

Affinity and Reaction Rates: Reconsideration of Theoretical Background and Modelling Results

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The phenomenological affinity approach to chemical kinetics based on mass-action rate expression is revised. It is shown that the reaction rate is not an unambiguous function of affinity and that in ideal mixtures with only elementary reactions thermodynamic coupling, i. e. a positive reaction rate and negative affinity of some reaction step at the same time, is not possible. Neither does thermodynamic coupling occur in a non-ideal system of elementary reactions where the mass-action rate equation is written with activities in place of concentrations. The non-ideality and/or non-equality of reaction orders to stoichiometric coefficients lead to more complex affinity-rate relationships than commonly given which puts no explicit restrictions on affinity and rate signs. Theoretical considerations are completed with results of numerical modelling made on several simple mechanisms. Various combinations of affinity and rate signs and complex affinity-rate profiles were obtained. Modelling results support the idea that affinity is much more a result of the time evolution of a reacting system and corresponding time profiles of concentrations than the actual cause of reaction rates.

Key words: Affinity; Chemical Kinetics; Reaction Rate.

1. Introduction

Affinity is often addressed in works that attempt to find a thermodynamic basis or even the thermodynamic causes of chemical reaction rates [1–9]. Two principal relations are used:

$$Ar \geq 0, \quad (1)$$

$$A = RT \ln(\vec{r} / \overleftarrow{r}), \quad (2)$$

sometimes called the de Donder inequality and equation, respectively [10]. Here A is the affinity, \vec{r} and \overleftarrow{r} are the forward and reverse reaction rate, respectively, and r is the overall rate: $r = \vec{r} - \overleftarrow{r}$. The rates are considered to be positive (negative overall rate means that reaction is running in the opposite direction, in other words, the reversed reaction rate is positive and just this direction is considered). The second relation, (2), is very often transformed in the vicinity of the equilibrium to an equation claimed to express a linear relationship between reaction rate and affinity close to equilibrium:

$$\begin{aligned} r &= \vec{r} (1 - \overleftarrow{r} / \vec{r}) = \vec{r} [1 - \exp(-A/RT)] \\ \Rightarrow r &\cong \vec{r} A / RT. \end{aligned} \quad (3)$$

Because the forward rate is generally not constant and is directly related to the overall rate r , this is generally not a linear relationship. The last equation has also motivated the declaration of the affinity as a “thermodynamic driving force” for a chemical reaction, i. e. as a force determining its rate.

The first relation, (1), is, in fact, a result of the entropic inequality (the second law of thermodynamics) and should be generally, for R reactions, formulated as follows:

$$\sum_{j=1}^R A_j r_j \geq 0. \quad (4)$$

Modern irreversible thermodynamics *proves* that inequality (4) should be valid, at least in simple material models [11–13]. Condition (4) is frequently and (unwarrantedly) extended to each individual reaction in a system of reactions and “thermodynamic coupling” is introduced. It is said that a reaction with negative affinity, called non-spontaneous, may be *coupled* to another reaction of positive affinity and may run with a positive overall reaction rate. For example, reaction 1 which with negative affinity and

$$A_1 r_1 < 0 \quad (5)$$

is coupled with reaction 2 such that

$$A_1 r_1 + A_2 r_2 > 0. \quad (6)$$

Thus, some reactions can be forced in their non-spontaneous direction by other ones. However, there is no direct proof that each individual reaction from a system should satisfy an equation like (1). The only thermodynamic requirement for a system of reactions is (4) and all discussions on coupling against spontaneity are in this sense superfluous. Spontaneity in a system of reactions should mean just conforming overall to condition (4) with no call for positive individual affinities. In a system of reactions, inequalities like (5) are quite natural, or “spontaneous”, providing condition (4) is maintained. It will be shown here that yet more restrictive conditions on the “coupling” can be derived. Let us also note that Boudart has given examples where potential coupled reactions do not occur in reality [10].

The second relation, (2), is also a special result of limited validity as will be shown below.

Affinity-rate relationships have been discussed for decades but several important points still remain overlooked. Previous work [14] analyzed published experimental proofs of linear relationship between reaction rate and affinity and of thermodynamic coupling and showed that the proofs are really doubtful. In this work, the theoretical background is analyzed. Phenomenological theory and relations like (1), (2), which are mostly used in published works, are discussed and traditional derivations are revised and extended. The limitations of (2) are stated and generalizations to non-ideal systems and systems of non-elementary reactions are derived. Computer modelling is used to illustrate the impacts on affinity time profiles and on the development of affinity-rate relationships during the course of the reaction. Affinity-rate relationships need not be monotonous, need not be a function in the mathematical sense and may include (in a system of reactions) any combination of signs. Modelling supports the idea that affinity is much more a result of the time evolution of a reacting system and corresponding time profiles of concentrations than the cause of reaction rates. It should be noted that modern irreversible thermodynamics treatments lead to more general results and these are reviewed elsewhere [15].

2. Theory

First, the traditional derivation of (2) (in a system of reactions) will be reviewed but made in a more precise

way which will clearly show what was tacitly assumed. A general chemical reaction j is supposed in a reacting mixture with the total number of components (symbolized by $[i]$) equal to n , and the first m are considered to be reactants:

$$0 = \sum_{i=1}^n \nu_{ij} [i] \quad (7)$$

(ν_{ij} is the stoichiometric coefficient, negative for reactants and positive for products). Reaction (7) may represent the overall stoichiometric equation or a single step in a reaction mechanism or network. The affinity of this reaction (A_j) is defined as

$$A_j = - \sum_{i=1}^n \nu_{ij} \mu_i,$$

where μ_i is the chemical potential of component i . Additional assumptions are as follows:

I. The thermodynamic equilibrium constant (K_j) can be identified with the kinetic equilibrium constant, which is given by the ratio of the forward (\vec{k}_j) and reverse (\overleftarrow{k}_j) rate constants (supposed to be non-negative):

$$K_j \equiv \vec{k}_j / \overleftarrow{k}_j \quad (8)$$

II. The traditional mass-action law for forward (\vec{r}_j) and reversed (\overleftarrow{r}_j) reaction rates, which are also supposed to be non-negative, applies.

III. Reaction orders are equal to the (absolute values of) stoichiometric coefficients.

IV. Ideal system and unit standard concentration are assumed.

Assumptions I and III mean that only elementary reactions are considered. Then the affinity definition can be reformulated:

$$\begin{aligned} A_j &= - \sum_{i=1}^n \nu_{ij} \mu_i \\ &= - \sum_{i=1}^n \nu_{ij} \mu_i^0 - RT \sum_{i=1}^n \nu_{ij} \ln(c_i / c^\circ) \\ &= RT \ln K_j - RT \sum_{i=1}^n \ln(c_i)^{\nu_{ij}} \\ &= RT \ln \left[K_j \prod_{i=1}^n 1 / (c_i)^{\nu_{ij}} \right] \\ &= RT \ln \frac{\vec{k}_j \prod_{i=1}^m (c_i)^{\bar{\nu}_{ij}}}{\overleftarrow{k}_j \prod_{i=m+1}^n (c_i)^{\bar{\nu}_{ij}}} = RT \ln(\vec{r}_j / \overleftarrow{r}_j). \end{aligned} \quad (9)$$

Here, c_i is the concentration of the component i , c° is the standard concentration ($= 1$ mol/L) and $\bar{v}_{ij} = |\nu_{ij}|$. Thus, for *the system under consideration only*, i. e. system satisfying assumptions I–IV, (2) is recovered and valid for each reaction in this system of reactions. Moreover, for any reaction in this system it is impossible to get a negative affinity and positive rate simultaneously:

$$r_j > 0 \Leftrightarrow \vec{r}_j > \overleftarrow{r}_j \Rightarrow A_j > 0, \quad (10)$$

compare (9), and the “thermodynamic coupling” is of no justification in this system.

Summarizing, (2) is a special result valid in an ideal system with elementary reactions and it excludes thermodynamic coupling. This was usually ignored in previous works on affinity-rate relationships and thermodynamic coupling. Previous treatments stopped at this equation, usually without stating clearly these four assumptions. Surprisingly, no discussion of the consequences of relaxing some of them can be found. A general modification of the affinity definition is therefore given here.

Chemical potentials and, consequently, affinities are generally expressed in terms of activities; suppose following model for activity: $a_i = \gamma_i c_i / c^\circ$, where γ_i is the activity coefficient of component i and standard concentration now need not be equal to one (in relevant units). Further, suppose the general mass-action rate equation for the reaction j , $r_j = \vec{k}_j \prod_{i=1}^m (c_i)^{n_{ij}} - \overleftarrow{k}_j \prod_{i=m+1}^n (c_i)^{n_{ij}}$, where n_{ij} is the reaction order of the component i . Finally, let us define equilibrium of the j -th reaction as follows:

$$(A_j = 0) \wedge (r_j = 0 \Leftrightarrow \vec{r}_j = \overleftarrow{r}_j). \quad (11)$$

From the affinity definition then follows:

$$\begin{aligned} A_j &= RT \ln \left[K_j \prod_{i=1}^n 1 / (\gamma_i c_i / c^\circ)^{\nu_{ij}} \right] \\ &= RT \ln K_j \frac{\vec{k}_j \overleftarrow{k}_j \prod_{i=m+1}^n (c_i)^{n_{ij}} \prod_{i=1}^m (c_i)^{n_{ij}} (\gamma_i c_i / c^\circ)^{\bar{v}_{ij}}}{\overleftarrow{k}_j \vec{k}_j \prod_{i=1}^m (c_i)^{n_{ij}} \prod_{i=m+1}^n (c_i)^{n_{ij}} (\gamma_i c_i / c^\circ)^{\bar{v}_{ij}}} \\ &= RT \ln K_j \frac{\vec{k}_j \overleftarrow{r}_j \prod_{i=1}^m (c_i)^{n_{ij}} (\gamma_i c_i / c^\circ)^{\bar{v}_{ij}}}{\overleftarrow{k}_j \vec{r}_j \prod_{i=m+1}^n (c_i)^{n_{ij}} (\gamma_i c_i / c^\circ)^{\bar{v}_{ij}}} \end{aligned}$$

$$= RT \ln K_j \frac{\vec{k}_j \overleftarrow{r}_j \prod_{i=1}^m (c_i)^{n_{ij} + \bar{v}_{ij}} (\gamma_i / c^\circ)^{\bar{v}_{ij}}}{\overleftarrow{k}_j \vec{r}_j \prod_{i=m+1}^n (c_i)^{n_{ij} + \bar{v}_{ij}} (\gamma_i c_i / c^\circ)^{\bar{v}_{ij}}} \quad (12)$$

where K_j now refers to the true thermodynamic equilibrium constant, i. e. no identification (8) is supposed. Equilibrium conditions (11) lead to the following identity:

$$K_{k,j} \equiv \vec{k}_j / \overleftarrow{k}_j = \frac{\prod_{i=m+1}^n (c_{i,\text{eq}})^{n_{ij}}}{\prod_{i=1}^m (c_{i,\text{eq}})^{n_{ij}}} \equiv K_{\text{cn},j}, \quad (13)$$

where “eq” stands for the equilibrium value. Alternatively, the relationship between thermodynamic (K_j) and concentration-kinetic equilibrium constants ($K_{k,j}$, $K_{\text{cn},j}$) can be expressed from (12) as follows

$$\begin{aligned} K_{k,j} &\equiv \vec{k}_j / \overleftarrow{k}_j \\ &= (1/K_j) \frac{\prod_{i=m+1}^n (c_{i,\text{eq}})^{n_{ij} + \bar{v}_{ij}} (\gamma_{i,\text{eq}} / c^\circ)^{\bar{v}_{ij}}}{\prod_{i=1}^m (c_{i,\text{eq}})^{n_{ij} + \bar{v}_{ij}} (\gamma_{i,\text{eq}} / c^\circ)^{\bar{v}_{ij}}} \\ &\equiv (K_{\gamma,j} / K_j) \frac{\prod_{i=m+1}^n (c_{i,\text{eq}})^{n_{ij} + \bar{v}_{ij}}}{\prod_{i=1}^m (c_{i,\text{eq}})^{n_{ij} + \bar{v}_{ij}}} \\ &= K_{\gamma,j} K_{\text{cn},j} K_{\text{cv},j} / K_j, \end{aligned} \quad (14)$$

where

$$K_{\gamma,j} = \frac{\prod_{i=m+1}^n (\gamma_{i,\text{eq}} / c^\circ)^{\bar{v}_{ij}}}{\prod_{i=1}^m (\gamma_{i,\text{eq}} / c^\circ)^{\bar{v}_{ij}}} \equiv \prod_{i=1}^n (\gamma_{i,\text{eq}} / c^\circ)^{\nu_{ij}}, \quad (15)$$

$$K_{\text{cv},j} = \frac{\prod_{i=m+1}^n (c_{i,\text{eq}})^{\bar{v}_{ij}}}{\prod_{i=1}^m (c_{i,\text{eq}})^{\bar{v}_{ij}}}. \quad (16)$$

The general relation between reaction affinity and rate (12) can also be written in the following shortened way:

$$A_j = RT \ln \frac{\overleftarrow{r}_j K_j K_{k,j}}{\vec{r}_j Q_j Q_{\text{cn},j}}, \quad (17)$$

introducing the thermodynamic reaction quotient $Q_j = \prod_{i=1}^n (a_i)^{\nu_{ij}}$, and concentration-kinetic reaction quotient

($Q_{\text{cn},j}$), similar to the corresponding concentration-kinetic equilibrium constant (13).

Equations (12) or (17) are the most general relationships between reaction affinity and rate for the activity model used and concentration mass-action kinetic law. From these equations no direct simple statements on the relationship between affinity and rate and their signs can be made, and the occurrence of a reaction with positive rate and negative affinity cannot be directly excluded. Moreover, (12) and (17) show that affinity is in general a rather complicated *function of concentrations*.

It should be also stressed that (17) is written to see the relationship between the reaction affinity and rate explicitly. Because the affinity definition can be rewritten as $A_j = RT \ln(K_j/Q_j)$ it follows from (17) that, in fact, $\bar{r}_j K_{k,j}/(\bar{r}_j Q_{\text{cn},j}) = 1$ as can be easily checked.

To obtain a consistent thermodynamic and kinetic description of the above defined equilibrium, rate constants should be determined for the known equilibrium composition and known thermodynamic equilibrium constant from (14). In other words, there is no identification of the thermodynamic equilibrium constant with the ratio of forward and backward rate constants.

General procedure of deriving the relationship (12) can be simplified for ideal systems and reaction orders equal to the absolute values of stoichiometric coefficients:

$$\begin{aligned}
 A_j &= RT \ln \prod_{i=1}^n K_j / (c_i/c^0)^{v_{ij}} \\
 &= RT \ln K_j \frac{\prod_{i=1}^m (c_i/c^0)^{\bar{v}_{ij}}}{\prod_{i=m+1}^n (c_i/c^0)^{\bar{v}_{ij}}} \\
 &= RT \ln K_j \frac{\bar{k}_j \bar{r}_j \prod_{i=1}^m (c_i/c^0)^{\bar{v}_{ij}}}{\bar{k}_j \bar{r}_j \prod_{i=m+1}^n (c_i/c^0)^{\bar{v}_{ij}}} \\
 &= RT \ln K_j \frac{\bar{r}_j \bar{k}_j Q_j^0}{\bar{k}_j \bar{r}_j}
 \end{aligned} \quad (18)$$

where

$$Q_j^0 = \prod_{i=1}^n (c^0)^{v_{ij}} \equiv (c^0)^{\sum_{i=1}^n v_{ij}}. \quad (19)$$

Equilibrium conditions (11) give:

$$\bar{k}_j / \bar{k}_j = K_j Q_j^0 \quad (20)$$

and finally the same equation as (9) is obtained, i. e. no negative affinity values for positive overall rate.

If reaction orders are equal to the absolute values of stoichiometric coefficients in non-ideal systems the situation is more complex:

$$\begin{aligned}
 A_j &= RT \ln \prod_{i=1}^n K_j / (\gamma_i c_i / c^0)^{v_{ij}} \\
 &= RT \ln K_j \frac{\bar{k}_j \bar{k}_j \prod_{i=1}^m (\gamma_i c_i / c^0)^{\bar{v}_{ij}}}{\bar{k}_j \bar{k}_j \prod_{i=m+1}^n (\gamma_i c_i / c^0)^{\bar{v}_{ij}}} \\
 &= RT \ln K_j \frac{\bar{k}_j \bar{r}_j \prod_{i=1}^m (\gamma_i / c^0)^{\bar{v}_{ij}}}{\bar{k}_j \bar{r}_j \prod_{i=m+1}^n (\gamma_i / c^0)^{\bar{v}_{ij}}}
 \end{aligned} \quad (21)$$

and equilibrium condition leads to the following equation:

$$\bar{k}_j / \bar{k}_j = \frac{\prod_{i=m+1}^n (c_{i,\text{eq}})^{\bar{v}_{ij}}}{\prod_{i=1}^m (c_{i,\text{eq}})^{\bar{v}_{ij}}} \equiv K_{\text{cv},j}. \quad (22)$$

Thus:

$$A_j = RT \ln \frac{\bar{r}_j K_j Q_j^0}{\bar{r}_j K_{\text{cv},j} Q_j}, \quad (23)$$

where

$$Q_j = \prod_{i=1}^n (\gamma_i)^{v_{ij}}. \quad (24)$$

Clearly, non-ideality and/or non-equality of reaction orders and stoichiometric coefficients destroy the simplicity of equations like (2) and do not a priori exclude possibility of having some reactions with positive rate and negative affinity in a system of reactions.

So far we have discussed the most common mass-action law written in concentrations regardless thermodynamic ideality or non-ideality. It is an easy task to show that writing the mass-action law in activities with reaction orders equal to the absolute values of stoichiometric coefficients and identifying kinetic and thermodynamic equilibrium constants also lead to (9) or (2), i. e. no thermodynamic coupling. Activity mass-action rate equations are sometime used with success [16–19]; however, they are not of “better generality” than concentration based equations [20–22]. Moreover, the

simple replacement of concentrations with activities in mass-action rate equations for ion reactions in solution does not work at all [23]. In this case, the Brönsted-Bjerrum approach [23, 24], which can be supported by the transition-state theory [24], may be used. Eckert and Boudart indicated [24] that the same procedure may be applied to non-ideal gas systems. For the reversible reactions this approach leads to some problems discussed elsewhere [15]. If we ignore them the reaction rate is expressed as

$$r_j = \vec{k}_j \prod_{i=1}^m (a_i)^{\bar{v}_{ij}} / \gamma_{j\neq} - \overleftarrow{k}_j \prod_{i=m+1}^n (a_i)^{\bar{v}_{ij}} / \gamma_{j\neq}$$

where $\gamma_{j\neq}$ is the activity coefficient of the activated complex (transition state) of j -th elementary step. This rate equation combined with equilibrium conditions (11) also leads to (9) or (7), i.e. no thermodynamic coupling. The problems mentioned above can be resolved by supposing different transition state activity coefficients in forward and backward directions [15]; then the following equation is obtained:

$$A_j = RT \ln K_j \frac{\overleftarrow{k}_j \vec{r}_j \vec{\gamma}_{j\neq}}{\vec{k}_j \overleftarrow{r}_j \overleftarrow{\gamma}_{j\neq}}. \quad (25)$$

To be consistent with the common equilibrium hypothesis of the transition-state theory both activity coefficients should equal in reaction equilibrium [15]. It is an easy task to verify that this supposition and equilibrium conditions (11) lead to (9) or (7) once more. If we relax this supposition the result is:

$$A_j = RT \ln \frac{\vec{r}_j \vec{\gamma}_{j\neq} \overleftarrow{\gamma}_{j\neq,eq}}{\overleftarrow{r}_j \overleftarrow{\gamma}_{j\neq} \vec{\gamma}_{j\neq,eq}} \quad (26)$$

and no a priori statement on affinity and rate signs can be given and thermodynamic coupling is not excluded.

At the end of this section one problem should be noted. Thermodynamic equations and relations are systematically expressed in terms of activities. Even an ideal system does not in general mean that activity is equal to concentration, but only that the activity coefficient is equal to one and activity is then equal to the ratio of the concentration and standard concentration. Activity cannot be equal to concentration, because it is a non-dimensional quantity whereas concentration has dimensions and units. Therefore, even introducing unity standard concentration in an ideal system does not lead to identifying activity with concentration, but at most to their identical numerical values (if proper

concentration units are selected). Furthermore, activity as well as many other thermodynamic quantities, including the equilibrium constant, refer to some standard state and may have different values for different standard states. On the contrary, mass-action rate equations do not refer to any standard state and are usually formulated in concentrations, and reaction rates are not measured (or determined from measured concentration data) relative to some standard state. Discussing relations between kinetics and thermodynamics, we have to check carefully if the selected standard state is consistent with our kinetic data. If we formulate mass-action rate equation in terms of activities, we should state the selected standard state and be aware of its effect on the values of the reaction rate. Perhaps it would be better to formulate the mass-action kinetic law in ratios of concentration and standard concentration instead of in concentrations. Then, all rate constants would have the same dimensions and units as the reaction rate and, of course, will refer to the selected standard state.

We have therefore systematically retained standard concentrations in the development given above, except for (9), which is just a reproduction of the traditional approach and, consequently, is valid relative to the standard state of unit molar concentration only. In some equations, we have combined expressions for affinity as a function of activities and reaction rate as a function of concentrations. Although in our deductions it is a matter of formal notation only, it causes no problem generally, because activity itself is a function of concentration.

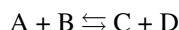
We are ready to sum up our theoretical development. In fact, we have not introduced any new theories or hypotheses. What we have done was to go several steps further in the derivation of commonly used equations. Extracting as much information as possible from classical relations, it was revealed that in many systems a reaction cannot have positive rate and negative affinity in the same time. In other words, “thermodynamic coupling” is not possible in such systems. In some systems, namely non-ideal or with reaction orders different from the absolute values of stoichiometric coefficients (i.e. in a system of non-elementary reactions), a positive reaction rate and negative affinity at the same time cannot be a priori excluded. Even here it is rather improper to say that such a reaction is driven by some other against its “spontaneous” direction. Thermodynamics only gives an overall summary statement on the sign of the product of the affinity and reaction rate for

a system of reactions, compare (4), and does not provide a “spontaneity” criterion for individual reactions in the system. The “spontaneity” of an isolated reaction is something other than the “spontaneity” of a system of reactions.

3. Modelling Method

Relationships between reaction affinity and rate were studied using computer simulation of simple reaction models and batch reacting system. All simulations were made with the Maple 6.02a package (Waterloo Maple, Inc., Canada). The following three models were used:

Model M1:



Model M2:

1. $A + B \rightleftharpoons C + D$
2. $C + B \rightleftharpoons E + D$

Model M3:

1. $A + B \rightleftharpoons C$
2. $C + B \rightleftharpoons D$

The standard state of unit concentration was supposed.

Model M1 can be solved analytically and was used as an ideal system with reaction orders equal to the absolute values of stoichiometric coefficients, i. e. with the thermodynamic equilibrium constant equal to the ratio of rate constants. Batch reactor differential balance equations for models M2 and M3 were solved numerically using the Gear multistep method embedded in the Maple software. These models were used in the same way as model M1, and also with reaction orders not equal to the absolute values of stoichiometric coefficients (in ideal system). In the latter, the following procedure was employed to ensure a consistent thermodynamic and kinetic description of equilibrium. For selected values of the initial concentrations and thermodynamic equilibrium constants of both reaction steps, the equilibrium concentrations were calculated from the expressions for the thermodynamic equilibrium constants. Due to the overall material stoichiometric balance, the concentrations of only two species needed to be calculated directly; the remaining ones were calculated from the former. Calculated equilibrium concentrations were introduced into equilibrium

rate equations (i. e. rate equations with zero overall rate of each step) together with selected values of reaction orders and rate constants \vec{k}_1, \vec{k}_2 . The resulting equations were used to calculate \vec{k}_1, \vec{k}_2 .

Parameters used in the simulations are given in Tables 1–5. Affinities were calculated from the reaction isotherm $A_j = RT \ln(K_j/Q_j)$ for 298.15 K, using the thermodynamic equilibrium constant and reaction quotient. Units of most variables are purely formal in this general modelling study and are therefore not given throughout the following text. However, the formula used to calculate the affinity gives its values in $\text{J} \cdot \text{mol}^{-1}$, and numbers in affinity figures are presented after division by 1000 and can be thus understood as given in $\text{kJ} \cdot \text{mol}^{-1}$.

4. Modelling Results; Discussion

Reaction model M1 in fact qualitatively represents many simple chemical reactions, even with numbers of reactants or products other than two. Parameter values used in simulations are given in Table 1.

The first example in Fig. 1 can be considered as “classical” or expected. The affinity monotonously decreases during the reaction run (Figure 1a). Time profiles of forward and overall reaction rates resemble that of affinity (data not shown). It has been shown [15] that a linear relationship between reaction rate and affinity can be obtained when the sum of the forward and reversed reaction rate is constant. The sum of forward and backward rates achieves essentially constant value at the time about 140. The backward reaction rate continuously increases up to the equilibrium value. The almost linear dependence between the overall reaction rate and affinity (Fig. 1b) falls well within the interval of the almost constant sum of the forward and backward rates.

Increasing the value of equilibrium constant (parameter set 2 in Table 1) did not change the shape of the affinity profile whereas rate-affinity relation became sigmoidal. The rate of the backward reaction was at least three orders of magnitude lower (in spite of continuous increase) than any of the other two rates that had very similar time profiles resembling that of affinity. Close to equilibrium, the rate-affinity relationship became almost linear; it is the region where the rate changed by less than a factor of two – as can be easily checked, the logarithm is well approximated by a straight line in any interval of twofold increase or decrease of its argument.

Table 1. Parameters used in model M1 calculations (reaction orders equal to the absolute values of stoichiometric coefficients)^a.

| Set | a | b | c | d | \vec{k} | \overleftarrow{k} |
|-----|-----|-----|-----|-----|-----------|---------------------|
| 1 | 0.5 | 0.5 | 0 | 0 | 10^{-2} | 10^{-2} |
| 2 | 0.5 | 0.5 | 0 | 0 | 10^{-2} | 10^{-5} |
| 3 | 0.5 | 0.5 | 0.1 | 10 | 10^{-2} | 10^{-2} |

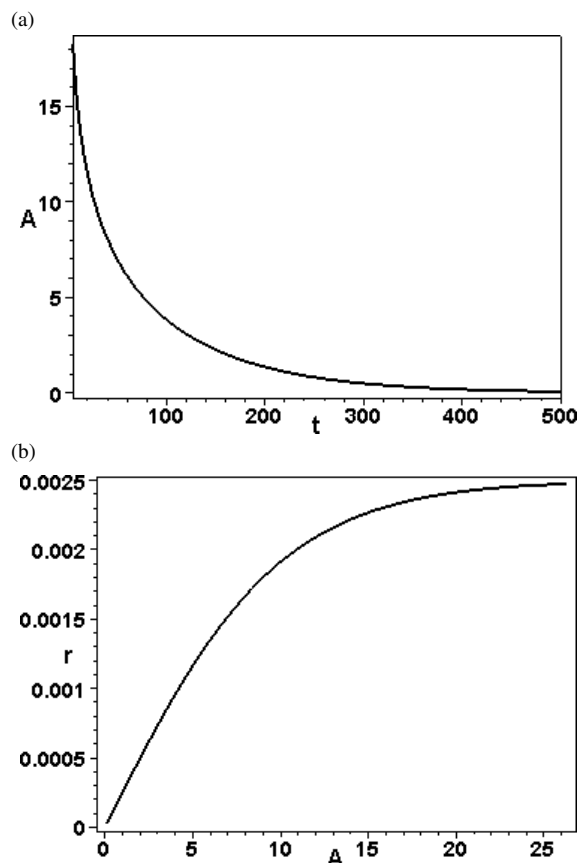
^a a, b, c, d denote the initial concentration of A, B, C, D, resp.

Fig. 1. Affinity time profile (a) and reaction rate-affinity relationship (b) in time interval (1; 500) for model M1 and parameter set 1 (see Table 1).

Preparing the initial mixture with sufficient amounts of “products” (species C and D) the course of reaction can be reversed. The affinity approaches equilibrium from the negative side as Fig. 2 shows and also the overall rate is everywhere negative (data not shown). Here, the relation between the rate and affinity was almost linear over the whole run, again due to the numeric properties of logarithm.

Model M2 combines the two reactions of model M1 into one mechanism. The two steps have common

Table 2. Parameters used in model M2 calculations with reaction orders equal to the absolute values of stoichiometric coefficients^a; $\vec{k}_1 = \vec{k}_2 = 10^{-2}$, $K_1 = K_2 = 10^{-1}$ and $\vec{k}_i / \overleftarrow{k}_i = K_i$.

| Set | a | b | c | d | e |
|-----|-----|-----|-----|-----|-----|
| 1 | 0.5 | 0.5 | 0.5 | 0 | 0 |
| 2 | 0.5 | 0.5 | 0 | 0 | 0 |
| 3 | 10 | 0.5 | 0 | 0 | 0.5 |

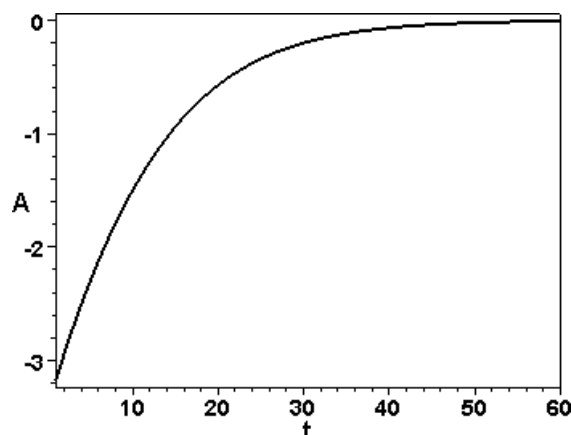
^a a, b, c, d, e denote the initial concentration of A, B, C, D, E, resp.

Fig. 2. Affinity time profile for model M1 and parameter set 3 (see Table 1).

components, and therefore time profiles of their affinities may be different from those obtained when studying each step individually as above. Parameter values are given in Table 2.

Figure 3a shows only the affinity change from positive to negative values during the course of the reaction (for the first reaction). In accordance with the theoretical development, the overall reaction rate crosses the time axis at the same time, see Figure 3b. On the rate-affinity curve, a “turning point” occurs – Fig. 3c, which corresponds to the minima of rate and affinity. Figure 3b also shows time profiles of the rates in both directions as well as of the sum of the forward and reversed reaction rates. Comparison of Figures 3b and 3c supports findings on the linear rate-affinity relationship within interval of the almost constant sum of the forward and reverse reaction rates. Figure 3c also clearly illustrates that the reaction rate *cannot* be viewed as a (mathematical) function of affinity because there can be found two rate values for one value of affinity. The rates of both steps decrease in the beginning, and decrease of the first reaction rate is more rapid because its reactant (B) is consumed in the second reaction also, and it supplies another reactant (C) for the second step,

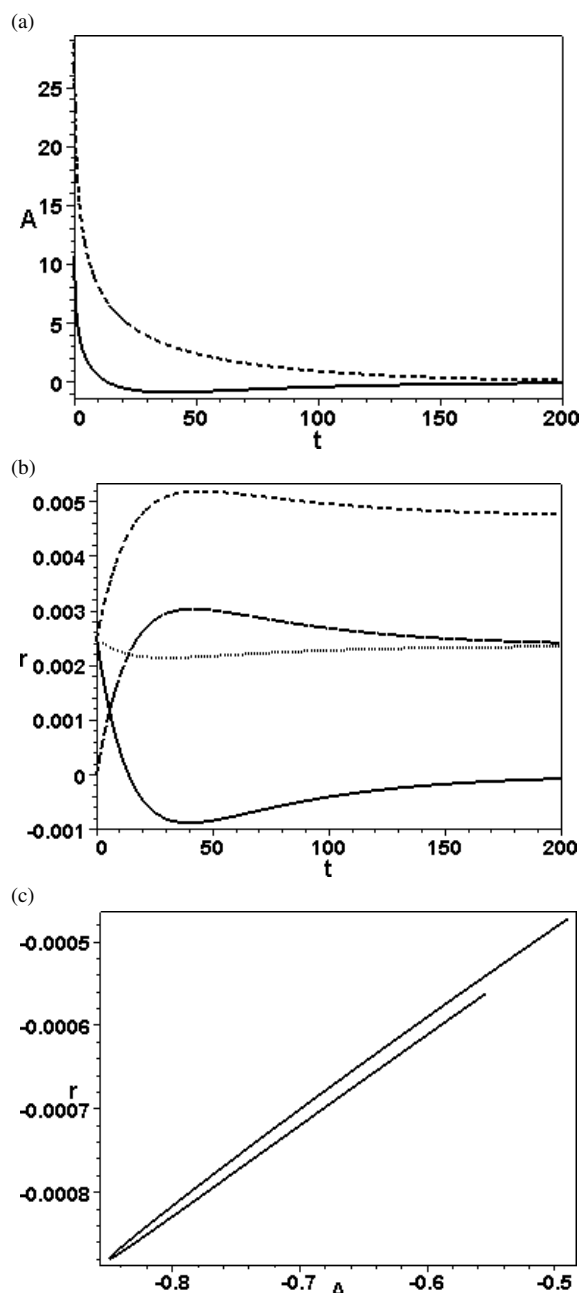


Fig. 3. (a) Affinity time profiles, A_1 (solid), A_2 (dashed); (b) reaction rate time profiles for the first reaction, r_1 (solid), \bar{r}_1 (dotted), \tilde{r}_1 (dashed), $(\bar{r}_1 + \tilde{r}_1)$ (dash-dotted); (c) reaction rate-affinity relationship for the first reaction in time interval (20; 80). Model M2 and parameter set 1 (see Table 2).

producing the common product (D). Finally, the concentrations of species C and D are so high that the first reaction is reversed.

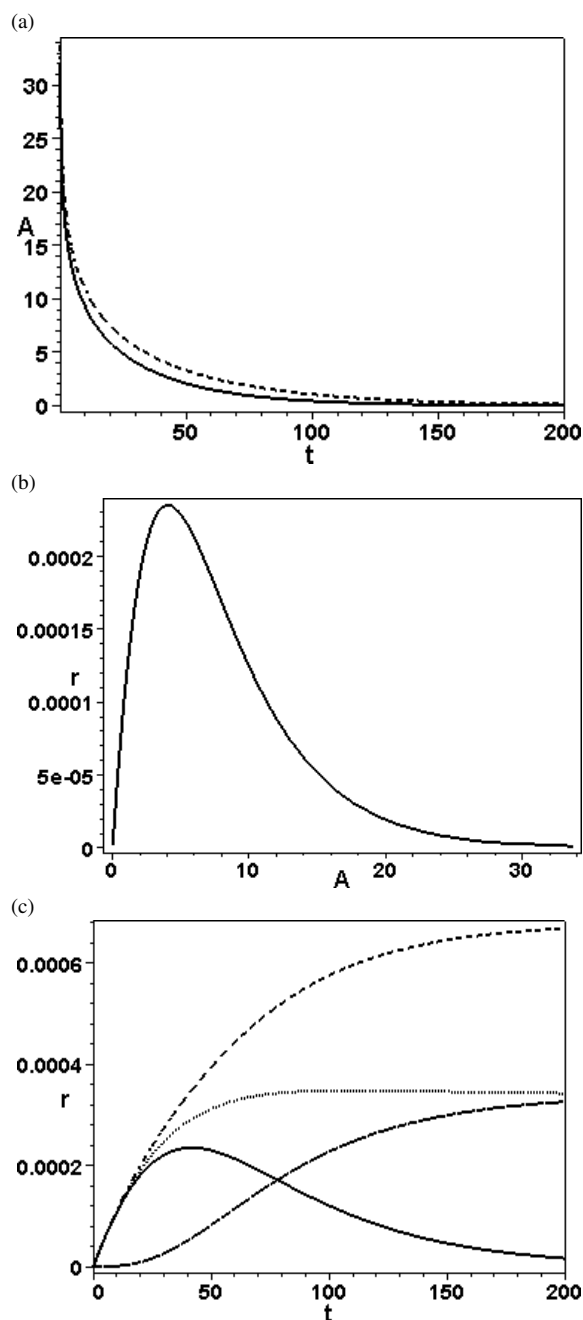


Fig. 4. (a) Affinity time profiles, A_1 (solid), A_2 (dashed); (b) reaction rate-affinity relationship for the second reaction in time interval (0.1; 300); (c) reaction rate time profiles for the second reaction r_2 (solid), \bar{r}_2 (dotted), \tilde{r}_2 (dashed), $(\bar{r}_2 + \tilde{r}_2)$ (dash-dotted) (c). Model M2 and parameter set 2 (see Table 2).

The example in Fig. 4a shows simple affinity profiles – both are monotonously decreasing as expected.

Table 3. Parameters used in model M2 calculations with reaction orders (n_{Xj}) not equal to the absolute values of stoichiometric coefficients^a; $\vec{k}_1 = \vec{k}_2 = 10^{-1}$, $K_1 = K_2 = 10^{-1}$.

| Set | a, b, c | d, e | 0.5 | 1 | 1.5 | \vec{k}_1 | \vec{k}_2 |
|-----|-----------|--------|------------------|---------------------------------------|------------------|-------------|-------------|
| 1 | 0.5 | 0 | n_{C1}, n_{D1} | $n_{B2}, n_{C2},$ n_{D2}, n_{E2} | n_{A1}, n_{B1} | 0.1339 | 10^{-2} |
| 2 | 0.5 | 0 | n_{D2}, n_{E2} | $n_{A1}, n_{B1},$ n_{C1}, n_{D1} | n_{B2}, n_{C2} | 10^{-2} | 0.2626 |

^a a, b, c, d, e denote initial concentration of A, B, C, D, E, resp.

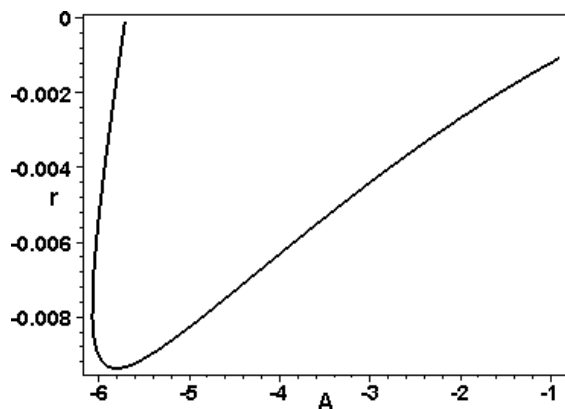


Fig. 5. Reaction rate-affinity relationship for the second reaction from model M2 and parameter set 3 (see Table 2) in time interval (0.1; 80).

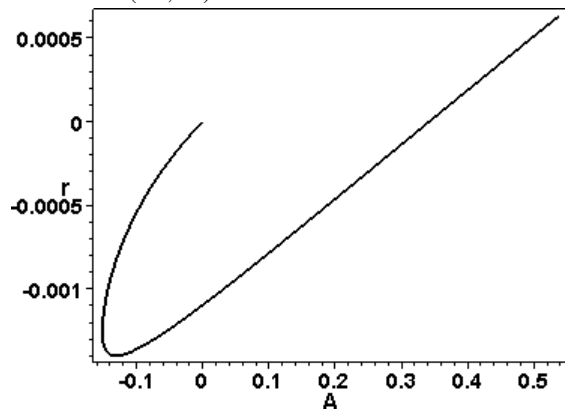


Fig. 6. Reaction rate-affinity relationship for the first reaction from model M2 and parameter set 1 (see Table 3) in time interval (5; 300).

However, the rate-affinity relationship of the second reaction, is not monotonous, see Figure 4b. Once more, the rate profile has little to do with the affinity profile and is not determined by it. Quite different rate profiles can be obtained for similar affinity profiles. The cause of the extreme in Figure 4b is the extreme in the overall reaction rate itself; see Figure 4c. The second reaction rate is zero at time zero, because of the lack of

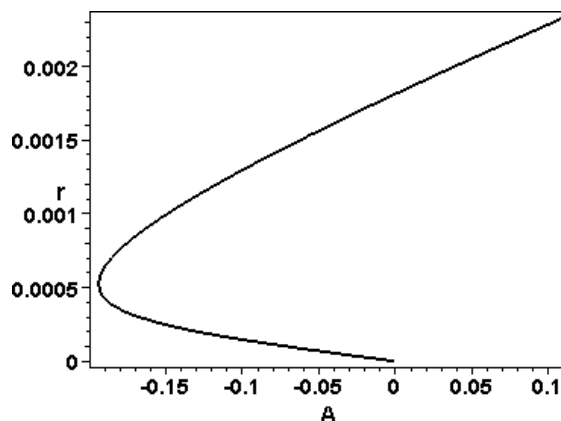


Fig. 7. Reaction rate-affinity relationship for the second reaction from model M2 and parameter set 2 (see Table 3) in time interval (12; 200).

one of its reactants (C), and continuously increasing as this reactant is formed. However, the other reactant (B) is still consumed by the first reaction as well. Consequently, its supply starts to be so small that the second reaction rate starts to decrease.

The effect of the initial mixture composition on reversing (second) reaction is shown in Figure 5. The affinity of this step is negative throughout the whole run as well as its overall rate, both having minima at time about 10. Again, two values of the reaction rate can be found for one value of affinity.

As indicated in the theoretical part, by manipulation of the reaction orders we can independently change the signs (and magnitudes) of the affinity and reaction rate. The corresponding examples, which now follow, are based on set 2 from Table 2, whereas actual parameter values are given in Table 3.

The first example, Fig. 6, shows that the rate of the first reaction can become negative (and reaction reversed) while the affinity still retains a positive sign. The second example, Fig. 7, shows a case where negative affinity is combined with a positive reaction rate (of the second reaction).

The last two examples should not be viewed as pure mathematical manipulations and merely formal results. They may represent a real situation when measured concentration profiles (simulated in the examples by computer) are used together with the *true thermodynamic* equilibrium constant to calculate affinity. The non-correspondence between the signs of the affinity and the rate may then occur when the sensitivity of the reaction rate to the concentrations of reacting species, determined by reaction orders, differs

Table 4. Parameters used in model M3 calculations with reaction orders equal to the absolute values of stoichiometric coefficients^a; $\vec{k}_1 = \vec{k}_2 = 10^{-2}$, $K_1 = 10^3$, $K_2 = 1$ and $\vec{k}_i/\vec{k}_i = K_i$.

| Set | a | b | c | d |
|-----|-----|-----|-----|-----|
| 1 | 1.5 | 0.5 | 0 | 0 |
| 2 | 1.5 | 0.5 | 0.2 | 0.2 |

^a a, b, c, d denote initial concentration of A, B, C, D, resp.

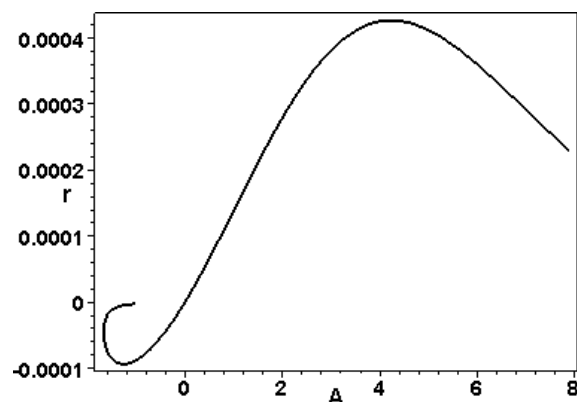


Fig. 8. Reaction rate-affinity relationship for the second reaction from model M3 and parameter set 1 (see Table 4) in time interval (8; 1000).

from what is expected from the stoichiometric equation (determined by stoichiometric coefficients). In other words, when the actual mechanism is different than what was used in the reaction quotient to calculate affinity. The sensitivity is manifested in concentration profiles.

The last model mechanism (M3) is a simpler version of mechanism M2 with a reduced potential of the second reaction to reverse the first one. For parameter values, see Table 4.

First example has two extremes in the rate-affinity curve of the second reaction; see Figure 8. The maximum corresponds to the maximum in its overall rate, which then decreases to negative values and achieves a minimum (data not shown) that is reflected as the minimum in the curve in Figure 8.

The last two examples show a stranger relation between the rate and affinity of the second reaction; see Figure 9. The curve in Fig. 9a is a result of the multiple extremes found in both individual time profiles. Figure 9b shows effect of reaction orders different than the absolute values of stoichiometric coefficients (for parameters, see Table 5) – for the second reaction from the reaction set M3, a positive overall reaction rate for a negative affinity can be achieved.

Table 5. Parameters used in model M3 calculations with reaction orders (n_{Xj}) not equal to the absolute values of stoichiometric coefficients^a; $\vec{k}_1 = \vec{k}_2 = 10^{-1}$, $K_1 = K_2 = 10^{-1}$.

| a | b | c | d | n_{A1} | n_{B1}, n_{C1} n_{C2}, n_{D2} | n_{B2} | \vec{k}_1 | \vec{k}_2 |
|-----|------|-------|-----|----------|--------------------------------------|----------|------------------------|------------------------|
| 1.5 | 1.99 | 0.308 | 0 | 0.7 | 1 | 1.2 | 2.304×10^{-3} | 1.380×10^{-2} |

^a a, b, c, d denote initial concentration of A, B, C, D, resp.

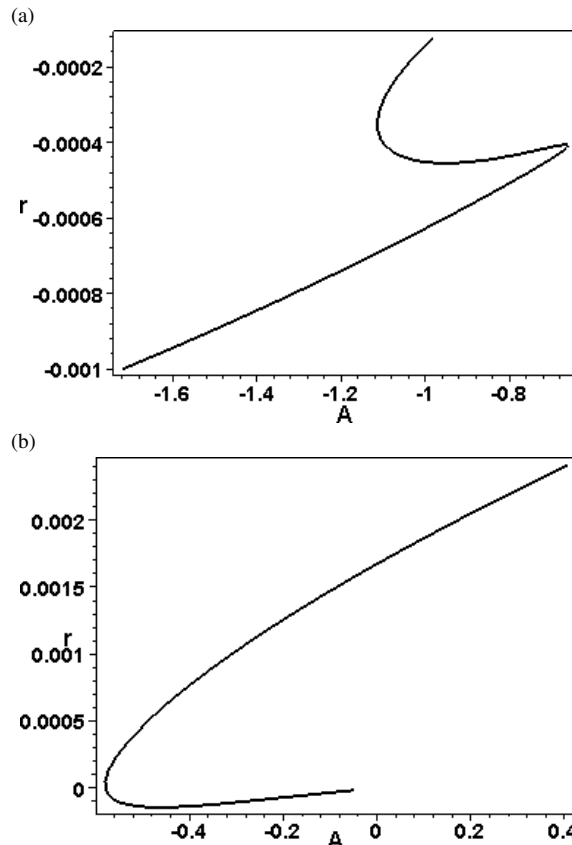


Fig. 9. Reaction rate-affinity relationship for the second reaction from model M3 and parameter set 2 (see Table 4) in time interval (0.1; 500) (a) and parameter set given in Table 5 in time interval (70; 3000) (b).

In conclusion it should be noted that in all examples (4) was fulfilled, and simulation results were thus consistent with the thermodynamic requirements, i. e. positive entropy production.

5. Conclusions

Affinity is much more a result of the time evolution of a reacting system and corresponding time profiles of concentrations than the genuine cause of the reac-

tion rate. Affinity itself does not control the reaction rate. Affinity is determined by the actual concentrations, which in turn are result of the actual reaction rate. Affinity is a specific and useful way of *describing* a reacting system and its time evolution.

Even from (3) it can be seen that the overall reaction rate is not an unambiguous function of affinity. This was lucidly proved by Samohýl within the framework of rational thermodynamics [12, 13] and reviewed with illustrative example and discussion in [15]. It was shown that the overall reaction rate (of independent reactions) can be expressed as a function of affinity *and* a quantity tentatively called constitutive affinity [15]. Interestingly, these findings are consequences of the algebraic properties of reaction stoichiometry revealed and analyzed by Bowen [25]. Other treatments within the theory of continuum thermodynamics have shown that rate-affinity relationships may be more complex and rich and that even in equilibrium affinity and rate need not vanish at the same time [26, 27].

A linear relationship between the reaction rate and its affinity, which is sometimes revealed, is a consequence of specific behaviour of the logarithm function

and not of some natural law (see also [14, 15]). Thermodynamic coupling is often either superfluous or a result of a rather improper combination of thermodynamics and kinetics and improper thermodynamic deductions. In many systems, including elementary reactions in thermodynamically ideal systems, it is even excluded. A positive reaction rate and negative affinity of the reaction at the same time may be a result of different types of dependence on concentrations. Whereas reaction rate depends usually on concentrations raised to reaction order powers, affinity depends on activities raised to stoichiometric coefficients. Non-ideality and/or non-equality of reaction orders and (the absolute values of) stoichiometric coefficients may lead, in multistep mechanisms or reaction networks, to any combination of signs of affinity and corresponding overall reaction rate for any step, providing the second law condition (4) is satisfied.

Acknowledgement

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