be described by an algorithm. The results of this procedure are shown in Table 1 for reaction 1 and illustrated schematically in Figure 1 as purely probabilistic curves.

Column 1 lists the reaction steps. For an actual reaction the steps would number perhaps three times the running time of the experiment in seconds. Column 2 lists the output of a random number generator for random numbers $n$ where $0 \leq n \leq 1$. Column 3 lists the probability $p_{i+1}$ for the next step of the reaction moving either forward or backward. Column 4 is the extent of reaction for each step calculated from eq 18b using the linearity assumption. Column 5 is the chemical affinity calculated from the extent of reaction.

The purpose of this exercise is to compare the affinity—step data $(\zeta_i, d_i)$ generated by the probabilistic analysis with the empirical affinity—time data $(\zeta_i, t_i)$ found in the literature. As the probabilistic analysis proceeds, the probabilistic chemical affinity tends to decay. Hence between any steps $\Delta t_i$ there is an affinity difference $\Delta \zeta_i$. Likewise, as an actual chemical reaction proceeds, the empirical chemical affinity decays. Hence between any time interval $\Delta t_i$ there is an affinity decay $\Delta \zeta_i$. To correlate the probabilistic affinity difference with the empirical affinity decay, it would necessitate adjusting the probabilistic affinity difference $\Delta \zeta_i$. This procedure is accomplished simply by introducing a fixed term $\Delta \zeta_0$, which is the probability difference $\Delta p_{i+1}$ between succeeding steps. The term $\Delta \zeta_0$ is adjusted until the probabilistic affinity agrees as closely as possible with the adjusted $\zeta_i$ according to eq 18b and hence $\Delta \zeta_i$ according to eq 19. Were this accomplished,
then \( \Delta d_i \) would presumably equal \( \Delta t_i \) and the data correlated. For each reaction, \( \Delta p \) has a single fixed value.

The affinity—step data \((\xi_i, d_i)\) are generated by this probabilistic analysis. From eq 18b the thermodynamic extent of reaction is zero at reaction initiation, as shown in Table 1. From eq 19 the affinity is infinite. For step 1 the value of the random number generator is compared to the probability. If the random number is smaller than the probability, the probability is decreased by the fixed value \( \Delta p \). In contrast, if the random number is larger than the probability, the probability is increased by a fixed value \( \Delta p \).

With the probability value 1.000 and the random number 0.802, the probability decreases to 0.985, in this instance by an arbitrary amount \( \Delta p \). Chosen simply to illustrate the approach to equilibrium as the number of steps approach 100. This procedure is in accordance with expression 17 that the reaction always has a greater tendency toward equilibrium than away from it. At step 2 the random number 0.157 is less than the probability 0.985 of step 1, and therefore the probability decreases again to 0.970 with the extent of reaction calculated from eq 18b and the affinity from eq 19. By step 29 the probability value of 0.685 indicates roughly a two-thirds possibility that the next step will be toward equilibrium. By step 71 the probability is just over one-half, indicating that the possibility of retrograde steps is almost equal to the possibility of forward steps. Hence this probabilistic analysis is in agreement with eqs 18a and 18b. These probabilistic data are then correlated with the empirical affinity data using solely \( \Delta p \).

**Empirical Verification**

The chemical affinity \( \xi_i \) not only unambiguously identifies each reaction step \( d_i \) from reaction initiation to equilibrium but also represents the actual thermodynamic driving force for chemical reactions. Accordingly, the decay rate of the chemical affinity is the most significant metric in examining the progress of chemical reactions, particularly in regard to empirical verification of the stochastic approach described herein.

For verification, the probabilistic extents-of-reaction \( \xi_0 \), are calculated from eq 18b and the experimental extents-of-reaction \( \xi_0 \), are calculated from eq 9 for each reaction examined. The probabilistic and empirical affinities \( \xi_i \) are then calculated from eq 10 and compared.

To accommodate this procedure, a Microsoft Excel 98 spreadsheet with its built-in random number generator was used to calculate the probabilistic \((\xi_i, d_i)\) data and plot the resultant curves. Six probability curves were generated for each experiment, differing only by the random numbers generated. These were compared with the experimental \((\xi_i, t_i)\) data entered onto the Excel spreadsheet and superimposed on the curves. The value of \( \Delta p \) was fixed for the six probability curves of each experiment and used to correlate the probabilistic data with the empirical. The chemical reactions examined were chosen to represent a wide selection of mechanisms, with reaction orders ranging from first to third. The number of steps \( d_i \) for each experiment was between 1000 and 4000.

The isomerization of 2-methylmethylene cyclopropane to ethylidenecyclopropane

This involves an intermediate activated complex (‡) in equilibrium with the reactants

\[
\text{C}_6\text{H}_5\text{CH} = \text{CH}_2 + \text{I}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}I \text{CH}_2 \text{I}
\]  

(22)

Six simulations of the affinity decay for this isomerization process are shown in Figure 2 for \( \Delta p = 6.7 \times 10^{-3} \) and compared with the experimental chemical affinities.\(^{29}\)

The reaction of styrene with iodine in carbon tetrachloride to form styrene diiodide is quite complex.

![Figure 2](image1.png)  
**Figure 2.** Affinity decay for the reaction of styrene with iodine in CCl$_4$.

![Figure 3](image2.png)  
**Figure 3.** Affinity decay for the isomerization of ethylidenecyclopropane.

The process apparently involves both a free-radical chain mechanism and a concurring nonchain reaction that has a first-order dependency on iodine concentration and a $3/2$-order dependency on styrene concentration.\(^{30}\) Six simulations of the affinity decay for this iodination process are shown in Figure 3.

\[
\text{C}_6\text{H}_5\text{CH} = \text{CH}_2 + \text{I}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}I \text{CH}_2 \text{I}
\]  

(22)
Figure 4. Affinity decay for the bromination of platinic ammonia chloride in KCl solution.

Figure 5. Affinity decay for the formation of acetone cyanohydrin.

The reaction proceeds in a simple stepwise fashion:

$$\text{Fe}^{2+} + 3(\text{C}_{10}\text{H}_6\text{N}_2) \rightarrow \text{Fe}(\text{C}_{10}\text{H}_6\text{N}_2)_3^{2+}$$ (26)

The reaction mechanism involves a free-radical chain reaction, with the postulated reaction rate depending on the equilibrium constant for iodine, where M is any molecule present.34

$$\text{I}_2 + \text{M} \leftrightarrow 2\text{I} + \text{M}$$ (29a)

$$\text{i-BuH} + \text{I} \rightarrow \text{t-Bu} + \text{HI}$$ (29b)

$$\text{t-Bu} + \text{I}_2 \rightarrow \text{t-Bu} + \text{I}$$ (29c)

$$\text{t-Bu} \rightarrow \text{i-Bu} + \text{HI}$$ (29d)

It is immediately evident that the overall reaction rate depends on the concentration of I\(_2\) and HI molecules. Six simulations of the affinity decay for this dehydrogenation process are shown in Figure 7 for \(\Delta_P = 5.0 \times 10^{-4}\) and compared with the experimental chemical affinities.

The dehydrogenation of isobutane by iodine vapor at 333 K is exceedingly complex.

$$\text{i-CH}_4 + \text{I}_2 \rightarrow \text{i-CH}_4 + 2\text{HI}$$ (28)

Discussion

According to the classical approach, the forward reaction rate \(v_1\) is proportional to the concentration of the reactants of reaction 1 and consequently is a maximum at reaction initiation and decreases as the reaction proceeds. Likewise, the reverse reaction velocity \(v_2\) is proportional to the concentration of products and is zero at reaction initiation and increases as the reaction proceeds. The value of the overall reaction velocity \(v_o\) is simply \(v_o = v_1 + v_2\), its value depending on the state of the system between reaction initiation and equilibrium. This formalism may superficially resemble the stochastic relationship between the probability for forward reaction \(P_{eq,eq+1}\), which is unity at reaction initiation and decreases as the reaction proceeds, and the probability for reverse reaction \(P_{eq,eq-1}\), which is zero at reaction initiation and increases as the reaction proceeds. However, the sum of these probabilities is always unity independently of the state of the system.

The only gap in this stochastic procedure is the lack of a relationship between the probability \(P_{eq,eq+1}\) and the extent-of-reaction \(\xi_0\). This gap, however, was bridged by the assumption of linearity, an assumption that has been demonstrated to be valid. The term \(\Delta_P\) represents the single degree of freedom.
generate only pseudorandom numbers that can impose patterns on resultant probabilities. Haggsrom et al. argue that such patterns can significantly affect reaction paths.35 This problem was somewhat alleviated in the present study by alternating between the generated pseudorandom number $n_i$ and number $1 - n_i$ each time the random number generator was accessed, where, of course, $0 \leq n_i \leq 1$. The resultant probabilistic paths are shown in Figure 8 for the bromination of platinic ammonia chloride in KCl solution, as previously discussed. No preferred paths appeared to be discernible.

### Conclusion

The description of homogeneous stoichiometric chemical processes using the probabilistic model matches experimental results exceedingly well, confirming the validity of the assumptions of a linear proportionality between reaction probability and extent of reaction. Accordingly, stoichiometric chemical reactions can be understood as purely stochastic processes amenable to a probabilistic analysis.

### References and Notes

(27) Ehrenfest, P.; Ehrenfest, T. *Phys. Z.* 1907, 8, 311.