

# The Thermodynamic Natural Path in Chemical Reaction Kinetics

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**The Natural Path approach to chemical reaction kinetics was developed to bridge the considerable gap between the Mass Action mechanistic approach and the non-mechanistic irreversible thermodynamic approach. The Natural Path approach can correlate empirical kinetic data with a high degree precision, as least equal to that achievable by the Mass-Action rate equations, but without recourse mechanistic considerations. The reaction velocities arising from the particular rate equation chosen by kineticists to best represent the kinetic behavior of a chemical reaction are the natural outcome of the Natural Path approach. Moreover, by virtue of its thermodynamic roots, equilibrium thermodynamic functions can be extracted from reaction kinetic data with considerable accuracy. These results support the intrinsic validity of the Natural Path approach.**

*Keywords:* Affinity decay, Irreversible thermodynamics, Natural Path, Mass Action, Reaction velocities

## INTRODUCTION

Stoichiometric chemical reactions have been classically perceived as systems of discrete reacting particles wherein reactant species transform to product species. However, because the extreme number of particles involved, generally a significant fraction of Avogadro's number, the classical analytic model based on the Kinetic Mass Action Law of Guldberg and Waage as expounded by Christianson (1964) treats chemical reactions as a continuum. According to this classical approach a stoichiometric chemical reaction proceeding from a reaction initiation state to a reaction equilibrium state involves the

transformation of reactants to products according to a specific reaction mechanism which can be delineated for each reaction by a mechanistic analysis.

Although the classical approach has served extremely well in the elucidation of reaction mechanisms, underlying the mechanistic changes in particle concentration is a more fundamental thermodynamic concern: the driving force for the chemical reaction. Since the mid-eighteenth century, according to Partington (1964), this generalized force has been given the generic name *chemical affinity*. Essentially the rate of decay of the chemical affinity controls the observed Mass Action reaction velocity.

The chemical affinity  $\mathcal{A}$  was formally introduced as a thermodynamic function by De Donder (1922) and defined as the chemical potential of a reaction, with the reaction proceeding in the direction to minimize the potential. To delineate the affinity decay path from the ordinarily measured *concentration: time*, kinetic data however, requires that the reacting system observed proceeds under certain restrictions which are not necessarily observed for the Mass Action approach:

- (1) The reacting system is isothermal and homogeneous in that all reacting species are uniformly distributed in a single fluid phase.
- (2) The reacting system is isochoric in that there is no mass transfer between the reacting system and its surroundings.
- (3) The reacting system can be described in terms of discrete reaction states which are defined in terms of a finite number of reactant and product particles present.
- (4) Transformation of one state to another can be viewed as proceeding in a single step involving transformations between reactant and product particles in a fixed ratio according to the reaction stoichiometry.

## 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 descriptions are possible, such as simply the fraction of reactant particles present relative to the initial number, a scheme consistent with the formalism of chemical thermodynamics will be chosen in which the characteristic identities of the initial state and the equilibrium state each have fixed values which can be related to thermodynamic functions.

Consider the homogeneous stoichiometric chemical reaction (1) proceeding in a closed system at fixed temperature  $T$  and volume  $V$  comprising

reacting components  $m$

$$\sum [\nu_m M_m]_{T,V} = 0 \quad (1)$$

where  $\nu_m$  is the stoichiometric coefficient and  $M_m$  is the molecular weight of reacting component  $m$ , with  $\nu_m < 0$  for reactants. The reaction proceeds from reaction initiation  $[\nu_m M_m]_0$  to reaction equilibrium  $[\nu_m M_m]_{\text{eq}}$ .

Although a chemical reaction physically proceeds stepwise in terms of the change in the number of reacting particles  $n_{m_i} \rightarrow n_{m_{i+1}}$  where  $i$  specifies any state of the system between initiation and equilibrium, the influence of each component on the progress of the reaction is represented by its thermodynamic activity  $a_{m_i}$ . The activity of component  $m$  is a measure of its chemical reactivity relative to the other reacting species present. Hence at any state  $i$  of the system each component  $m$  has a specific activity  $a_{m_i}$ , the product of which

$$Q_i = \prod (a_{m_i})^{\nu_m} \quad (2)$$

can fully define that state in terms of all of the reacting components present where  $Q_i$  is identified as the *activity ratio* at state  $i$ .

However kineticists experimentally measure the change in concentration of reacting species with time, not their activities. Accordingly, to determine the value of  $Q_i$  at state  $i$  requires that activities  $a_{m_i}$  be calculated from measured concentrations  $c_{m_i}$ . Although  $c_{m_i}$  and  $a_{m_i}$  are related by  $c_{m_i} = a_{m_i}/\gamma_{m_i}$  where  $\gamma_{m_i}$  is the activity coefficient of component  $m$ ,  $\gamma_{m_i}$  is a very complex function of component concentration  $c_{m_i}$ .

Fortunately, chemical reactions are customarily investigated under conditions of sufficient dilution that  $\gamma_{m_i} \rightarrow 1$  and therefore  $c_{m_i} \rightarrow a_{m_i}$ , permitting  $Q_i$  to be represented in terms of the instantaneous concentration of each of the reacting particles at state  $i$ .

$$Q_i = \prod (c_{m_i})^{\nu_m}. \quad (3)$$

However, as defined  $Q_i$  requires that the instantaneous concentration of all of the reactants  $c_{m_i}$  be known at state  $i$ . This complication can be remedied however by resorting to the *reaction advancement* term  $\xi_i$  conventionally defined as

$$\xi_i = (c_{m_0} - c_{m_i})/(-\nu_m) \quad (4)$$

where  $c_{m_0}$  is the initial concentration of component  $m$ . The reaction advancement has the same value for all of the reacting components present. Substituting for  $c_{m_i}$  in Eq. (3) yields

$$Q_i = \prod (c_{m_0} + \nu_m \xi_i)^{\nu_m}. \quad (5a)$$

As defined  $Q_i$  has a unique state value of  $Q_0 = 0$  at reaction initiation and  $Q_{\text{eq}} = K$  at reaction equilibrium, where  $K$  is the thermodynamic equilibrium constant defined as

$$K = \prod (c_{m_0} + \nu_m \xi_{\text{eq}})^{\nu_m}. \quad (5b)$$

Taking the ratio of Eq. (5a) to Eq. (5b) permits a thermodynamic *extent of reaction* term  $\zeta_{Q_i}$  to be defined as

$$\zeta_{Q_i} = Q_i/K. \quad (6)$$

Consequently reaction initiation and reaction equilibrium are uniquely defined states  $\zeta_{Q_0} = 0$  and  $\zeta_{Q_{\text{eq}}} = 1$ , respectively. Evidently  $\zeta_{Q_i}$  remains absolutely invariant under transformations such as the units selected to represent reacting components: either by number of particles, partial pressures, mol fractions, concentrations or whatever.

## AFFINITY DECAY

What will now be considered is a thermodynamic approach to chemical reaction kinetics that dispenses entirely with mechanistic considerations. A chemical reaction is accordingly viewed as simply an isothermal sink or source of energy in which kinetic behavior is described in term of the time dependency of a thermodynamic function.

Unfortunately such a time dependence is not generally accepted by classical thermodynamicists. The admonishment of Brostow (1972) that thermodynamicists are mistaken in assuming that the scope and contents of thermodynamics are time independent has not been appreciated, neither by thermodynamicists, let alone by kineticists.

Because there is no theoretical foundation on which to base a thermodynamic description of close-system reactions, this study was undertaken to determine whether it was possible to base such a description on a heuristic approach involving a numerical analysis of empirical data.

Prigogine and DeFay (1962) redefined the chemical affinity as a generalized force in terms of potential difference as

$$\mathcal{A}_i = -\sum [\nu_m \mu_{m_i}]_{T,V} \quad (7)$$

where  $\mu_m$  is the chemical potential of component  $m$ . According to this definition at equilibrium  $\mathcal{A}_i = 0$  and in any state prior to equilibrium  $\mathcal{A}_i > 0$ . All thermodynamic functions are relative quantities and consequently to calculate the value of  $\mathcal{A}_i$  as Reaction (1) proceeds from initiation to equilibrium requires that  $\mathcal{A}_i$  in state  $i$  be compared to its value in some other state, conventionally designated as the standard state. In this regard the standard state will be defined as the state at which the affinity  $\mathcal{A}_i = \mathcal{A}^0$ .

Classically the chemical potential  $\mu_m$  of component  $m$  can be related to its chemical potential  $\mu_m^0$  in some arbitrary state by an equation of the form

$$\nu_m \mu_{m_i} = \nu_m \mu_{m_i}^0 + RT \ln(a_{m_i})^{\nu_m}. \quad (8a)$$

This arbitrary state will be defined as the *standard state* and is the state at which the affinity  $\mathcal{A}$  equals its standard state value  $\mathcal{A}^0$ .

Substituting from Eq. (7) yields

$$\mathcal{A}_i = \mathcal{A}^0 - RT \sum \ln(a_{m_i})^{\nu_m} \quad (8b)$$

where  $\mathcal{A}^0$  is the standard affinity. Substituting from Eq. (2) yields

$$\mathcal{A}_i = \mathcal{A}^0 - RT \ln(Q_i). \quad (9a)$$

At equilibrium  $\mathcal{A}_i = 0$  and  $Q_{\text{eq}} = K$  and therefore  $\mathcal{A}^0 = RT \ln(K)$ . From Eq. (6) therefore

$$\mathcal{A}_i = -RT \sum \ln(\zeta_{Q_i}) \quad (9b)$$

thereby relating the chemical affinity to a determinable quantity: the extent of reaction.

Accordingly, for Reaction (1) proceeding towards equilibrium the affinity decays towards zero and

$$\dot{\mathcal{A}}_{T,V} < 0 \quad (10)$$

where  $\dot{\mathcal{A}}_{T,V} = [\partial \mathcal{A} / \partial t]_{T,V}$ . Expression (10) represents the furthest extent to which classical thermodynamic considerations alone can be carried in describing a chemical reaction proceeding towards equilibrium. Because chemical thermodynamics does not involve itself with mechanistic concerns and because chemical reactions involve reacting particles that are finite in number and indivisible, no fractional steps occur. Accordingly, in relation to a chemical reaction:

- (1) the decay of a thermodynamic function would be independent of reaction mechanism, and
- (2) this stepwise process would reach any state of the system from its initial state in a finite time.

Because the limit of thermodynamic considerations has been reached with Expression (10) resort will now be made to an empirical analysis of experimental reaction data to ascertain the time dependency of the chemical affinity  $\mathcal{A}_i$  consistent with Expression (10). To ascertain the form of the required analytical expression necessitates that actual values of  $\mathcal{A}_i$  be calculated from concentration data measured by kineticists for the reactions examined.

The required kinetic data for a number of reactions, found in the literature or solicited from kineticists, were used to calculate  $\zeta_{Q_i}$  at the measured

time intervals. Equilibrium data were obtained from diverse sources, but primarily from Latimer (1952) or the JANAF Tables (1971). From this information the values of the  $(\mathcal{A}_i, t_i)$  coordinates were calculated according to Eq. (8b). The values of  $\mathcal{A}_i$  were plotted directly against the elapsed time  $t_i$ . Although computer-aided integration is a quick and accurate procedure, this is not so in the case of computer-aided differentiation, according to La Fara (1973) integration is an error enhancing procedure. Consequently a manual chord-area method of differentiation reported by Klotz (1957) was employed to determine  $\dot{\mathcal{A}}_{T,V}$  from the plotted  $(\mathcal{A}_i, t_i)$  curves. The result was a series of  $(\dot{\mathcal{A}}_{T,V}, t_i)$  coordinates for each reaction examined.

The calculated values of  $\dot{\mathcal{A}}_{T,V}$  were correlated with various functions of elapsed time  $t_i$  by a regression analysis to determine the best data fit. However as soon as the reciprocal-time relationship was examined it was apparent that  $\dot{\mathcal{A}}_{T,V}$  was inversely proportional to the elapsed time:

$$\dot{\mathcal{A}}_{T,V} \propto 1/t_i. \quad (11)$$

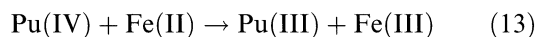
Using this reciprocal-time function four reactions representative of those investigated will be discussed.

The isomerization of ethylenecyclopropane to 2-methylmethylenecyclopropane examined by Chesick (1963) is a simple unimolecular reaction involving a two-step process requiring an activated complex.



Figure 1 illustrates the reciprocal-time dependence of  $\dot{\mathcal{A}}_{T,V}$  for this unimolecular reaction according to Expression (11).

The bimolecular reduction of Pu(IV) by Fe(II) in perchloric acid



is probably catalyzed by chloride or hydroxyl ions according to Newton and Cowan (1960). An

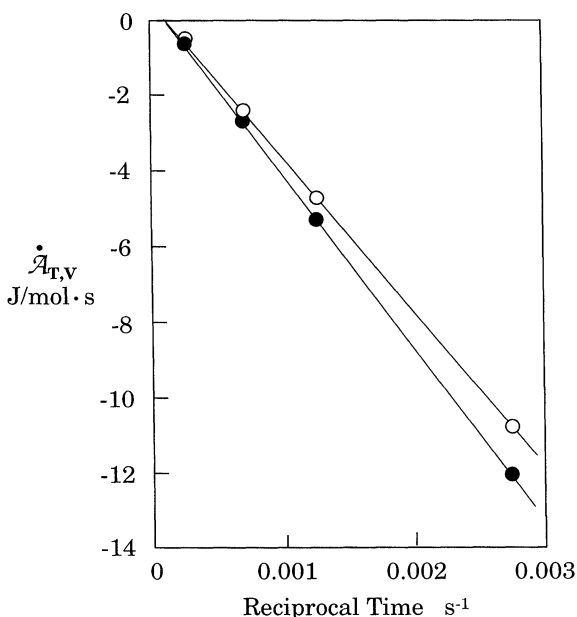


FIGURE 1 Unimolecular isomerization reactions at 507 K.

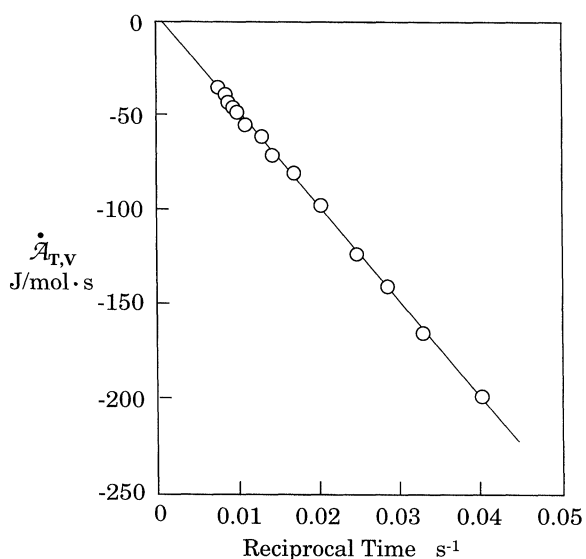


FIGURE 2 Bimolecular electron-transfer process at 289 K.

$[\text{Pu}(\text{I}) \cdot \text{X} \cdot \text{Fe}(\text{V})]^\ddagger$  activated complex supposedly is involved in the reaction, where X is either a chloride or hydroxyl ion (Fig. 2).

The formation of nitrosyl chloride was examined by Welinsky and Taylor (1938). This reaction

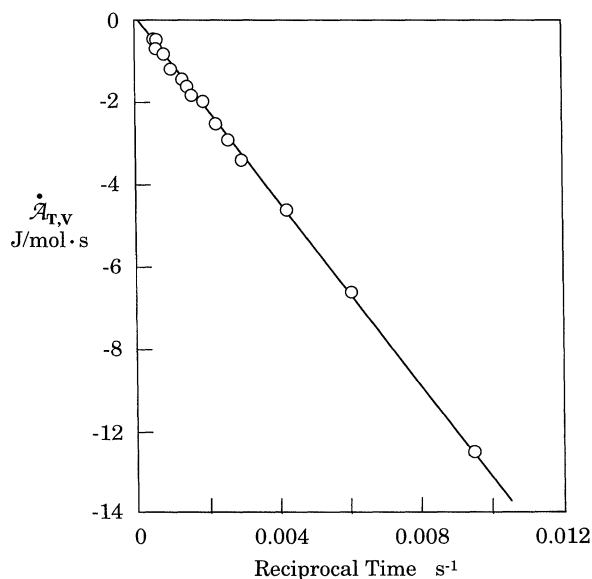


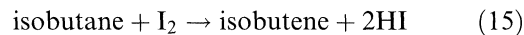
FIGURE 3 Trimolecular process at 333 K.

ostensibly depends on ternary collisions, which are estimated to be about 100 times as rare as binary collisions according to Benson (1960).



This process can also be explained by a two-stage bimolecular process according to Sykes (1966), although the process does follow trimolecular kinetics (Fig. 3).

The dehydrogenation of isobutane by iodine



involves a free-radical chain mechanism according to Terinishi and Benson (1963). The overall reaction velocity is a very complex function of intermediate reaction velocities (Fig. 4).

The four reactions illustrated represent diverse mechanism, yet  $\dot{A}_{T,V}$  was inversely proportional to the elapsed time for all of them, which suggests that Expression (11) is a valid description of affinity decay path. In no case did the lines of regression shown pass through the origin however but rather intersected the abscissa at a finite time interval, as it did for all of the reactions observed. Consequently

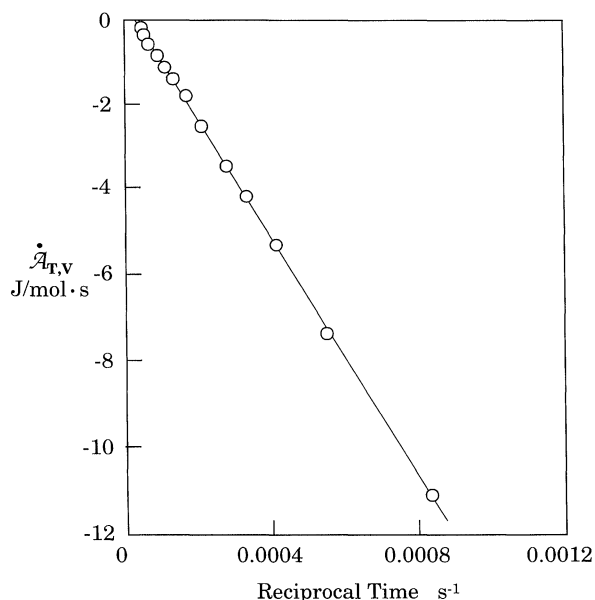


FIGURE 4 Free-radical chain reaction at 525 K.

an intercept term must be represented in Expression (11).

$$\dot{A}_{T,V} \propto 1/t + I. \quad (16a)$$

Inasmuch as  $\dot{A}_{T,V} = 0$  indicates reaction termination or equilibrium then the intercept must be related to the expected time to attain equilibrium, which will be denoted  $t_K$ . Accordingly Expression (16a) can be rearranged to yield

$$\dot{A}_{T,V} = \mathcal{A}_r [1/t_i - 1/t_K] \quad (16b)$$

where  $\mathcal{A}_r$  is a constant of proportionality: denoted the *affinity rate constant*.

Equation (16b) is in agreement with the two restrictions placed on the reacting system: that the affinity decay path is independent of reaction mechanism and that the elapsed time to attain any state is finite, and therefore  $t_K < \infty$ . Because Eq. (16b) describes the decay of the chemical affinity along a reaction path independently of reaction mechanism it was denoted by Garfinkle (1989) as the *Natural Path*.

## NATURAL PATH

The development of irreversible thermodynamics was a reaction to the limitations inherent in the classical approach. To overcome these limitations Landsberg (1970) proposed to expand the classical laws to include irreversible processes. Kestin (1984) went further and proposed that the distinction between reversible and irreversible processes should be dispensed with entirely: the former being a special case of the latter, only lacking direction.

In regard to this particular investigation what functionally distinguishes the reversible from the irreversible path is that in the former case the role of the investigator is quite limited. The investigator can only alter the surroundings at an infinitesimal rate to effect a reversible change in the system between an initial equilibrium state and a final equilibrium state, with the intermediate states themselves equilibrium states. According to Bataille *et al.* (1978) this is not the case as far as irreversible processes are concerned.

To distinguish a *natural* irreversible process from all other irreversible processes will also require that the role of the investigator be limited, for otherwise a multitude of paths would be possible between these equilibrium states. Accordingly for an irreversible process to be natural, the degrees of freedom permitted to the investigator must be severely limited.

If no constraints are placed on the investigator then the system can be forced in any arbitrary fashion whatsoever and is therefore simply one of many irreversible processes. If the most stringent restraint is placed on the investigator then the system cannot be altered at all from its initial configuration and consequently would be denoted a static system.

For example consider an ideal monatomic gas at equilibrium confined to an inert isochoric isothermal chamber. Because the volume and the temperature of the system are invariant the role of the investigator is limited to setting the initial conditions. The possible path traversed is unique but as the system is static the case is trivial.

However there is one exception to this trivial case concerning a closed isothermal system. The exception involves a chemical reaction such as the association of the ideal monatomic gas to form a homonuclear diatomic molecule. For example, upon initiation of this exothermic process the system would be displaced from its initial condition by essentially an infinitesimal amount and heat would flow out of the system at temperature  $T + \delta T$  into the surroundings at  $T$ .

The mechanistic differences between the static system and the dynamic system concerns the nature of the molecular collisions. In the static example the gas collisions are simple elastic impact collisions resulting solely in a redistribution of kinetic energy.

In the dynamic case a change in identity also occurs. Generally under experimental conditions simple impact collisions are at least  $10^6$  times more prevalent than are reaction collisions. Hence on average only after  $10^6$  impact collisions does a reaction collision occur, and between every reaction collision some  $10^6$  impact collisions occur.

What will now be assumed is that  $10^6$  impact collisions are sufficient to redistribute the heat evolved by any one reaction collision that full energy level equilibrium is restored at a uniform system temperature of  $T + \delta T$ , and that the molecular heat of reaction passes uniformly through the walls of the chamber by virtue of the temperature difference  $\delta T$ . Essentially full quantization occurs during this quiescent period of pseudo-equilibrium. Consequently  $T$ ,  $V$ ,  $P$  and  $\mu_m$  are definable.

Accordingly, for the reaction considered both  $P$  and  $\mu_m$  would decrease discontinuously as the system configuration passes from one pseudo-equilibrium state to another. Integrated over many such periods the variables would apparently change at a continuous rate, defining a reaction path. It is this unique reaction path that differs from all other irreversible paths because it is not forced by the investigator and is consequently the Natural Path.

To ascertain the validity of the Natural Path a comprehensive examination of almost 100 homogeneous closed-system reactions was conducted. These included reactions with mechanisms

sufficiently diverse so as to preclude the possibility that the observed correlations might be anomalies. The reactions examined by Garfinkle (1982) included thermal decompositions, electron and proton transfer, isomerization, and direct combination in the gas phase and in aqueous and organic solvents.

In order to directly correlate the calculated values of the chemical affinity with the measured values of the elapsed time Eq. (16b) must be integrated, which yields

$$\mathcal{A}_i = \mathcal{A}_r \ln[\zeta_i \cdot \exp(1 - \zeta_i)] \quad (17)$$

where  $\zeta_i = (t_i/t_K)$ . Similarly to  $\zeta_{Q_i}$ , the extent of reaction  $\zeta_i$  is limited to the range  $0 \leq \zeta_i \leq 1$ . However the value of  $\zeta_i$  must be known to correlate empirical data by Eq. (17) so as to determine the value of  $t_K$ , but  $\zeta_i$  itself depends on  $t_K$ .

This obstacle was overcome by generating values of  $t_K$  by an iterative subroutine. This involves a multiple regression analysis that is satisfied by the requirement of Eq. (17) that the intercept vanishes. The input data required for each reaction examined is the reaction temperature  $T$  and equilibrium constant  $K$ , along with an array of  $(Q_i, t_i)$  coordinates. The correlation procedure is described in Fig. 5.

Because the value of the intercept  $I$  increases towards zero from large negative values with decreasing values of  $t_K$ , the value of  $t_K$  as initially chosen must be larger than its final, but unknown, value. To insure that this condition is met the initial value of the exponent  $z$  in the relationship  $t_K = 10^z$  is arbitrarily placed at seventy and is decreased incrementally.

The following synthetic data Table I was used to test the computational procedure for the hypothetical decomposition reaction:



Input Data:

$$T = 550 \text{ K}$$

$$[\text{W}_2]_0 = 0.100 \text{ atm}$$

$$K = 4.119 \text{ atm}$$

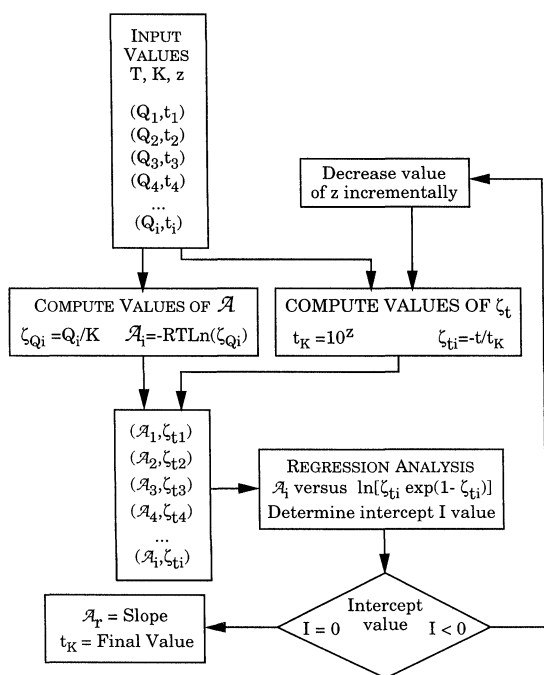


FIGURE 5 Affinity rate equation algorithm.

TABLE I Synthetic reaction rate data

$t/s$	$[W_2]/atm$	$t/s$	$[W_2]/atm$	$t/s$	$[W_2]/atm$
1000	0.05887	4000	0.02344	7000	0.01434
2000	0.04028	5000	0.01926	8000	0.01283
3000	0.02984	6000	0.01639	9000	0.01169

Output Data:

$$\mathcal{A}_r = -8000 \text{ J/mol}$$

$$t_K = 20,000 \text{ s}$$

The condition that the intercept term vanishes is considered to be met when  $I < \mathcal{A}_{\min}/10^6$  where  $\mathcal{A}_{\min}$  is the minimal value of the  $\mathcal{A}$  calculated from Eq. (9b) from the input data array.

## EMPIRICAL DATA CORRELATION

Consider now the time dependency of the chemical affinity for the following four reactions with diverse mechanisms according to Eq. (17). Figure 6

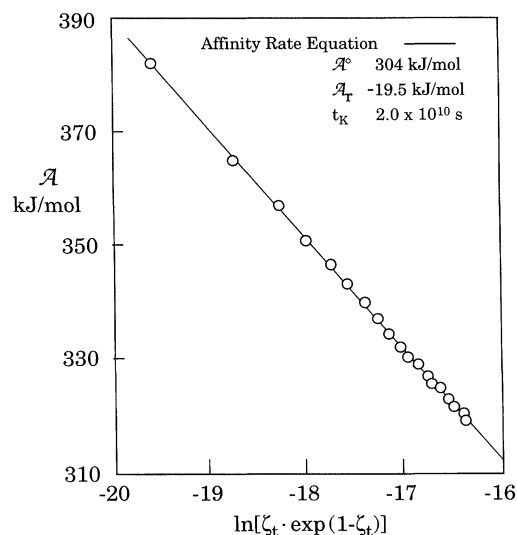
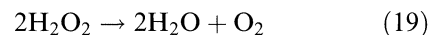


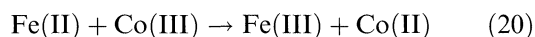
FIGURE 6 Suppressed heterogeneous process at 705 K.

illustrates the affinity decay for the thermal decomposition of hydrogen peroxide vapor investigated by Forst (1958).



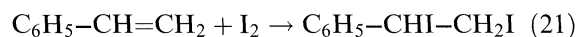
This unimolecular process is normally heterogeneous. However when an inert gas is present its preferential adsorption on reactor surfaces reduces the number of sites available for reaction. This effectively suppresses the heterogeneous process, the conditions under which the decomposition was examined in this study.

The oxidation of Fe(II) by Co(III) in perchloric acid solution probably involves an activated intermediate molecule containing the hydroxyl ion.



The affinity decay for this bimolecular electron-transfer reaction is shown in Fig. 7.

The reaction of styrene with iodine in carbon tetrachloride to form styrene diiodide apparently involves both a free-radical chain mechanism.





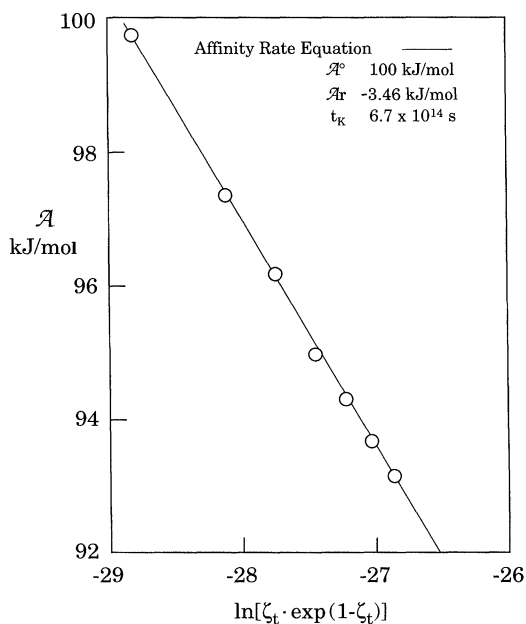


FIGURE 7 Electron-transfer reaction at 298 K.

There is a concurring non-chain reaction that has a first-order dependency on iodine concentration and a 3/2 order dependency on styrene concentration according to Fraenkel and Bartlett (1959). Figure 8 illustrates the affinity decay for this process.

The kinetics of the recombination of monatomic species examined by Strong *et al.* (1957) requires the flash photolysis of the diatomic molecules. The bromine was diluted with argon to minimize thermal excursions due to the rapid recombination.



These reactions are extremely rapid, with  $t_K$  just over a second as shown by Garfinkle (1983) in Fig. 9.

These several figures illustrate that the chemical reactions examined in fact follow the Natural Path and consequently that the time dependency of a thermodynamic function can be described by an analytical function independently of mechanistic complications.

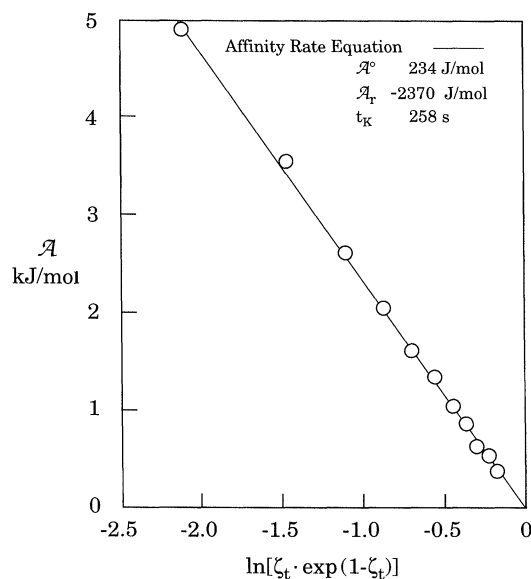


FIGURE 8 Chain reaction at 295 K.

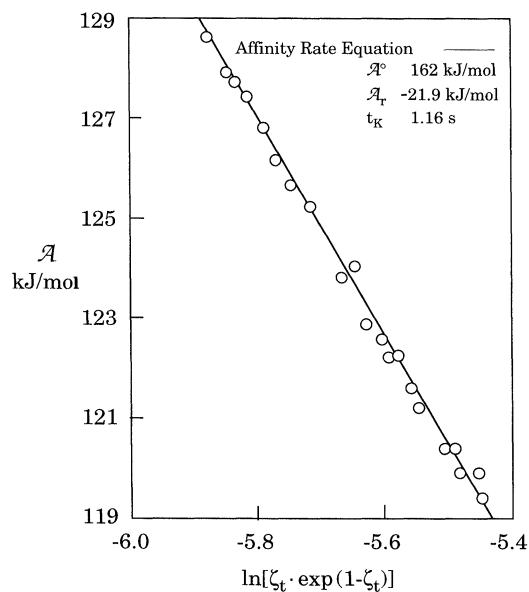


FIGURE 9 Reaction initiation by flash photolysis at 298 K.

## STANDARD STATE CONSIDERATIONS

Inasmuch as the thermodynamic standard state is a specifically defined state, then the elapsed time  $t_1$

TABLE II Thermodynamic states along the Natural Path

System state ( <i>i</i> )	Elapsed time ( <i>t<sub>i</sub></i> )	Activity ratio ( <i>Q<sub>i</sub></i> )	Extent of reaction ( <i>ζ<sub>i</sub></i> )	Extent of reaction ( <i>ζ<sub>Q<sub>i</sub></sub></i> )	Chemical affinity ( <i>A<sub>i</sub></i> )	Affinity rate ( <i>Ȧ<sub>i</sub></i> )
Initial	0	0	0	0	+∞	-∞
Standard	<i>t<sup>0</sup></i>	1	<i>ζ<sub>t<sup>0</sup></sub></i>	<i>ζ<sub>Q<sup>0</sup></sub></i>	<i>A<sup>0</sup></i>	—
Equilibrium	<i>t<sub>K</sub></i>	<i>K</i>	1	1	0	0

required to attain this state at which  $Q^0 = 1$  must be considered. From Eq. (6) the standard state extent of reaction must be  $\zeta_{Q^0} = 1/K$ . Substituting into Eq. (8b) yields

$$\mathcal{A}^0 = -RT \sum \ln(\zeta_{Q^0}). \quad (23)$$

This formalism can now be used to define a standard state value of the extent of reaction  $\zeta_t^0 = t_1/t_K$  from Eq. (17).

$$\mathcal{A}^0 = \mathcal{A}_r[\zeta_t^0 \cdot \exp(1 - \zeta_t^0)]. \quad (24)$$

With the initial, standard, and equilibrium states now defined, all of the thermodynamic parameters have been introduced, and are summarized in Table II.

## CLASSICAL KINETIC APPROACH

Having described the progress of chemical reactions in terms of the decay of the chemical affinity rather than the change in the concentrations of the reacting species, it would be instructional to consider just how compatible are these diverse approaches. The thermodynamic velocity calculated from the Natural Path approach will be compared with the velocity calculated from the Mass Action laws.

According to Garfinkle (1983a) in order to calculate the thermodynamic velocity Eq. (8b) is differentiated with respect to the elapsed time to yield

$$\dot{\mathcal{A}}_{T,V} = -RT \sum \frac{\nu_m^2}{c_m} \left( \frac{dc}{\nu_m dt} \right) \quad (25)$$

where  $c_m$  is the concentration of component  $m$  and can be assumed to approximate its corresponding

activity. The term in parentheses is the reaction velocity  $\mathcal{V}$ . Rearranging terms yields

$$-\mathcal{V}_i = \frac{\dot{\mathcal{A}}_i/RT}{\sum \nu_m^2/c_m}. \quad (26)$$

All of the terms in Eq. (26) have been introduced previously and all can be calculated from empirical kinetic data, with  $\dot{\mathcal{A}}_{T,V}$  calculated from Eq. (16b). Because  $\mathcal{V}_i$  was calculated from thermodynamic consideration alone, there is no mechanistic contribution to its computed value at any state  $i$  between initiation and equilibrium. In contrast the value of the velocity calculated from Mass Action law depends directly on the mechanism chosen by the investigator to best represent the kinetic behavior of the reaction under observation.

For example the oxidation of U(IV) by hydrogen peroxide in perchloric acid solution proceeds according to the stoichiometric reaction



because autocatalytic decomposition of the  $\text{H}_2\text{O}_2$  was essentially absent. From Eq. (26)

$$-\mathcal{V}_i = [\dot{\mathcal{A}}_{T,V}/RT]/[1/[\text{U}^{++++}] + 1/[\text{H}_2\text{O}_2] + 1/[\text{UO}_2^{++}] + 4/[\text{H}^+]]. \quad (28)$$

Figure 10 illustrates three possible mechanistic velocities: 2nd order, a 3rd order, and a 4th order.

Baker and Newton (1961) determined that this reaction was first order in both U(IV) and hydrogen peroxide, the curve followed by the Natural Path velocity. Only points are plotted to represent the Natural Path velocities because Eq. (26) is not in

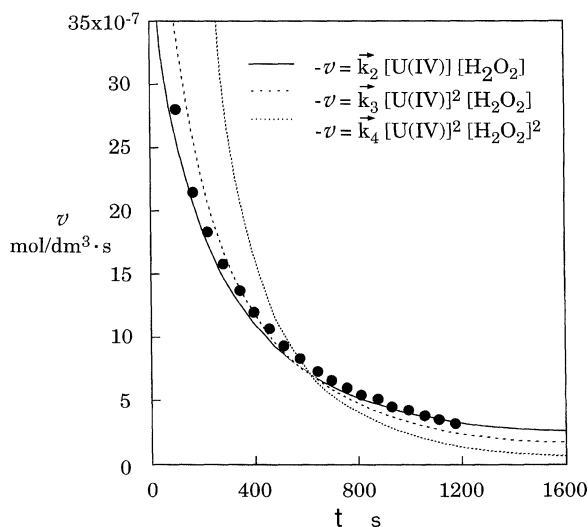


FIGURE 10 Oxidation of U(IV) by hydrogen peroxide at 298 K.

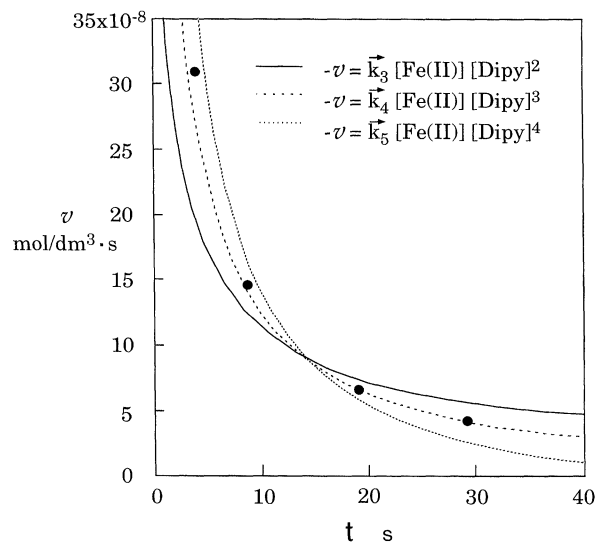
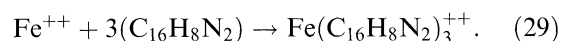


FIGURE 11 Formation of ferrous tris-dipyridyl ion at 290 K.

closed form, requiring the empirical data points for the concentration term.

The formation of the ferrous tris-dipyridyl ion in acetic acid solution was determined by Baxendale and George (1950) to be fourth order, with the  $\text{Fe}^{++}$  ion reacting with each of the three dipyridyl

molecules in a stepwise fashion.



The final step involving  $\text{Fe}(\text{C}_{16}\text{H}_8\text{N}_2)_2^{++}$  was the slowest and hence rate determining.

As is evident from Fig. 11, the Natural Path velocity computed from

$$-\mathcal{V}_i = [\dot{\mathcal{A}}_{T,V}/RT]/[1/[\text{Fe}^{++}] + 9/[\text{Dipy}] + 1/[\text{Fe}(\text{Dipy})_3^{++}]] \quad (30)$$

follows the fourth order mechanism, although this velocity computed from Eq. (25) had no mechanistic input. It is interesting to note that Eq. (25) resembles the expression derived by King (1979) to describe the rate at which a reacting system perturbed from equilibrium returns to equilibrium.

## PHENOMENOLOGICAL APPROACH

For well over a century the analytical description of rate processes has been based on a linear phenomenological description of irreversible thermodynamics wherein a flux term  $\mathcal{J}_i$  identified with an escape tendency or velocity is related to a force term  $\mathcal{X}_i$  which generally take the form of a spatial gradient.

$$\mathcal{J}_i \propto f(\mathcal{X}_i). \quad (31)$$

For non-equilibrium processes such as heat, charge and mass flow the linear approach has been found to be extremely successful. In fact, this approach so excels in the study of these non-equilibrium processes, particularly with regard to reciprocity as discovered by Onsager (1931), that the linear phenomenological approach might be termed the first law of irreversible thermodynamics. However, as Van Rysselberge (1962) indicated the flux-force approach has been uniformly unsuccessful for describing homogeneous chemical reactions. Although  $\mathcal{J}_i$  can be readily identified with the reaction velocity  $\mathcal{V}_i$ , according to Anderson and Boyd (1971) a spatial gradient  $\mathcal{X}_i$  cannot be identified.

Prigogine *et al.* (1948) attempted to relate the force term  $\mathcal{X}$  to the chemical affinity  $\mathcal{A}_i$ .

$$\mathcal{V}_i \propto \mathcal{A}_i. \quad (32)$$

However, Manes *et al.* (1950) found that correlation of the empirical data by Expression (31) is not successful.

By comparing Expression (36) with Eq. (26) it is evident that there is a direct contradiction between them. According to the Natural Path approach  $\mathcal{V}_i$  is proportional to the affinity rate  $\mathcal{A}_{T,\mathcal{V}}$  while according to the phenomenological approach  $\mathcal{V}_i$  is proportional to the affinity  $\mathcal{A}_i$ .

Figure 12 illustrates the correlation between  $\mathcal{V}_i$  and  $\mathcal{A}_i$  according to Expression (36) for the isomerization of ethylenecyclopropane to 2-methyl-methylenecyclopropane at 507 K and indicates that even on close approach to equilibrium a linear relationship is contrary to observations.

In contrast the Natural Path velocity was derived directly from thermodynamic considerations and is correlated by the empirical data. A simple isomerization reaction was chosen because it involves minimal complications and experimental data is

available on close approach to equilibrium. All that can be definitely concluded about these two approaches is that the two affinity decay paths vanish concurrently.

## MECHANISTIC CONSIDERATIONS

It is axiomatic that thermodynamics concerns itself with equilibrium states, not the mechanism required for a chemical reaction to attain any equilibrium state from any other. For example consider the recombination of monatomic iodine in various inert diluents.



Figure 13 illustrates the decreasing gas pressure  $P_1$  of the monatomic iodine with elapsed time for five inert diluents M.

It is evident that inert gases have a pronounced effect on the reaction velocity. As generally agreed by kineticists, according to Kondratiev and Nikitin (1981) the most probable mechanism involves two

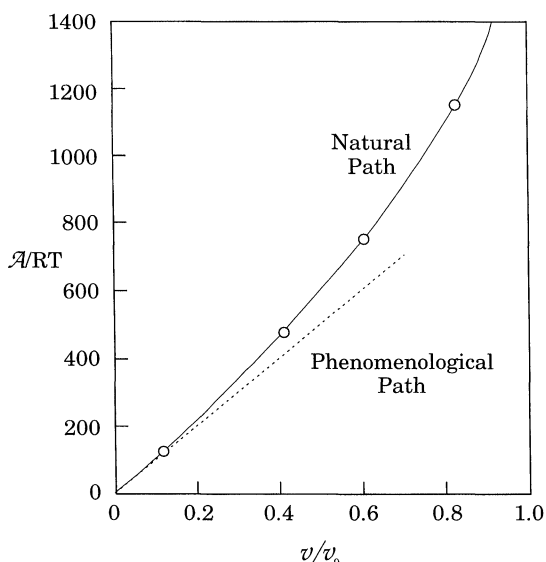


FIGURE 12 Approach to equilibrium.

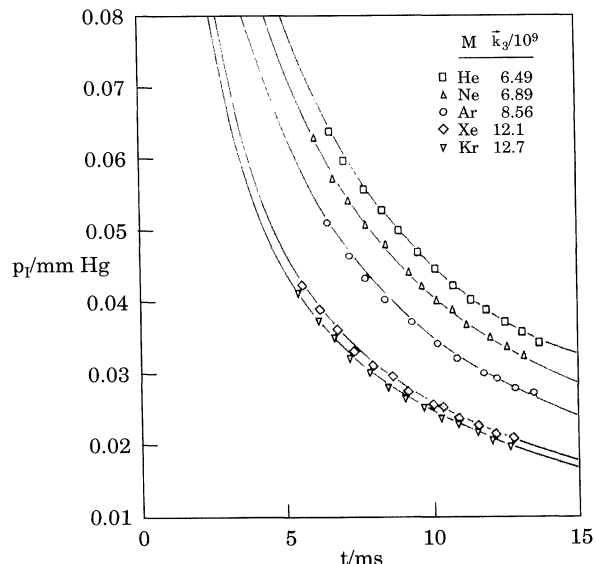


FIGURE 13 Recombination of monatomic iodine at 290 K.

intermediate steps:



where M represents either He, Ne, Ar, Xe or Kr. This model involves a metastable molecule IM in equilibrium with the reactant and diluent.

The rate equation for the recombination reaction according to the rate controlling step (34b) is simply

$$-\mathcal{V} = \vec{k}_2[IM][I] \quad (35)$$

where  $\vec{k}_2$  is the second-order rate constant. The reverse reaction is negligible over the experimental period of observation.

Because IM is in equilibrium with I and M according to Reaction (34a) the equilibrium constant  $K = [IM]/[I][M]$ . Consequently Reaction (35) can take the form

$$-\mathcal{V} = \vec{k}_3[I]^2[I] \quad (36)$$

where the third-order rate constant  $\vec{k}_3 = \vec{k}_2 K$ . According to Eq. (36) the reaction velocity is directly dependent on the concentration of the inert gas present.

Integrating Eq. (36) yields

$$1/[I] = \vec{k}_3[M]t + 1/[I]_0 \quad (37)$$

where  $[I]_0$  is the initial concentration of monatomic iodine. Figure 14 illustrates this third-order recombination reaction.

The different slopes shown in Fig. 14 do not arise from thermodynamic considerations inasmuch as the initial  $T_1$ ,  $V_1$ ,  $P_1$  and  $\mu_1$  of the monatomic iodine were essentially identical for the five reactions examined. Hence these differences must arise solely from mechanistic considerations which should have no effect on thermodynamic considerations in general and the Natural Path in particular.

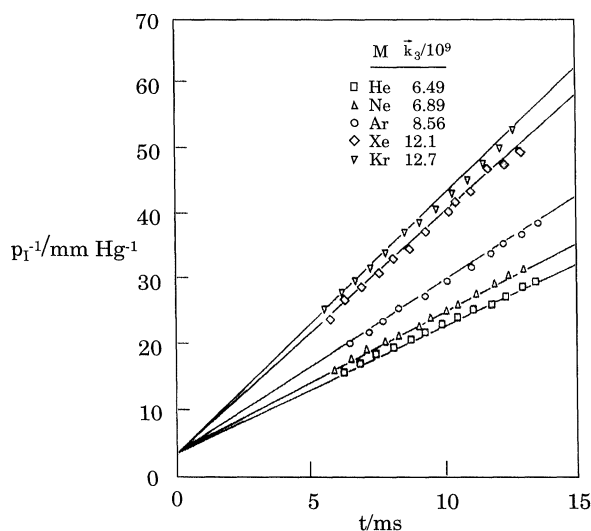


FIGURE 14 Third-order recombination reaction.

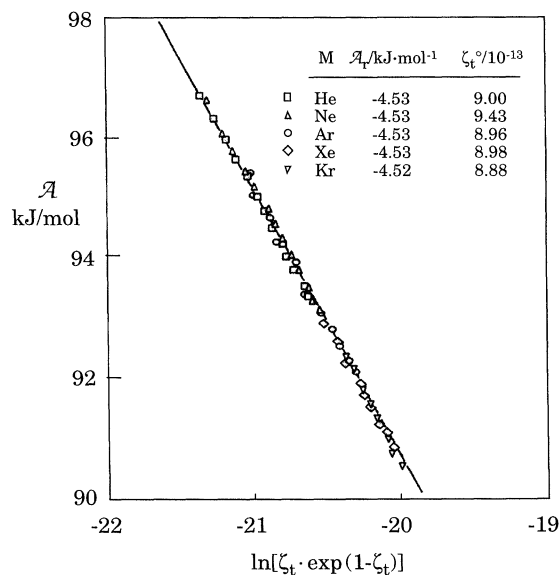


FIGURE 15 Recombination along a Natural Path.

Figure 15 illustrates the empirical data for the five recombination reactions plotted according to Natural Path Eq. (17).

Figures 14 and 15 illustrate the high degree of correlation of the empirical data possible with these diametrically opposite approaches to chemical

reaction dynamics. *Mechanistically*, the particular inert gas present has a pronounced effect on the rate of the recombination reaction, as shown by the five reaction paths illustrated in Fig. 14. *Thermodynamically*, the particular inert gas present has no effect whatsoever on the rate of the recombination reaction, as shown by the single reaction path illustrated in Fig. 15. This apparent paradox is not too surprising however for mechanistic considerations cannot be introduced into a relationship involving thermodynamic functions otherwise, for example, catalysis would affect chemical equilibrium.

This point can be demonstrated by considering the previously discussed standard state where  $t_1$  is the expected time for the chemical affinity  $\mathcal{A}_i$  to reach its standard value  $\mathcal{A}^0$ . From Eq. (24) the standard chemical affinity, a thermodynamic function, can be represented as a function of two constants:  $\mathcal{A}_r$  and  $\zeta_i^0$ .

The values of these two constants can be calculated from the experimental data for the five recombination reactions and are listed in Fig. 15. They are essentially invariant, indicating that  $\mathcal{A}_r$  and  $\zeta_i^0$  are themselves thermodynamic constants. In contrast the reaction rates  $\vec{k}_3$ , listed in Fig. 14, have roughly doubled in value, indicating their essentially mechanistic nature.

Although  $\zeta_i^0$  is a thermodynamic constant, recall that  $\zeta_i^0 = t_1/t_K$ , and this thermodynamic qualification is not necessarily valid individually for  $t_1$  and  $t_K$ . As is evident from Fig. 16 these quantities vary systematically and consequently, like  $\vec{k}_3$ , are mechanistic constants. This being the case, the possibility presents its self that these quantities can be correlated, finally establishing a relationship between the thermodynamic and the mechanistic approaches. That such a possibility is not valid can be demonstrated.

If  $t_1$ ,  $t_K$  and  $\vec{k}_3$  were related then  $t_1$  and  $t_K$  must be inversely proportional to some function of the rate constant  $f(\vec{k}_3)$  as the more rapid the reaction the shorter period required to reach any defined state.

$$t_1^{-1} \propto f_i(\vec{k}_3) \quad t_K^{-1} \propto f_{ii}(\vec{k}_3). \quad (38a)$$

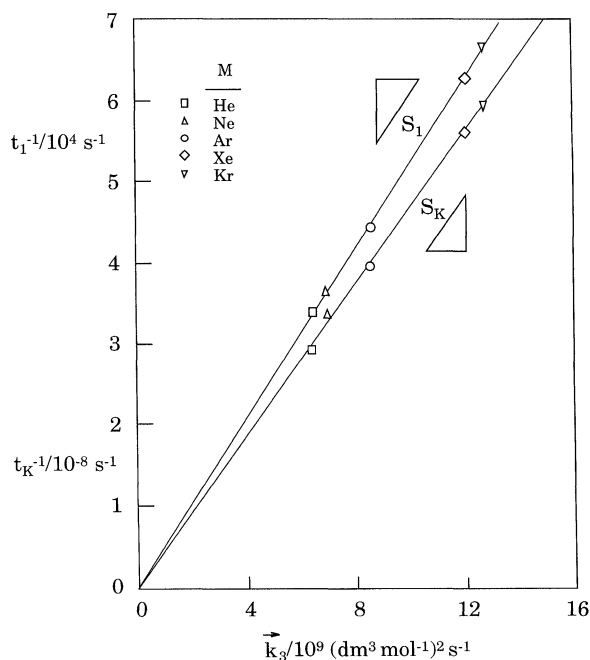


FIGURE 16 Correlation of reaction constants.

Accordingly

$$\zeta_i^0 = t_1/t_K = f_i(\vec{k}_3)/f_{ii}(\vec{k}_3). \quad (38b)$$

The least complex form that the functions  $f_i(\vec{k}_3)$  and  $f_{ii}(\vec{k}_3)$  can assume for the purpose of correlating  $t_1$ ,  $t_K$  and  $\vec{k}_3$  is simply  $f_i(\vec{k}_3) = \vec{k}_3$  and  $f_{ii}(\vec{k}_3) = \vec{k}_3$ , and consequently

$$t_1^{-1} \propto \vec{k}_3 \quad t_K^{-1} \propto \vec{k}_3. \quad (39a)$$

Figure 16 illustrates that Expression (38b) effectively correlates  $t_1$  and  $t_K$  with  $\vec{k}_3$ . Because the lines of regression of Fig. 16 pass through the origin

$$t_1^{-1} = \vec{k}_3 S_1 \quad t_K^{-1} = \vec{k}_3 S_K \quad (39b)$$

where  $S_1$  and  $S_K$  are the appropriate slopes of Fig. 16. Consequently

$$\zeta_i^0 = t_1/t_K = \vec{k}_3 S_K / \vec{k}_3 S_1. \quad (40)$$

Although Fig. 16 ostensibly illustrates an inverse correlation of  $t_1$  and  $t_K$  with  $\vec{k}_3$  this is without mechanistic significance because  $\vec{k}_3$  cancels out of the equation. What remains is the trivial relationship  $\zeta_i^0 = S_K/S_1$ . Expectedly, any thermodynamic quantity such as  $\zeta_i^0$  cannot be related to any mechanistic quantity such as  $\vec{k}_3$ .

## THERMODYNAMIC CORRELATIONS

To extract equilibrium thermodynamic functions such as the standard Helmholtz function  $\Delta F^0$  from non-equilibrium quantities such as the affinity rate constant  $\mathcal{A}_r$  would not appear to be possible inasmuch as the standard affinity  $\mathcal{A}^0$  is required to calculate  $\mathcal{A}_r$  while  $-\mathcal{A}^0 \equiv \Delta F^0$ . That this limitation can be overcome was demonstrated by Garfinkle (1985).

Substituting for the chemical affinity in Eq. (17) from Eq. (9a) and  $\zeta_{t_i} = (t_i/t_K)$  yields

$$RT \ln(Q_i) = \mathcal{A}_r \ln[(t_i/t_K) \exp(1 - t_i/t_K)] + I \quad (41)$$

where the intercept term  $I$  is presumably equal to the standard affinity  $\mathcal{A}^0$ . However with  $\Delta F^0$  unknown and consequently  $\mathcal{A}^0$  unknown this assumption has no foundation. All that is really apparent is that Eq. (41) relating the variables  $Q_i$  to  $t_i$  has three unknowns:  $\mathcal{A}_r$ ,  $t_K$  and  $I$ . Knowledge of any one unknown would allow the other two to be determined from a regression analysis. Because the resultant slope of the analysis is  $\mathcal{A}_r$  and the intercept is  $I$  according to Eq. (41) the value  $t_K$  can be systematically varied until the best correlation is achieved, in this case measured by the coefficient of determination ( $r^2$ ) reaching a maxima.

For example consider the dehydrogenation of isobutane by iodine vapor at 525 K described by Eq. (15). The effect of the chosen values of  $t_K$  on the regression analysis is shown in Table III.

As is evident from this tabulation the intercept  $I$  varies monotonically with  $t_K$ . However the regression analysis conducted for each value of  $t_K$  exhibits

TABLE III Determination of intercept term

$t_K$ (ks)	$I$ (kJ/mol)	Coefficient of determination
25.2	-29.8	96.5
26.0	-29.7	97.0
26.6	-29.5	97.5
27.5	-29.3	98.0
28.8	-29.1	98.5
30.2	-28.8	99.0
32.7	-28.3	99.5
39.8	-26.9	99.9
53.1	-24.7	99.5
63.8	-23.3	99.0
75.9	-21.8	98.5
91.2	-20.2	98.0
112	-18.3	97.5
141	-16.2	97.0
191	-13.3	96.5
275	-9.71	96.0
501	-3.62	95.5
2510	+13.5	95.0

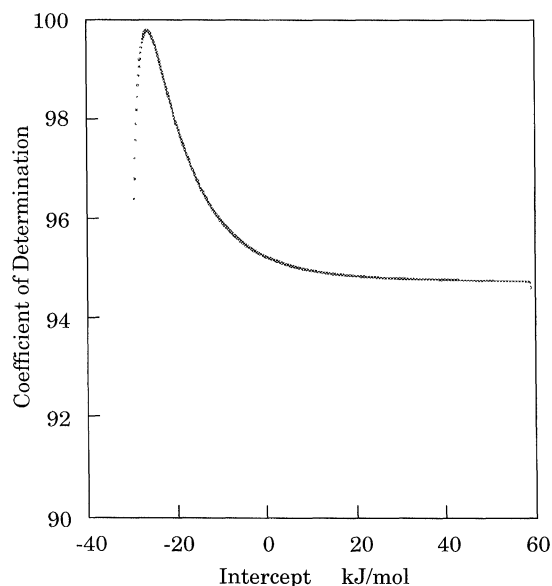


FIGURE 17 Iterative regression analysis for dehydration of isobutane at 525 K.

a distinct maxima in the coefficient of determination as illustrated in Fig. 17. Each point is the iterative result of a separate regression analysis. The intercept value at the maxima in the coefficient of determination  $-26.9$  kJ/mol. The value of  $-\Delta F^0$  at 525 K reported by Stull *et al.* (1969) is  $-26.8$  kJ/mol.

TABLE IV Determination of Helmholtz functions

Reaction	Temp (K)	$\Delta F^0$ (experimental)	kJ/mol (extracted)	Error (%)	$1/\zeta_r$ (max)	References
Dehydrogenations of isobutane by iodine	525	-26.8	-26.9	0.37	1.6	Benson (1963)
Isomerization of ethylenecyclopropane	507	-0.994	-0.758	-23.7	2.0	Chesick (1963)
Styrene and iodine in carbon tetrachloride	295	-0.234	-0.304	29.9	2.0	Fraenkel and Bartlett (1959)
Reduction of Pu(IV) by Fe(II) in perchloric Acid	279	-18.5	-16.5	-10.8	23	Newton and Cowan (1960)
Formation of ferrous tris-dipyridyl Ion	290	-94.7	-85.4	-9.8	217	Baxendale and George (1950)
Formation of nitrosyl chloride	333	-36.5	-30.1	-17.5	416	Welinsky and Taylor (1938)

Using this technique kinetic data was subject to a regression analysis to extract Helmholtz functions. The results for six reactions are listed in Table IV.

Considering the extent of extrapolation  $1/\zeta_r$  required to extract the Helmholtz functions, in the most extreme case shown in Table IV: more than 400 fold, the resultant correlation is quite remarkable in terms of the absolute nature of the extraction. The height of the determination peak above the plateau, as shown in Fig. 17 for comparison with Fig. 16, diminishes with extent of extrapolation and is not present at all for most of the reactions examined (Fig. 18).

An alternative technique was also found by Garfinkle (1983b) to extract standard thermodynamic functions using the temperature dependency of the standard Helmholtz function.

The standard affinity  $\mathcal{A}^0$  has the same temperature dependency as does the standard Helmholtz function  $\Delta F^0$  and accordingly

$$\left[ \frac{\partial(\mathcal{A}^0/T)}{\partial(1/T)} \right]_V = -\Delta U^0 \quad (42)$$

where  $\Delta U^0$  is the standard internal energy difference between the products and reactants of a chemical reaction.

Integrating Eq. (24) with respect to  $1/T$  in accordance with Eq. (42) yields

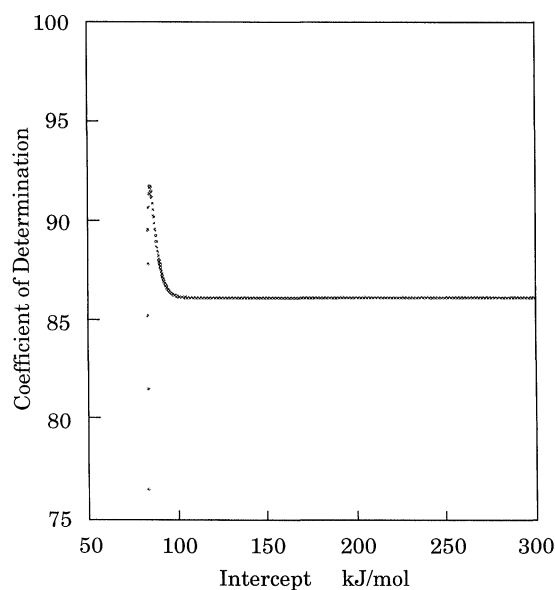


FIGURE 18 Iterative regression analysis for formation of dipyrindyl ion at 290 K.

$$-\Delta U^0 = \ln[\zeta_r^0 \exp(1 - \zeta_r^0)] \left[ \frac{\partial(\mathcal{A}_r/T)}{\partial(1/T)} \right]_V + \frac{\mathcal{A}_r}{T} \left[ \frac{\partial \ln[\zeta_r^0 \exp(1 - \zeta_r^0)]}{\partial(1/T)} \right]_V \quad (43)$$

Inasmuch as  $\Delta U^0$  is essentially constant over the temperature range at which chemical reactions are ordinarily observed, then the quantities in brackets



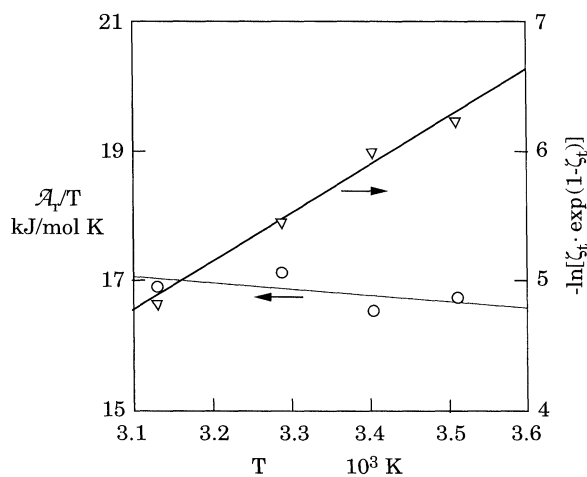


FIGURE 19 Temperature dependency of the affinity rate constants.

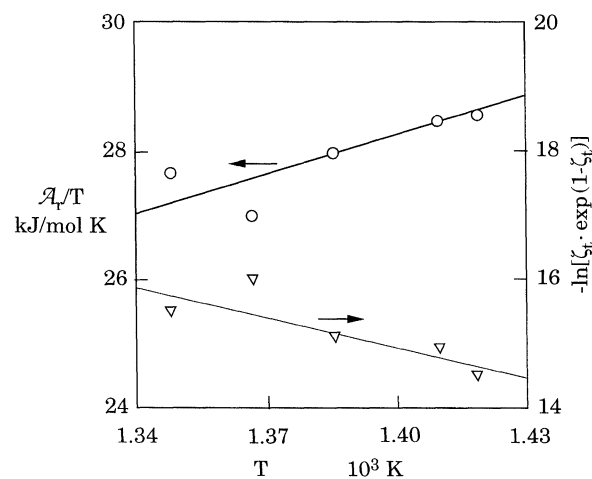
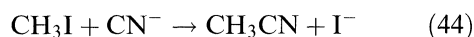


FIGURE 20 Temperature dependency of the affinity rate constants.

must themselves be essentially constant over the same temperature range. Two reactions will be examined in regard to these expectations.

Consider first the temperature dependency for the affinity decay constants for the reaction of methyl iodide with cyanide in aqueous solution.



This was investigated by Lynn and Yankwich (1960) in the temperature range of 280–335 K.

The second reaction examined is the pyrolysis of hydrogen peroxide by Forst (1958) as described by Eq. (19).

Using the slopes shown in Figs. 19 and 20 and the data points shown in Table V the standard internal energies  $\Delta U^0$  were calculated according to Eq. (43).

The absolute nature of these calculations should be noted: classical thermodynamic functions are computed from non-equilibrium thermodynamic parameters. The agreement between values obtained from these widely diverse sources is quite good, confirming that the temperature dependency of the affinity decay rate is analogous to the temperature dependency of the Helmholtz free energy of the equilibrium system.

## DISCUSSION

The veracity of this thermodynamic approach to chemical reaction kinetics is explicitly dependent upon the validity of the reciprocal time dependency of the affinity decay as represented by Expression (11), and in large measure the objective of this paper is to demonstrate this validity. Because Expression (11) was not derived nor has any recognized antecedents in the field of irreversible thermodynamics this difficult task was accomplished by approaching validation from several directions.

Primarily validation was effected by demonstrating that stoichiometric chemical reactions in a closed isothermal system follow a specific affinity-decay path independent of reaction mechanism. The analytical description of this reaction path was derived from Expression (11) and the high degree of data correlation achieved was convincing evidence that this approach had merit. Because the reaction path was not forced by the investigator it is sufficiently distinguishable to be denoted as Natural Path.

A thermodynamic reaction velocity was derived from Expression (11) that could be compared to the reaction velocity derived from Mass Action considerations. Kineticists derive the appropriate

TABLE V Calculated and experimental internal energy values

Reaction	$T$ (K)	Eq. (24) parameters		$\Delta U^0$ (kJ/mol)	
		$\mathcal{A}_r$ (kJ/mol)	$\zeta_r^0$	Eq. (40)	Thermo data
$\text{CH}_3\text{I} + \text{CN}^- \rightarrow \text{CH}_3\text{CN} + \text{I}^-$	285	-4.76	$7.22 \times 10^{-4}$	-59.3	
	294	-4.85	9.17	-58.8	
	304	-5.21	16.4	-61.5	
	319	-5.40	30.2	-61.3	
				Av -60.2	-60.0
$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	705	-19.5	$6.35 \times 10^{-8}$	-206	
	713	-19.2	4.73	-187	
	722	-20.2	9.81	-219	
	732	-20.8	14.3	-234	
	442	-21.2	17.4	-239	
				Av -217	-212

reaction rate equation for a particular chemical reaction from consideration of reaction mechanism. Hence there is a choice of Mass-Action rate equations depending on the chosen mechanism. In contrast, because the Natural Path is independent of reaction mechanism, only a single rate equation could be derived from thermodynamic considerations. Invariably the thermodynamic rate equation coincided with the Mass-Action rate equation most appropriate to the reaction mechanism, demonstrating the probable validity of Expression (11).

The principal discrepancy between these two approaches concerns the expected time to attain equilibrium  $t_K$ . According to Mass Action considerations  $t_K = \infty$  while the Natural Path is predicted to terminate at  $t_K < \infty$ . Equilibrium can be defined as a state whose macroscopic properties are time invariant but this definition does not preclude microscopic fluctuations about a mean value of these properties. Percival (1961) relates that Boltzmann argued that the energy probability distribution in an isolated system is itself an almost periodic function of time that effectively never repeats itself. That is, the probability distribution itself fluctuates with a period that approaches infinity. Hence some displacement must always be present between a system approaching equilibrium and the state defined as equilibrium by virtue of its canonical distribution. In contrast Prigogine *et al.* (1961) argued that as long as the system has a finite

volume encompassing a finite number of particles, its energy distribution must in some finite period attain its canonical form.

From either of these arguments the conclusion can be reached that the displaced system can attain macroscopic equilibrium within any desired degree of precision without having to attain microscopic equilibrium. That is, microscopic time invariance is possible in some finite period depending on how the elapsed time is represented. Because this study pertains to the time dependence of a thermodynamic function, it only macroscopic time variance which concerns us.

Evidently the crucial consideration in this analysis of the approach to equilibrium is that it is concerned with probabilities: the probability of an event occurring in accordance with some statistical probability function. Under these circumstance the absolute certainty of any specific event occurring must require an infinite period of time, whether the time to attain equilibrium or to attain any other state. Fortunately, it is only the *expected* time to attain equilibrium with which we are concerned, and must have a finite period according to any distribution function.

Accordingly, when Baierlein (1971) asserts that the nuclear spin in LiF attains equilibrium on the order of  $10 \mu\text{s}$ , or that it requires as long as five minutes for vibration equilibrium to be attained, these values of  $t_K$  can only be interpreted as

expected times. There exists an exceedingly small but finite probability that equilibrium might instantaneously be attained, or not at all. Similarly with chemical reaction equilibrium: only expected times such as  $t_K$  have significance, and these are finite.

Probably the strongest validation of the Natural Path concerns the extraction of thermodynamic functions from empirical kinetic data because this process requires that Expression (11) and  $t_K < \infty$  both be valid. Essentially the kinetic data of the reactions examined were extrapolated from the range of empirical observations out to  $t_K$  in order to extract standard Helmholtz functions. The results were quite good considering the absolute nature of the extrapolation, with the experimental and extracted values generally agreeing within ten percentage points, and for several extrapolations within a few percentage points.

Having ostensibly established the validity of the Natural Path approach to the study of chemical reaction kinetics the question arises as to the ramifications of the approach.

Substituting for the chemical affinity in Eq. (17) from Eq. (9b) yields

$$\zeta_{Q_i} = [\zeta_{t_i} \cdot \exp(1 - \zeta_{t_i})]^{A_r^*} \quad (45)$$

where  $A_r^* = A_r/RT$ . All of the quantities involved in Eq. (45) are unitless ratios, a rather intriguing outcome. Accordingly this extent of reaction relationship can be considered the most basic description of the Natural Path inasmuch as it is free of any dimensions whatsoever. Essentially this extent of reaction relationship is the master equation of the Natural Path. Figure 21 is a plot of Eq. (45) for various value of  $A_r^*$ .

According to the formalism of Gontar (1993) the extent of reaction  $\zeta_{Q_i}$  would be a secondary variable related to the primary concentration variable  $\xi_i$ . Unlike primary variables, for example  $c_{m_i}$  or  $a_{m_i}$ , the secondary variables are dimensionless. In this regard Gontar and Il'in (1991) developed his  $\pi$ -theorem of the theory of similarity and dimensionality in relation to stoichiometric chemical reactions as a bridge between the continuous time and space

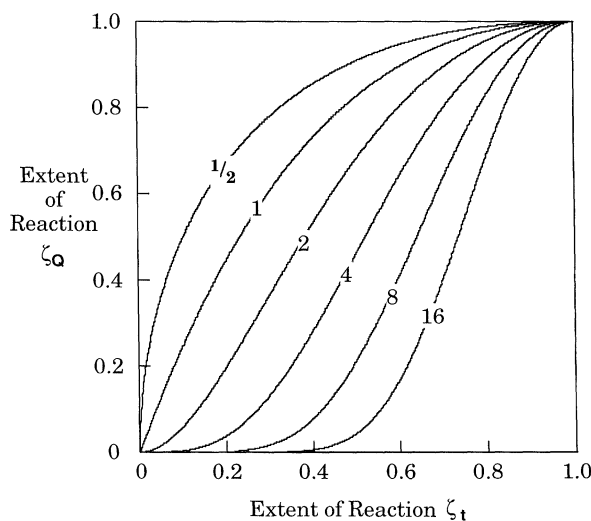


FIGURE 21 Extent of reaction relationship for various values of  $A_r^*$ .

of differential equations and the discrete stepwise process of calculation. What is most intriguing about the  $\pi$ -theorem in relation to Eq. (45) is that Gontar's proposal essentially supports the concept that empirical dimensions are essentially artificial (societal) and consequently contrivances (arbitrary).

As an example Gontar considered a chemical reaction comprising three interdependent reactions. The relationship between the five reacting components present in the reacting system along with an elapsed time function Gontar arranged as a matrix to account for all of the practical reactions between these reacting species, which amounted to three.

By coincidence one of these three reactions is Reaction (33) of this paper: the formation of a homonuclear molecule from monatomic reactants. Gontar broke with the conventional Mass Action representation of this reaction however and instead expressed the time-dependent concentration term as

$$X_6/X_2^2 = \pi_3 \quad (46)$$

which is equivalent to  $I_2/I^2 = Q_i$  of Eq. (3). Accordingly  $\pi_3 \equiv Q_i$  and these are secondary quantities

with the virtue of *absoluteness of relation*. Moreover, by dividing both  $\pi_3$  and Gontar's time function  $\theta_t$  by a constant, in regard to the Natural Path the constants  $K$  and  $t_K$  respectively, these ratios are equivalent to  $\zeta_{Q_i}$  and  $\zeta_{t_i}$  and are related by Eq. (45). Accordingly, Gontar's approach using the theory of similarity and dimensionality is in complete agreement with the Natural Path approach.

## CONCLUSION

The Natural Path approach to chemical reaction kinetics is not only a break with the Mass Action approach to chemical kinetics but also with the phenomenological approach to chemical kinetics of irreversible thermodynamics. Ostensibly the great weakness of the Natural Path approach is that it depends absolutely on an affinity rate equation that has no antecedents. Nevertheless this approach can correlate empirical kinetic data with a high degree of precision, at least equal to that achievable by the Mass-Action rate equations, but without recourse to mechanistic considerations. The reaction velocities arising from the particular rate equation chosen by kineticists to best represent the Mass Action behavior of a chemical reaction are the natural outcome of the Natural Path approach. Moreover, by virtue of its thermodynamic roots, equilibrium thermodynamic functions can be extracted from reaction kinetic data with considerable accuracy. These results support the intrinsic validity of the Natural Path approach.

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