Extraction of Standard Helmholtz Functions from Affinity Rate Data

BY MARVIN GARFINKLE

Department of Materials Engineering, Drexel University, Philadelphia, Pennsylvania 19104, U.S.A.

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An extrapolation procedure to extract standard Helmholtz functions from empirical kinetic data without reference to reaction mechanisms has been developed using an analytical description of the affinity decay rate.

The kinetic behaviour of chemical reactions is conventionally described in terms of the change in concentration of reacting components with elapsed time. In this concentration-time coordinate system the description of the reaction path is found to be dependent on the reaction mechanism,¹ and so the diverse analytical expressions required to describe these paths have a distinct derivation and formulation that is also dependent on reaction mechanism. Consequently this microscopic approach to chemical kinetics is most advantageous in elucidating reaction mechanisms and specifying transitory reactions and species required for reactions to occur. A further advantage is that the reacting components can be considered to be classical oscillators, and so the approach is ideally suited to a statistical-mechanical analysis. With suitable quantum-mechanical corrections where applicable, this formalism has allowed the kinetic behaviour of some very simple reactions to be fully characterised from energy-partition considerations alone and has permitted very important insights to be gained concerning more complex reactions.^{2,3} However, because it is dependent on reaction mechanism, it emphasizes the dissimilarities between diverse reactions. Thus even the rate constants computed from empirical data or analytical models have units that permit direct comparisons only with reactions with similar mechanisms.

Descriptive diversity is not required when kinetic behaviour is examined by the alternative macroscopic approach in which the reacting system is considered simply as a sink or source of energy. When the reaction paths are described in this energy-time coordinate system, fundamental similarities are evident between diverse reactions despite significant mechanistic differences.

The results of such a macroscopic examination have been published in a series of papers in which the time rate of change of the chemical affinity A, a thermodynamic function introduced by de Donder,⁴ was examined for homogeneous stoichiometric chemical reactions proceeding in a closed isothermal system. Only for reactions proceeding under these restrictive conditions can the affinity be computed as a function of state. The kinetic data required for this study were gathered from tabulations that had appeared in the literature or from investigators whose results had appeared in the literature. Fortunately, most reaction-kinetics investigations are conducted under precisely the conditions required.

As a consequence of this investigation, it was demonstrated that (a) kinetic

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behaviour can be described in terms of an affinity rate equation, ${}^{5}(b)$ the kinetic elapsed time does not necessarily coincide with the thermodynamic elapsed time, ${}^{6}(c)$ reaction velocities can be related to the affinity decay rate⁷ and (d) the temperature dependence of the affinity decay rate is analogous to that of the Helmholtz function.⁸

The sine qua non of this thermodynamic analysis of reacting systems was the derivation of the affinity rate equation. This derivation was predicated on two propositions: (1) that the affinity decay rate is independent of mechanistic considerations and (2) that the most probable time required for the reaction to attain any thermodynamically defined state is finite; *i.e.* the reaction is assumed to follow a unique path in an affinity-time coordinate system that can be described without reference to reaction mechanism, and this path's *terminus a quo* and its *terminus ad quem* occur at states that can be explicitly defined by thermodynamic and temporal coordinates. Accordingly, with the initial and final states of the system defined in an energy-time coordinate system, it was demonstrated that the reaction path along which a thermodynamic function varies with time can be described explicitly in the same coordinate system.

The objective of the present paper is to demonstrate, with only the initial state defined, that the terminal state can be described from an analytical description of the path alone without reference to mechanistic consideration. The concentration-time data gathered by kineticists have concealed within them the required description of the terminal state of the system: thermodynamic equilibrium.

METHOD OF APPROACH

The affinity rate equation previously derived⁵ takes the form

$$\dot{A}_{T,V} = A_{\rm r} \left(\frac{1}{t - 1} \right) \tag{1}$$

for a homogeneous stoichiometric reaction proceeding in a closed isothermal system of fixed volume V and constant temperature T, where $\dot{A}_{T,V}$ is the affinity decay rate $(\partial A/\partial t)_{T,V}$, A_r is a proportionality constant, t is the elapsed time and t_K is the most probable time required for the reaction to attain its equilibrium state. The significance of these parameters was discussed previously,⁵ along with the means by which they are computed from empirical kinetic data.

The reactions considered in this study are assumed to commence from a thermodynamically defined initial state Q = 0 at t = 0. The activity ratio Q is defined by the relationship

$$Q = \prod_{i} (a_i)^{\nu_i} \tag{2}$$

where a_i is the activity and v_i is the stoichiometric coefficient of reacting component *i*. Thus, the reaction proceeds from the initial state Q = 0 and t = 0 to the terminal state Q = K and $t = t_K$, where K is the thermodynamic equilibrium constant. The progress of the reaction from its initial to its terminal state can thus be expressed by two dimensionless extents of reaction: $\zeta_t = t/t_K$ and $\xi_Q = Q/K$.

The chemical affinity in any arbitrary state as defined by Prigogine and Defay⁹ can be related to its standard-state value A° by an equation of the form

$$A = A^{\circ} - \mathbf{R}T \ln Q. \tag{3}$$

Consequently $A^\circ = \mathbf{R}T \ln K$, and the initial and terminal states of the system can be represented in the affinity-time (A, t) coordinate system by the coordinates $(\infty, 0)$ and $(0, t_K)$, respectively.

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	internet T	coefficient
	intercept, I	or
t_K/ks	/kJ mol ⁻¹	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

Table 1. Affinity decay rate intercept terms for the dehydrogenation of isobutane
by iodine $vapour^a$

^a T = 525 K, $[C_4H_{10}]_0 = 0.264$ atm and $[I_2]_0 = 0.127$ atm.

Integrating eqn (1) and substituting for ζ_t yields

$$A = A_{\rm r} \ln \left[\zeta_t \exp \left(1 - \zeta_t \right) \right]. \tag{4}$$

Eqn (4) constitutes the integrated affinity rate equation that describes the reaction path joining the initial and terminal states as defined in the affinity-time coordinate system. To correlate the empirical data according to eqn (4), the value of A is calculated from eqn (3), where activities are assumed equal to concentrations and the standard affinity has the same absolute value as the standard Helmholtz function: $A^{\circ} = -\Delta F^{\circ}$. The correct value for ζ_t is determined by a least-squares regression analysis in which various values of t_K are tested until the intercept vanishes. The affinity rate constant A_r is equal to the slope.

It is apparent that the Helmholtz function must be known to correlate empirical data according to eqn (4). However, it is precisely the value of the Helmholtz function that we are seeking from a correlation of the kinetic data. That such a determination is ostensibly not feasible can be illustrated by substituting for A in eqn (4) from eqn (3) to yield

$$\boldsymbol{R}T \ln Q = -A_{\rm r} \ln \left[\zeta_t \exp\left(1 - \zeta_t\right)\right] + I \tag{5}$$

where the intercept term I is presumably equal to the standard affinity A° . However, with the Helmholtz function unknown, this assumption has no foundation. All that is really apparent is that we have one equation with three unknowns: A_r , t_K and I. Knowledge of any one would allow the other two to be determined by regression analysis. However, with all three unknown, it is evident that no analytical expression

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is available that relates a standard thermodynamic function to kinetic parameters. This observation can be illustrated by example.

Consider the dehydrogenation of isobutane by iodine vapour at 525 K. Using the tabulated⁵ kinetic data supplied by Teranishi and Benson¹⁰ with arbitrary values of t_K , various intercept values were computed using eqn (5). These are listed in table 1.

As is evident from this tabulation, increasing values of t_K simply result in increasing values of the intercept term *I*. No points of inflection or maxima or minima in the intercept tabulation are discernible that might indicate some special value for *I*. Nevertheless, if the affinity rate equation is valid, then the reaction path described by eqn (5) must terminate at a singular state whose coordinates are concealed within the information listed in table 1. An analytical procedure will now be described that permits the values of these three unknowns to be determined from kinetic data alone without *a priori* knowledge of the Helmholtz function.

ANALYTICAL PROCEDURE

Because regression analysis is required to determine the value of the intercept term in eqn (5), the degree of data correlation achieved is sensitive to the factors used in this analytical expression, in this case the value of t_K . Consequently, at some arbitrary value of t_K data correlation should be optimized. The most sensitive test of data correlation is the coefficient of determination,¹¹ which in this case measures the percentage of the variance in **R**T ln Q that is attributable to ζ_t in accordance with eqn (5). It is a test of association between variables.

For an infinite number of possible values of t_K there is a corresponding number of values of the coefficient of determination. The maximum value of the coefficient of determination will indicate the corresponding value of t_K responsible for optimum data correlation. Thus, the coordinates of the equilibrium state $(0, t_K)$ are specified.

This correlation test is a process of extrapolation in which the coordinates of the terminal state of the reaction path are determined beyond the range of empirical data observations. However, a correlation test is not necessarily an unequivocal test of analytical validity. Fortunately, because the determination of any one of the three unknowns of eqn (5) will permit all of them to be determined by the regression analysis, the value of I at optimum data correlation can be determined. That is, for every value of t_K there is a corresponding value of I, as can be seen from table 1. Moreover, according to the derivation of eqn (5), the value of I at optimum data correlation is met it would constitute an unequivocal test of the validity of the affinity rate equation and demonstrate that a standard thermodynamic function can be determined from kinetic data alone without recourse to mechanistic considerations.

The following empirical analysis was conducted in order to test this condition at optimum data correlation. Five chemical reactions with various degrees of mechanistic complexity are examined. Fig. 1(a)-(e) are direct reproductions of computer-generated graphics and show the variation of the coefficient of determination with the intercept term *I*. Because no analytical expression is available to relate these variables, the results are displayed as points, each of which represents the results of a separate regression analysis.

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EMPIRICAL ANALYSIS

First let us consider the dehydrogenation of isobutane by iodine vapour:

$$C_4 H_{10} + I_2 \to C_4 H_8 + 2HI.$$
 (6)

The reaction proceeds by means of a free-radical chain mechanism. As illustrated in fig. 1(*a*), the coefficient of determination for this reaction attains a maximum value. Using this information, the third column of table 1 lists the values of the coefficients of determination that correspond to the values of the intercept term *I*. The coefficient of determination reaches its maximum value at $t_K = 39800$ s, which defines the coordinates of the equilibrium state in the affinity-time coordinate system.

Because the 25000 s period of observation was > 60% ($\zeta_t = 0.62$) of the most probable time to attain equilibrium, the extent of extrapolation is not extreme. Consequently, the coefficient of determination curve of fig. 1(*a*) exhibits a sharp maximum. From the tabulated coordinates of the points of fig. 1, the optimum value of the intercept term *I* is shown in table 1 to be -26.9 kJ mol⁻¹. The accepted value¹² for the standard Helmholtz function $-\Delta F^{\circ}$ for this reaction 525 K is -26.8 kJ mol⁻¹.

The value of a standard thermodynamic function was extracted from reactionkinetic data without the need of either an explicit analytical expression or *a priori* knowledge of thermodynamic equilibrium data. That this close agreement between the extrapolated value of the intercept term and the known value of the Helmholtz function is not an anomaly will be demonstrated by the following examples.

Fig. 1 (b) illustrates the same coordinates as fig. 1, but for an isomerization reaction: the conversion of 2-methylmethylenecyclopropane to ethylidenecyclopropane at 507 K:



According to Chesick,¹³ for this first-order reaction $-\Delta F^{\circ} = 990$ J mol⁻¹. Because the 3500 s experimental period of observation was almost one-half ($\zeta_t = 0.47$) of the most probable time required to attain equilibrium ($t_K = 7400$ s), the extent of extrapolation was minimal. Accordingly, a sharp maximum appears in the coefficient of determination curve corresponding to a value of I = 996 J mol, indicating excellent agreement between I and $-\Delta F^{\circ}$.

According to Newton and Cowan,¹⁴ an ionic activated complex is involved in the second-order reduction of Pu^{IV} by Fe^{II} in perchloric acid solution at 289 K :

$$\mathbf{P}\mathbf{u}^{\mathrm{iv}} + \mathbf{F}\mathbf{e}^{\mathrm{ii}} \to \mathbf{P}\mathbf{u}^{\mathrm{iii}} + \mathbf{F}\mathbf{e}^{\mathrm{iii}}.$$
 (8)

The value of the standard Helmholtz function $-\Delta F^{\circ}$ computed from half-cell potentials¹⁵ is 18.5 kJ mol⁻¹. Because the 480 s period of experimental observations was short ($\zeta_t = 0.043$) compared with the most probable time required to attain equilibrium ($t_K = 11200$ s), a 20-fold extent of extrapolation beyond the period of observation was required to maximize the coefficient of determination. Nevertheless, the optimum value of the intercept of 16.5 kJ mol⁻¹ determined from the regression analysis and illustrated in fig. 1(c) indicates reasonable agreement between I and $-\Delta F^{\circ}$.

Carrying this analysis one step further, consider the illustration fig. 1(d) of the



Fig. 1. (a) Dehydrogenation of isobutane by iodine vapour at 525 K; $[C_4H_{10}]_0 = 0.264$ atm, $[I_{2}]_0 = 0.0127$ atm and $A^\circ = -26.8$ kJ mol⁻¹. (b) Conversion of 2-methylmethylenecyclopropane (2-Me) into ethylidenecyclopropane at 507 K; $[2-Me]_0 = 0.329$ atm and $A^\circ = 991$ J mol⁻¹. (c) Reduction of Pu^{IV} by Fe^{II} in perchloric acid solution at 279 K; $[Pu^{IV}]_0 = 0.00115$ mol dm⁻³, $[Fe^{II}]_0 = 0.00117$ mol dm⁻³ and $A^\circ = 18.6$ kJ mol⁻¹. (d) Formation of tris(bipyridyl)iron(II) ion in acetic acid solution at 290 K; $[Fe^{II}]_0 = 9.6 \times 10^{-6}$ mol dm⁻³, $[bipy]_0 = 28.8 \times 10^{-6}$ mol dm⁻³ and $A^\circ = 85.4$ kJ mol⁻¹. (e) Formation of nitrosyl chloride at 333 K; $[NO]_0 = 0.168$ atm, $[Cl_2]_0 = 0.0791$ atm and $A^\circ = 36.5$ kJ mol⁻¹.

intercept/kJ mol⁻¹

fourth-order formation of the tris(bipyridyl)iron(11) ion in acetic acid solution at 290 K:

$$Fe^{2+} + 3(bipy) \rightarrow Fe(bipy)^{2+}_3.$$
 (9)

According to Baxendale and George,¹⁶ the reaction rate is controlled by the stepwise addition of bipyridyl groups to the ferrous ion. Because the 29.5 s period of observation was exceedingly short ($\zeta_t = 0.0047$) compared with the most probable time required to attain equilibrium ($t_K = 6340$ s), a 200-fold extrapolation was required to determine the optimum value of the intercept term I = 85.4 kJ mol⁻¹. The standard Helmholtz function $-\Delta F^{\circ}$ determined for this reaction has the value 94.7 kJ mol⁻¹, indicating reasonable agreement despite the extent of extrapolation.

The final reaction to be considered illustrates the limit to which this extrapolation process can be carried. Welinsky and Taylor¹⁷ have examined the third-order formation of nitrosyl chloride at 333 K:

$$2NO + Cl_2 \rightarrow 2NOCl. \tag{10}$$

Their 2170 s period of observation was virtually insignificant ($\zeta_t = 0.0024$) compared with the most probable time required to attain equilibrium ($t_K = 8.92 \times 10^5$ s). Although the peak in the curve of fig. 1(e) is barely discernible, it did indicate the optimum value for the intercept term as determined from the regression analysis to be 28.8 kJ mol⁻¹. Considering the 400-fold extrapolation of the 36 min period of observation to the ten days most probably required to attain equilibrium, surprisingly good agreement is achieved with the value of the standard Helmholtz function, $-\Delta F^{\circ} = 36.5$ kJ mol⁻¹.

DISCUSSION

A line of regression described by an analytical expression can be extrapolated beyond the range of experimental observations to any distance reference point provided that that reference point can be specified in the same coordinate system as the analytical expression. However, information so gained decreases in reliability with increasing extrapolation. There are three causes of this lack of reliability. (1) The analytical expression that describes the line of regression, although ostensibly valid in accounting for the variance in the empirical data over the limited range of experimental observations significantly bias the line of regression over an extended extrapolation. (3) Random experimental errors that result in statistical uncertainties in the information obtained that are many times greater than the uncertainties in the experimental data. Generally, useful information can be gained by extrapolation only when the line of regression is extended by an amount not greater than a small fraction of the experimental range of observations.

Let us now consider the situation in which the information obtained by extrapolation can also be obtained independently by a direct determination using an alternative procedure. Accordingly, the uncertainties arising from the three sources discussed would together reduce any agreement between the information gained by extrapolation and by direct determination. Under these circumstances, actual agreement between the information would tend to confirm the validity of the analytical expression used to describe the line of regression. Such a critical comparison can therefore be used to test the validity of an analytical expression, for the very arguments normally used against extrapolation because of the uncertainty of the results would be precisely the reasons that reliance could be placed on the analytical expression. Any source which contributes to unreliability would be insignificant.

In the light of these observations, we consider again the five reactions examined in this study. For the first two, the extent of extrapolation did not exceed approximately one-half of the experimental periods of observation, and the extrapolated values of the standard Helmholtz function agreed with the direct values to within a fraction of 1%. For the next two reactions, extrapolations of up to 200-fold were required and yet the extrapolated and direct values agree to within 10%. For the last reaction examined, a 400-fold extrapolation was required and the values agree to within 20%, although the extrapolation process was carried to its limit, even using double-precision computations. Clearly, the affinity rate equation can be extrapolated well beyond the experimental period of observation.

It is evident from this analysis that the thermodynamic approach to chemical kinetics is distinct from the mechanistic approach in that kinetic behaviour is described in an energy-time coordinate system, and within that coordinate system empirical data can be extrapolated to equilibrium. In contrast, within the concentration-time coordinate system of the mechanistic approach there are obstacles to such an extrapolation.

For example, the reaction mechanism must be known *a priori* for both the forward and reverse reaction in order to express the line of regression analytically in the concentration-time coordinate system; *i.e.* any intermediate steps involved in either the forward or reverse reactions must be recognized and if relevant the rate-controlling steps determined. For complex processes such as free-radical chain reactions, equilibrium information must be known in order to formulate the rate equation. In addition, these equations can be so complex that only integration by numerical means is possible, which renders the extrapolation procedure inoperative because an analytical expression is not available. Moreover, kineticists concede that on approach to equilibrium, reactions become first order with respect to each of the reacting components, so the analytical expression required to describe the line of regression for reactions displaced far from equilibrium cannot be extrapolated to equilibrium.

Because the thermodynamic approach does not depend on mechanistic considerations, these factors do not enter into the extrapolation procedure. Of course the thermodynamic approach reveals nothing of mechanism, but it is not intended to.

CONCLUSIONS

It is apparent from this analysis that although there may be an infinite number of possible reaction paths between the initial and terminal states in the affinity-time coordinate system, these paths do not touch. Hence, the reactions considered follow a singular path from $(\infty, 0)$ to $(0, t_R)$. Because the termination point of the reaction path is simply a defined state in the affinity-time coordinate system, analytical data sufficient to describe any portion of the reaction path are also sufficient to specify the equilibrium state.

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