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A Thermodynamic-Probabilistic Analysis of Diverse Homogeneous Stoichiometric Chemical Reactions

Moishe Garfinkle†

Department of Materials Engineering, Drexel University, Philadelphia, Pennsylvania 19104

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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 Deterministic	Mechanistic Probabilistic
Thermodynamic Deterministic	Thermodynamic 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

$$\Sigma[\nu_m M_m]_{T,V} = 0 \tag{1}$$

proceeding in a closed system at fixed temperature T and volume V from reaction initiation to reaction equilibrium, where ν_m is the stoichiometric coefficient and M_m is the molecular weight of reacting component m, with $\nu_m < 0$ 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.[1] This formalism constitutes the classical Mechanistic-Deterministic description of reaction 1 from reaction initiation to 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:

$$v = k_\mathrm{f}\Pi[\mathrm{R}_m]^{\nu_m} - k_\mathrm{r}\Pi[\mathrm{P}_m]^{\nu_m} \tag{2}$$

where k_f and k_r are the forward and reverse reaction rate constants, respectively, and $[\mathrm{R}_m]$ and $[\mathrm{P}_m]$ 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

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† E-mail: garfinkm@mail.drexel.edu.

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the reaction velocity as reaction 1 proceeds, indicating a singular reaction path from initiation to equilibrium. Because the values of the reaction rate constants k_f and k_r depend on the reaction mechanism for all but the very simplest reactions, Kinetic Mass Action constitutes a purely mechanistic approach.

In contrast to the Mechanistic-Deterministic description, a Mechanistic-Probabilistic description of a chemical reaction results in a myriad of reaction paths inasmuch as the paths are described as a succession of stochastic reaction steps. This approach is based on the general *Master Equation* formalism, which, when derived for chain processes is known as the *Kolmogorov forward differential equation*[2] and was formulated to investigate the rate of return to equilibrium of a perturbed system originally at equilibrium.[3]

For example, consider as a specific case of reaction 1: the reversible transformation A ↔ B for which the concentration of reactant [A] at reaction initiation ($t = 0$) is $[A]_0$ and product $[B]_0 = 0$, generally the condition under which kineticists observe chemical reactions. Essentially, the probability $p_{[A]_n,[A]_{n+1}}$ that the reactant concentration at state n transforms to the concentration at state $n + 1$: $[A]_n \rightarrow [A]_{n+1}$, depends solely on the concentration $[A]_n$, not on any prior concentration $[A]_{n-1}$. Accordingly, $p_{[A]_n,[A]_{n+1}} \propto [A]_n$ with the condition that as $[A]_n \rightarrow [A]_{eq}$ the probability $p_{[A]_n,[A]_{n+1}} \rightarrow 0$. Hence any perturbation from equilibrium requires an infinity period to return to equilibrium inasmuch as $p_{[A]_{eq-1},[A]_{eq}} = 0$, as in the Mass Action approach.

Compare now the deterministic Mass Action approach to the probabilistic Master Equation approach. Integrating deterministic eq 2 and solving for concentration of $[A]_t$ at time t yields

$$[A]_t = [k_f[A]_0/(k_f + k_r)][1 - e^{-(k_f+k_r)t}] \qquad (3a)$$

Now contrast eq 3a with the expected concentration of reactant $\{A\}_t$ at time t derived from the stochastic approach, which is expressed in eq 3b:

$$\{A\}_t = [k_f[A]_0/(k_f + k_r)][1 - e^{-(k_f+k_r)t}] \qquad (3b)$$

The similarity is not too surprising for this very simple reaction considering that the probability for reactant A to transform to product B depends on the concentration of reactant [A] and product [B], exactly as does the reaction velocity for the deterministic Mass Action approach.[4] For highly complex reactions, however, this Mechanistic-Probabilistic approach becomes exceedingly difficult.[5,6] Essentially, the Kolmogorov approach cannot be rigorously tested for complex reactions.[7]

The thermodynamics of irreversible processes remains the classical example of the Thermodynamic-Deterministic approach to the study of chemical reactions. According to the Clausius inequality irreversible processes are characterized by entropy production $dS > dQ/T$ greater than that for reversible processes $dS = dQ/T$. For equilibrium of course $dS = 0$. Hence for a chemical reaction proceeding irreversibly toward equilibrium $dS/dt \rightarrow 0$. The rate of this process dS/dt, however, is not directly discernible, although the linear phenomenological equation had offered hope in this regard.

The Linear Phenomenological Equation is an irreversible thermodynamic formalism that had been devised to describe transport phenomena such as electrical conductivity, thermal conductivity, and atomic diffusion.[8,9] According to this theory, a flux (flow) term and a force (driving) term for transport phenomena are assumed to be linearly related. For example, for electric conduction the current is the flow and the potential gradient the driving force and similarly for thermal conduction heat is the flow and the temperature gradient the force. The unqualified success of this linear assumption is universally recognized.[10,11] With the success of reciprocity, the Linear Phenomenological Equation is fully established as the basis of irreversible thermodynamics of transport phenomena.[12]

When the Linear Phenomenological Equation is applied to chemical reactions, however, difficulties arise: identifying the flux and force terms. Logically, the flux term can be identified with the reaction velocity v and the force term with the driving force or chemical affinity $\mathcal{A}_i$, a function of state introduced by De Donder to quantify the force driving a chemical reaction.[13,14]

$$v_i \propto \mathcal{A}_i \qquad (4)$$

It is precisely in the case of homogeneous chemical reactions, however, that the Linear Phenomenological Equation has proven a failure.[15] In fact, Manes et al.[16] cast doubt on the validity of the linear equation even on close approach to chemical equilibrium. What is straightforward as far as transport phenomena is concerned is not so in the case of closed chemical reactions. In transport phenomena the flux and force terms have spatial coordinates. In chemical reactions they do not. Hence there is no independent means of describing the time-dependency of dS/dt. The true value of this Thermodynamic-Deterministic approach, however, is in validating thermodynamic variables as time-dependent quantities although originally derived for reversible processes.[17−19]

Three of the four possible formalisms involved in describing the reaction path of chemical reactions have been considered. As far as the literature is concerned, no Thermodynamic-Probabilistic formalism has been developed to describe the progress of a chemical reaction along some probabilistic reaction path. To determine whether such formalism is possible and the extent of its validity is the subject of this study.

Rather than relying on the chemical concentration $[A]_i$ to distinguish the states of a reacting system, De Donder's chemical affinity $\mathcal{A}_i$ will admirably fulfill this role. It is furthermore proposed that in a closed homogeneous reacting system comprising a temporal succession of states i between reaction initiation and equilibrium the reacting system can be fully characterized at any such state i by the intensive variables T_i, P_i, V_i, and $\mathcal{A}_i$.

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 i, 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 *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_i, P_i, V_i, and $\mathcal{A}_i$, the difficulty with these intensive variables is that they are classically defined only for states at equilibrium. It is immediately evident that V_i as a physical constant can describe a nonequilibrium system as easily as an equilibrium system. The principal difficulties arise with T_i and P_i, for they are not necessarily uniform across a reacting system at any temporal state, as required to define a unique $\mathcal{A}_i$ for any state i in a succession of states $i \rightarrow i + 1$ between reaction initiation i_0 and equilibrium $i_{\mathrm{eq.}}$ This obstacle can be overcome, however, by modifying the postulate of local equilibrium derived from Landsberg's so-called Fourth Law of Thermodynamics.[20]

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.[21]

In theory, the minimum period $\tau_{\mathcal{D}}$ required for the homogeneous equilibrium cells to occupy the entire system is simply

$$\tau_{\mathcal{D}} \propto V^{1/3}/v_{\mathcal{D}} \tag{5}$$

where V is the volume of the reacting cell and $v_{\mathcal{D}} = \mathcal{D}/V^{1/3}$, for which $\mathcal{D}$ is the diffusion coefficient.[22] 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.[23] Happily, this position is strongly supported by Garcia-Colin[24] and Bhalekar[25] who demonstrated that the nonequilibrium contibutions 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: $\delta T_i \rightarrow 0$ and $\delta P_i \rightarrow 0$. Hence, for practical purposes both T_i and P_i have unique instantaneous values at any state i, permitting $\mathcal{A}_i$ 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 $\mathcal{A}_i$ 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 $n_{m_i} \rightarrow n_{m_{i\pm1}}$, 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

$$Q_i = \Pi(a_m)^{\nu_m} \tag{6}$$

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 $c_m = a_m/\gamma_m$ at state i where γ_m is the activity coefficient of component m, unfortunately γ_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 $\gamma_m \rightarrow 1$ and therefore $c_m \rightarrow a_m$, permitting Q_i to be approximated by the instantaneous number of each of the reacting particles at state i.

$$Q_i = \Pi[(n_m)^{\nu_m}(VN)^{\nu_m}] \tag{7a}$$

However, as defined, Q_i requires that the instantaneous number of all reacting particles n_{m_i} be known at state i. This complication can be remedied, however, by resorting to the reaction advancement term ξ_i, conveniently defined as

$$\xi_i = (n_{m_i} - n_{m_0})/(-\nu_{m_i}) \tag{7b}$$

where n_{m_0} is the number of particles m present at reaction initiation. Substituting for n_{m_i} in eq 5 yields

$$Q_i = \Pi[(n_{m_0} + \xi_i \nu_{m_i})^{\nu_m}(VN)^{\nu_m}] \tag{7c}$$

relating the system variable Q_i to a single concentration term $\xi_{0,i}$.

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

$$K = \Pi[(n_{m_0} + \xi_{\mathrm{eq}}\nu_{m_i})^{\nu_m}(VN)^{\nu_m}] \tag{8}$$

Taking the ratio of eqs 7c to 8 permits a thermodynamic extent-of-reaction term ζ_{Q_i} to be defined as

$$\zeta_{Q_i} = Q_i/K \tag{9}$$

Accordingly, reaction initiation and reaction equilibrium are the uniquely defined states $\zeta_{Q_0} = 0$ and $\zeta_{Q_{\mathrm{eq}}} = 1$, 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 $\zeta_{Q_0} = 0$ toward a specific equilibrium state $\zeta_{Q_{\mathrm{eq}}} = 1$. 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 ζ_{Q_i}, then a transformation toward equilibrium can be defined as the forward reaction $\zeta_{Q_i} \rightarrow \zeta_{Q_{i+1}}$ and a transformation away from equilibrium can be defined as the reverse reaction $\zeta_{Q_{i-1}} \leftarrow \zeta_{Q_i}$.

According to this probabilistic analysis $p_{i,i+1}$ is defined as the probability of reaction transformation from state ζ_{Q_i} forward to state $\zeta_{Q_{i+1}}$ and $p_{i,i-1}$ is the probability for transformation from state ζ_{Q_i} backward to state $\zeta_{Q_{i-1}}$. Because any state $\zeta_{Q_{0-1}}$ prior to the initiation state ζ_{Q_0} by definition cannot occur, any reverse transformation from ζ_{Q_0} is precluded, and therefore $p_{0,0-1} = 0$, which indicates that the transformation probability $p_{i,i\pm1}$ clearly depends on the state of the system ζ_{Q_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 $p_{i,i\pm1}$ and ζ_{Q_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 $\mathcal{A}_i$.[28] Accordingly,

$$p_{i,i\pm1} \propto \zeta_{Q_i} \tag{10}$$

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

$$p_{i,i-1} \equiv \text{the probability of transformation } \zeta_{Q_{i-1}} \leftarrow \zeta_{Q_i} \tag{11}$$

and for the forward reaction

$$p_{i,i+1} \equiv \text{the probability of transformation } \zeta_{Q_i} \rightarrow \zeta_{Q_{i+1}} \tag{12}$$

Because the only allowable transformations from ζ_{Q_i} are either to $\zeta_{Q_{i-1}}$ or to $\zeta_{Q_{i+1}}$, clearly

$$p_{i,i-1} + p_{i,i+1} = 1 \tag{13}$$

Accordingly, the reacting system can either transform forward toward equilibrium or backward toward reaction initiation, with the probability of transformation $p_{i,i\pm1}$ dependent on state ζ_{Q_i} in accordance with expression 12. Consequently, some relationship $p_{i,i\pm1} = c_{\mathrm{p}}\zeta_{Q_i}$ must be elucidated, where c_{p} is a constant of proportionality to be determined. This objective can be accomplished by relating the values of $p_{i,i\pm1}$ to the corresponding state ζ_{Q_i} at specific boundary conditions.

At reaction, initiation products are not present and thus $\zeta_{Q_0} = 0$. Because state $\zeta_{Q_{0-1}}$ cannot exist, there can be no reverse transformation from reaction initiation as previously discussed, hence

$$p_{0,0-1} = 0\text{:} \quad \text{the probability of transformation } \zeta_{Q_{0-1}} \leftarrow \zeta_{Q_0} \tag{14a}$$

From eq 13, for the forward reaction

$$p_{0,0+1} = 1\text{:} \quad \text{the probability of transformation } \zeta_{Q_0} \rightarrow \zeta_{Q_{0+1}} \tag{14b}$$

Accordingly, the probability of transformation forward $p_{i,i+1}$ (away from reaction initiation) is greater than the probability of transformation backward $p_{i,i-1}$ (toward reaction initiation). Consequently, following reaction initiation the probability of transformation in the direction shown

$$\zeta_{Q_0} \rightarrow \zeta_{Q_1} \rightarrow \zeta_{Q_2} \rightarrow \cdots \rightarrow \zeta_{Q_{\mathrm{eq}-2}} \rightarrow \zeta_{Q_{\mathrm{eq}-1}} \rightarrow \zeta_{Q_{\mathrm{eq}}} \tag{15}$$

is always greater toward equilibrium inasmuch as $p_{i,i-1} < p_{i,i+1}$. It is evident, therefore, that as a reaction progresses: $p_{i,i-1}$ increases from its initial zero value and $p_{i,i+1}$ decreases from its initial unit value.

Accordingly, as a reaction proceeds, the decreasing probability $p_{i,i+1} \rightarrow 0$ for forward reaction must eventually intersect the increasing probability $p_{i,i-1} \rightarrow 1$ for backward reaction. Stochastically, equilibrium is defined as the state of the system $\zeta_{Q_{\mathrm{eq}}}$ at intersection $p_{i,i-1} = p_{i,i+1}$. Hence, at equilibrium the probabilities for the forward and reverse transformations are equal. From eq 13 for the backward reaction

$$p_{\mathrm{eq,eq}-1} = {}^1/_2 \equiv \text{the probability of transformation } \zeta_{Q_{\mathrm{eq}-1}} \leftarrow \zeta_{Q_{\mathrm{eq}}} \tag{16a}$$

and for the forward reaction

$$p_{\mathrm{eq,eq}+1} = {}^1/_2 \equiv \text{the probability of transformation } \zeta_{Q_{\mathrm{eq}}} \rightarrow \zeta_{Q_{\mathrm{eq}+1}} \tag{16b}$$

According to this stochastic model, following reaction initiation the probability of transformation in the direction shown

$$\zeta_{Q_0} \rightarrow \zeta_{Q_1} \rightarrow \zeta_{Q_2} \rightarrow \cdots \rightarrow \zeta_{Q_{\mathrm{eq}-2}} \rightarrow \zeta_{Q_{\mathrm{eq}-1}} \rightarrow$$
$$\zeta_{Q_{\mathrm{eq}}} \leftarrow \zeta_{Q_{\mathrm{eq}+1}} \leftarrow \zeta_{Q_{\mathrm{eq}+2}} \leftarrow \cdots \leftarrow \zeta_{Q_{\mathrm{c}-1}} \leftarrow \zeta_{Q_{\mathrm{c}}} \quad (17)$$

between initiation ζ_{Q_0} (no products present) and completion ζ_{Q_c} (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 $p_{i,i\pm1}$ and ζ_{Q_i} identified at reaction initiation (eq 14b) and at reaction equilibrium (eqs 16a and 16b) the following equalities follow. For the backward reaction

$$p_{i,i-1} = {}^1\!/_2\zeta_{Q_i} \quad (18a)$$

and consequently from eq 13

$$p_{i,i+1} = 1 - {}^1\!/_2\zeta_{Q_i} \quad (18b)$$

for the forward reaction. Equations 18a and 18b describe the progress of chemical reaction 1 from reaction initiation ζ_{Q_0} to reaction equilibrium $\zeta_{Q_{\mathrm{eq}}}$ 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 ζ_{Q_i}.

(2) The process must be periodic in that the number of reaction steps $\Delta_{i,i\pm n}$ between steps d_i and $d_{i\pm n}$ required to return to any state ζ_{Q_i} from any other state $\zeta_{Q_{i\pm n}}$ is a multiple of some positive integer.

(3) The process must be irreducible in that the probabilities $p_{i,i\pm1}$ associated with the transformation of any present state ζ_{Q_i} to any future state $\zeta_{Q_{i\pm n}}$ must be independent of any past state $\zeta_{Q_{i-n}}$ or $\zeta_{Q_{i+n}}$.

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

$$\mathscr{A}_i = -RT \ln(\zeta_{Q_i}) \quad (19)$$

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 $p_{i\pm1}$ 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.

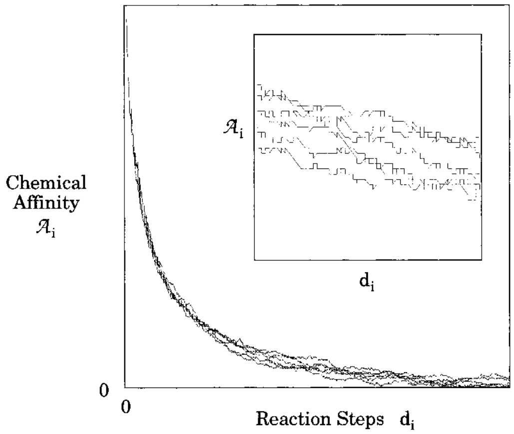


Figure 1. Probabilistic affinity decay curve.

TABLE 1: Determination of the Chemical Affinity Decay

1 step	2 random number	3 probability	4 extent of reaction	5 chemical affinity
0	-	1.000	0.000	∞
1	0.802	0.985	0.030	5831
2	0.157	0.970	0.060	4678
3	0.019	0.955	0.090	4004
4	0.115	0.940	0.120	3526
5	0.259	0.925	0.150	3155
25	0.367	0.715	0.570	935
26	0.483	0.700	0.600	849
27	0.933	0.685	0.630	768
28	0.211	0.700	0.600	849
29	0.277	0.685	0.630	768
50	0.246	0.580	0.840	290
51	0.814	0.565	0.870	232
52	0.078	0.580	0.840	290
53	0.417	0.565	0.870	232
54	0.249	0.550	0.900	175
70	0.294	0.520	0.960	68
71	0.531	0.505	0.990	17
72	0.700	0.520	0.960	68
73	0.079	0.535	0.930	121
74	0.738	0.520	0.960	68
96	0.721	0.490	1.020	−33
97	0.133	0.505	0.990	17
98	0.259	0.490	1.020	−33
99	0.993	0.475	1.050	−81
100	0.880	0.490	1.020	−33

The purpose of this exercise is to compare the affinity−step data ($\mathscr{A}_i$, d_i) generated by the probabilistic analysis with the empirical affinity−time data ($\mathscr{A}_i$, t_i) found in the literature. As the probabilistic analysis proceeds, the probabilistic chemical affinity tends to decay. Hence between any steps Δd_i there is an affinity difference $\Delta\mathscr{A}_i$. Likewise, as an actual chemical reaction proceeds, the empirical chemical affinity decays. Hence between any time interval Δt_i there is an affinity decay $\Delta\mathscr{A}_i$. To correlate the probabilistic affinity difference with the empirical affinity decay, it would necessitate adjusting the probabilistic affinity difference $\Delta\mathscr{A}_i$. This procedure is accomplished simply by introducing a fixed term Δ_p, which is the probability difference $\Delta p_{i,i\pm1}$ between succeding steps. The term Δ_p is adjusted until the probabilistic affinity agrees as closely as possible with the adjusted ζ_Q according to eq 18b and thence $\Delta\mathscr{A}_i$ according to eq 19. Were this accomplished,

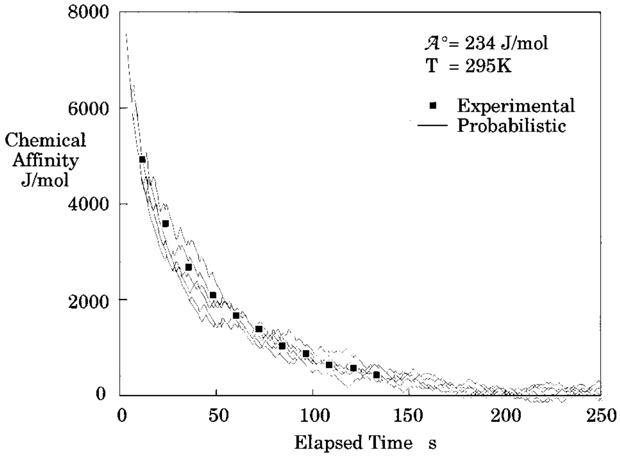


Figure 2. Affinity decay for the reaction of styrene with iodine in CCl_4.

then Δd_i would presumably equal Δt_i and the data correlated. For each reaction, Δ_p has a single fixed value.

The affinity−step data ($\mathcal{A}_i$, 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 Δ_p. In contrast, if the random number is larger than the probability, the probability is increased by a fixed value Δ_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 $\Delta_p = 0.015$, 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 Δ_p.

Empirical Verification

The chemical affinity $\mathcal{A}_i$ 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 ζ_{Q_i} are calculated from eq 18b and the experimental extents-of-reaction ζ_{Q_i} are calculated from eq 9 for each reaction examined. The probabilistic and empirical affinities $\mathcal{A}_i$ 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 ($\mathcal{A}_i$, 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 ($\mathcal{A}_i$, t_i) data entered onto the Excel spreadsheet and superimposed on the curves. The value of Δ_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.

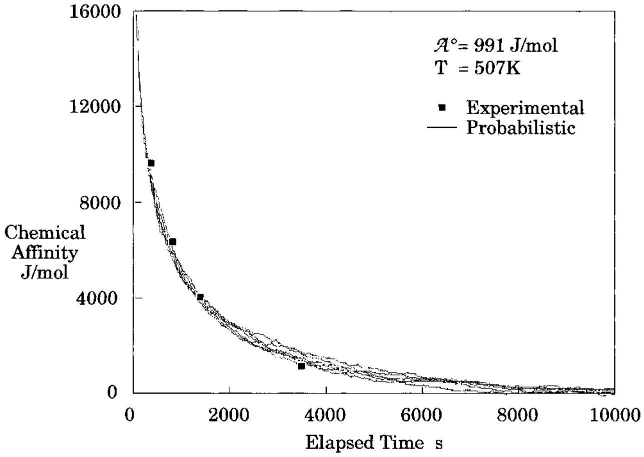
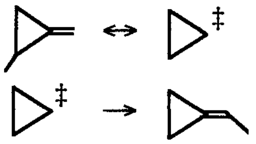


Figure 3. Affinity decay for the isomerization of ethylidenecyclopropane.

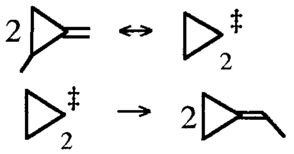
The isomerization of 2-methylmethylenecyclopropane to ethylidenecyclopropane


(20)

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


(21a)

whose configuration is not precisely known. Alternatively, the activated complex may be bimolecular:


(21b)

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.

$$C_6H_5{-}CH{=}CH_2 + I_2 \rightarrow C_6H_5{-}CHI{-}CH_2I \quad (22)$$

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

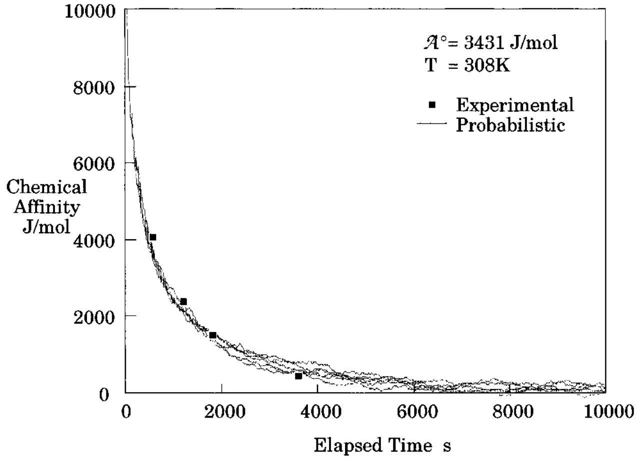


Figure 4. Affinity decay for the bromination of platinic ammonia chloride in KCl solution.

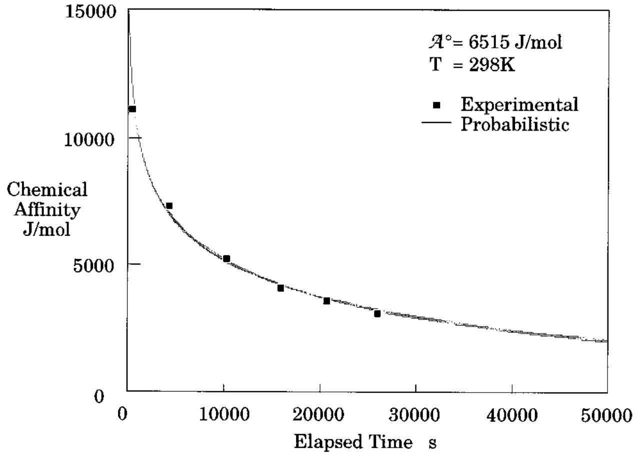


Figure 5. Affinity decay for the formation of acetone cyanohydrin.

for $\Delta_p = 9.0 \times 10^{-4}$ and compared with the experimental chemical affinities.

The bromination of platinic ammonia chloride ion in KCl solution is probably a simple substitution reaction wherein

$$\mathrm{Pt(NH_3)Cl^+ + Br^- \rightarrow Pt(NH_3)Br^+ + Cl^-} \tag{23}$$

although an activated intermediate species is possibly involved.[31] Six simulations of the affinity decay for this substitution process are shown in Figure 4 for $\Delta_p = 2.2 \times 10^{-3}$ and compared with the experimental chemical affinities.

Unexpectedly, the formation of acetone cyanohydrin in aqueous solution does not involve catalysis, as does many other such cyanohydrin-formation processes.

$$\mathrm{CH_3COCH_3 + HCN \rightarrow (CH_3)_2C(OH)CN} \tag{24}$$

Rather, the formation reaction is a two-step process

$$\mathrm{CH_3COCH_3 + CN^- \rightarrow (CH_3)_3COCN^-} \tag{25a}$$

$$\mathrm{(CH_3)_3COCN^- + H^+ \rightarrow (CH_3)_3C(OH)CN} \tag{25b}$$

with the slower reaction 25a controlling the overall reaction.[32] Six simulations of the affinity decay for this cyanohydrin process are shown in Figure 5 for $\Delta_p = 1.1 \times 10^{-4}$ and compared with the experimental chemical affinities.

The formation of ferrous tris(dipyridyl) ions in acetic acid is unusual in that the reaction is third order.[33]

$$\mathrm{Fe^{2+} + 3(C_{10}H_6N_2) \rightarrow Fe(C_{10}H_6N_2)_3{}^{2+}} \tag{26}$$

The reaction proceeds in a simple stepwise fashion:

$$\mathrm{Fe^{2+} + (C_{10}H_6N_2) \rightarrow Fe(C_{10}H_6N_2)^{2+}} \tag{27a}$$

$$\mathrm{Fe(C_{10}H_6N_2)^{2+} + (C_{10}H_6N_2) \rightarrow Fe(C_{10}H_6N_2)_2{}^{2+}} \tag{27b}$$

$$\mathrm{Fe(C_{10}H_6N_2)_2{}^{2+} + (C_{10}H_6N_2) \rightarrow Fe(C_{10}H_6N_2)_3{}^{2+}} \tag{27c}$$

where reaction 27c is the rate-determining step. Six simulations of the affinity decay for the formation of ferrous tris(dipyridyl) ions are shown in Figure 6 for $\Delta_p = 5.0 \times 10^{-6}$ and compared with the experimental chemical affinities.

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

$$\mathrm{i\text{-}CH_6 + I_2 \rightarrow i\text{-}CH_4 + 2HI} \tag{28}$$

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]

$$\mathrm{I_2 + M \leftrightarrow 2I + M} \tag{29a}$$

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

$$\mathrm{t\text{-}Bu + I_2 \rightarrow t\text{-}BuI + I} \tag{29c}$$

$$\mathrm{t\text{-}BuI \rightarrow i\text{-}Bu + HI} \tag{29d}$$

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.

It is evident from these examples that excellent correlations were achieved between the probabilistic model with the empirical kinetic data for highly complex processes. Moreover, only one degree of freedom was allowed: the value of Δ_p. As would be expected, the probabilistic curves become increasingly more erratic as they approach equilibrium with $p_{i,i\pm1} \rightarrow {}^1/_2$.

Discussion

According to the classical approach, the forward reaction rate v_f 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_r 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 $v_o = v_f + v_r$, 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 $p_{eq,eq\pm1}$ and the extent-of-reaction ζ_{Q_i}. This gap, however, was bridged by the assumption of linearity, an assumption that has been demonstrated to be valid. The term Δ_p represents the single degree of freedom

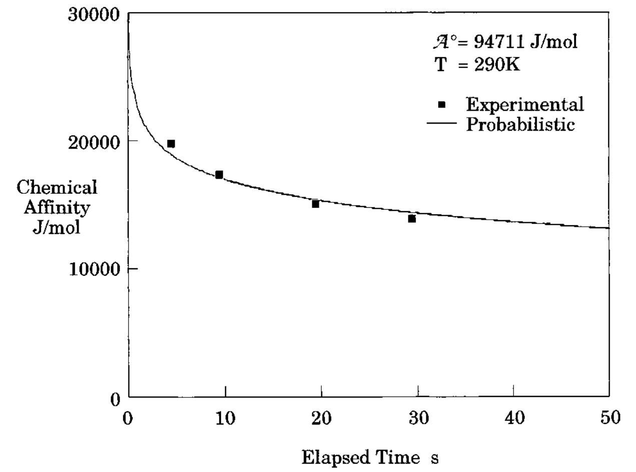


Figure 6. Affinity decay for the formation of ferrous tris(dipyidyl) ion in acetic acid.

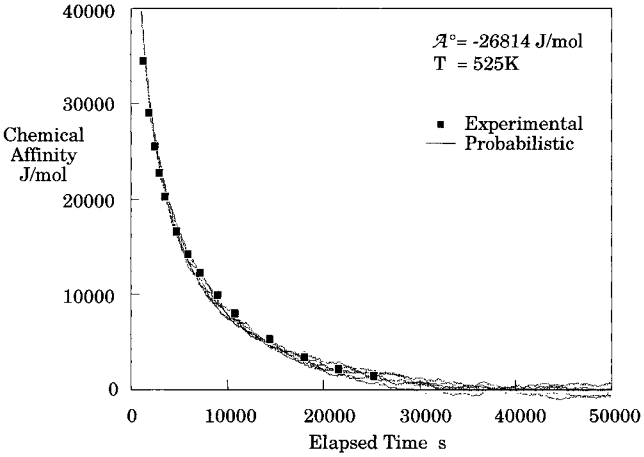


Figure 7. Affinity decay for the dehydrogenation of isobutane by iodine vapor.

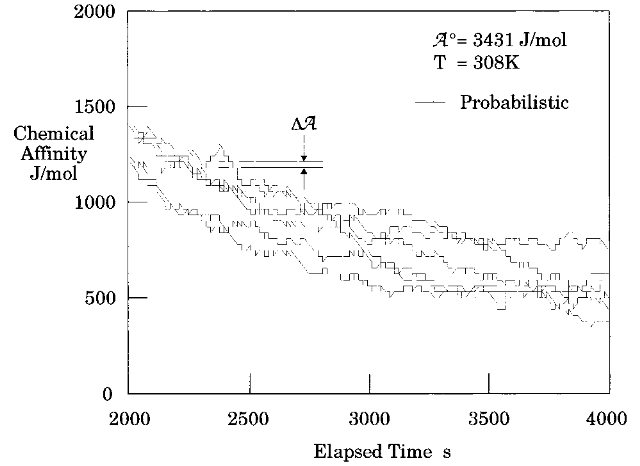


Figure 8. Detail of the affinity decay for the bromination of platinic ammonia chloride.

allowed, which proved to suffice in correlating the probabilistic to the experimental data. The necessity for Δ_p is obvious. The time units used for the actual chemical reaction are arbitrary, generally seconds, while the number of probabilistic steps is simply a tabulation. The value of Δ_p is chosen to align d_i to t_i.

The requirement for a source of random-numbers, however, imposes a potentially serious impediment to the application of this stochastic approach, as it does for all such approaches, including Monte Carlo simulations. In practice, such sources generate only pseudorandom numbers that can impose patterns on resultant probabilities. Haggstrom 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.

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