Affinity and Reaction Rates: Reconsideration of Experimental Data

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Two published experimental confirmations of either the linear relationship between the reaction rate and its affinity, or the 'thermodynamic coupling' are revised. It is shown that 'proved' results are more consequences of a given experimental arrangement or of methods used for the treatment of experimental concentration data than outcomes of some general thermodynamic law. The affinity should be considered not as a quantity determining the value of the reaction rate but as an alternative quantity for description of the evolution of a reacting system, its distance from equilibrium. The affinity, perhaps, expresses some potential for a reaction, but its manifestation in the reaction rate is controlled by the very kinetics.

1. Introduction. – Affinity is often considered as a principal quantity in determining the rate of a chemical reaction, as the reaction driving force, especially within the classical or extended irreversible thermodynamics [1–13]. Despite of evidences that relationships between the affinity and reaction rate are much more complicated [14–19], and that the affinity is definitely not the only one quantity which might affect the rate [17–20], attempts to formulate some equations describing dependence of the rate on the reaction affinity still occur. However, practical applications of the rate–affinity relationships or experimental confirmations of them are scarce. In this work, perhaps the only two published experimental works devoted to this aim will be revised.

For readers' convenience and explanation of the nomenclature, the basic principles of introduction of the affinity into the chemical kinetics are briefly reviewed. The affinity was originally introduced by *de Donder* and *van Rysselberghe* [21]. However, they used rather a strange hypothesis on dependence between independent variables, as explained in details in [20]; therefore the affinity should be preferably defined much more simply as the reaction *Gibbs* energy with reversed (minus) sign or using the chemical potentials of constituents of a reacting mixture. For a general chemical reaction

$$0 = \sum_{i=1}^{n} \nu_i A_i \tag{1.1}$$

under conditions of *constant temperature and pressure*, the *Gibbs* energy can be expressed as a function of the extent of reaction only. The partial derivative of the *Gibbs* energy with respect to the reaction extent is called the reaction *Gibbs* energy (ΔG_r) and can be expressed through the constituent activities (a_i) by the well-known reaction isotherm:

$$\Delta G_{\mathrm{r}} = \Delta G_{\mathrm{r}}^{\circ} + RT \ln \prod_{i=1}^{n} a_i^{\nu_i} \equiv \Delta G_{\mathrm{r}}^{\circ} + RT \ln Q_{\mathrm{r}} \tag{1.2}$$

where Q_{r} is called the reaction quotient and $\Delta G_{\mathrm{r}}^{\circ} = -RT \ln K$, K is the equilibrium constant and '$^{\circ}$' states for the standard state. The affinity can be defined by $A = -\Delta G_{\mathrm{r}}$ or through the chemical potentials (μ_i):

$$A = -\sum_{i=1}^{n} \nu_i \mu_i = -\sum_{i=1}^{n} (\nu_i \mu_i^{\circ} + \nu_i RT \ln a_i) = -\Delta G_{\mathrm{r}}^{\circ} - RT \ln Q_{\mathrm{r}} \tag{1.3}$$

In fact, many irreversible thermodynamics approaches to the affinity – rate problem are rooted in the reaction isotherm *Eqns. 1.2* or *1.3* derived within the framework of a reversible theory. This is acceptable if the *Gibbs* energy can be considered as a function of temperature, pressure, and composition. *Eqn. 1.3* can be in *ideal systems and for an elementary reaction* modified as follows:

$$\begin{aligned} A &= RT \ln K - RT \ln C^{\circ} \prod_{i=1}^{n} c_i^{\nu_i} = RT \ln K - RT \ln C^{\circ} \prod_{i=1}^{n} (\vec{k}\overleftarrow{k}/\vec{k}\overleftarrow{k}) c_i^{\nu_i} \\ &= RT \ln K - RT \ln C^{\circ} [(\vec{k}/\overleftarrow{k})(\overleftarrow{r}/\vec{r})] \end{aligned} \tag{1.4}$$

Here, C° formally denotes the standard concentration factor converting the activities to concentrations c_i, $\vec{k}, \overleftarrow{k}$ are the rate constants in respective directions. *Identifying* the equilibrium constant with the ratio of the rate constants and *selecting* unit standard concentrations the following equation is obtained:

$$A = RT \ln(\vec{r}/\overleftarrow{r}) \tag{1.5}$$

From *Eqn. 1.5*, other versions can be derived. Very popular is the following relation:

$$r = \vec{r}(1 - \overleftarrow{r}/\vec{r}) = \vec{r}[1 - \exp(-A/RT)] \tag{1.6}$$

which can be close to equilibrium ($A/RT \ll 1$) linearized as follows:

$$\exp(-A/RT) = 1 - (A/RT)/1 + (A/RT)^2/2 - \cdots \quad \Rightarrow \quad r \cong \vec{r} A/RT \tag{1.7}$$

It is said that the linear relationship between the overall reaction rate r and affinity is thus obtained. However, because the forward-reaction rate is not generally constant and is directly related to the overall rate, this is generally no linear relationship.

The second law of thermodynamics, as *de Donder* observed, calls for

$$Ar \geq 0 \tag{1.8}$$

Because the rate of some running reaction is considered to be positive, it is deduced that all spontaneous reactions must have positive affinity. Especially the latter statement is unfoundedly transferred to *systems of reactions*, requiring that any reaction from the system should have positive affinity to be able to occur; otherwise, it is called to be coupled with other reactions and forced by them *against* its spontaneous direction ('thermodynamic coupling'). However, the only proved statement of irreversible thermodynamics reads [18][19][22]:

$$\sum_i A_i r_i \geq 0 \tag{1.9}$$

In a system of R reactions, the best way to introduce the affinity is through the chemical potentials:

$$A_j = -\sum_{i=1}^{n} \nu_{ij}\mu_i; \; j = 1,\ldots,R \tag{1.10}$$

where ν_{ij} is the stoichiometric coefficient of a species i in the reaction j. The affinity A_j can be alternatively viewed as a partial derivative of the *Gibbs* energy with respect to the extent of reaction j (under constant temperature and pressure).

The main aim of this work is to revise the conclusions of the two published studies on the relationship between the affinity and reaction rate. The first of them [1] was devoted to an experimental proof of the linear relationship between the reaction rate and affinity in the vicinity of equilibrium. Lately, using the same data, it was claimed that the linearity is maintained fairly far from equilibrium [23]. The second paper [2] tried to check the thermodynamic coupling. The reconsideration developed here takes into account that affinities are not measured but only calculated from measurable quantities (usually concentrations), and, therefore, we have to pay attention to what was really measured, and what are the consequences of calculations and mathematics. The aim is not to invalidate the experimental work or the theory expressed by *Eqns. 1.7* or *1.9* but to re-check if the data really and unambiguously prove the theory.

2. Reconsideration of Data by *Prigogine et al.* – The data published by *Prigogine et al.* [1] seem to be the first report on an experimental test of the affinity–rate relationship. The authors studied two opposite directions of a single reaction – the hydrogenation of benzene and cyclohexane dehydrogenation. They reported linear relationship between the reaction rate and the fraction A/RT up to $|A/RT| = 2.3$. Because the linearity originates in the approximation of an exponential (*cf. Eqn. 1.7*), it can be easily checked that this approximation is not realistic for such high values [20]. As stressed above, we must carefully inspect what was really measured. It was not the affinity, of course, and even directly not the reaction rate but just the concentration(s). From the description of experiments given in the original paper [1] and its predecessors [24][25] follows that the stationary flow-through differential reactor was used. The reaction rate was determined from the difference between the hydrogen flow rates in the reactor entrance and exit, which was then recalculated by the pertinent molecular weight and division by three to the grams of benzene hydrogenated per one hour (the rate of benzene hydrogenation). Further, the hydrogen partial pressure was much higher than that of the other two constituents and almost did not change with changing reaction rate under constant temperature (Table 2 in ref. [1]). Thus, one component of the reacting mixture was in high excess, and the reaction and its rate was controlled by the other two components, one of which being the reactant and the other the product. In fact, the experiments tested how far is the stationary composition, established in the mixture initially containing both reactant and product, from the equilibrium composition. Not too surprisingly, this distance is linearly related to the initial composition. Let us analyze the experiments in more details. They were presented in two main tables [1]1)).

Table 1 in the original paper [1] presents the results of experiments performed at several different temperatures, with a given initial composition. In total, four different compositions (four experimental runs) at various temperatures were used. The dependence of the reaction rate on the affinity (divided by the universal gas constant) was linear for each initial composition. As the reactor used in experimental work was differential [24] [25], the affinity was calculated from the partial pressures at the reactor inlet, *i.e.*, from the composition of prepared initial reacting mixture, using the *Eqn. 2.1:*

$$A/R = T(\log K + \log P_{\mathrm{c}} - \log P_{\mathrm{b}} - 3\log P_{\mathrm{h}}) \tag{2.1}$$

where K is the equilibrium constant, Ps are the (inlet) partial pressures of cyclohexane (subscript 'c'), benzene ('b'), or hydrogen ('h'). Because the initial composition was constant, any change in the (calculated) affinity in a particular run is *solely* due to the *temperature*. The temperature effect on the affinity in each run can be expressed with *Eqn. 2.1* and the equation for the temperature dependence of the equilibrium constant given on p. 327 in [1] as:

$$A/R = T\log K + T\log(\text{const.}) = (\text{const.} - 20.69)T + 51\,500/4.573 \tag{2.2}$$

(units are calories, mol, and Kelvin), *i.e.*, the affinity is 'by definition' a linear function of temperature. Consequently, if also the experimental reaction rate (symbol v' was used by *Prigogine et al.* [1]) is a linear function of the temperature, then the rate would naturally depend linearly on the affinity:

$$(A/R = k'T + q' \wedge v' = k''T + q'') \Rightarrow v' \propto A/R \tag{2.3}$$

The data given by *Prigogine et al.* [1] really indicate the linear relationship between the *measured* reaction rate and temperature which was actually *preset* in the experiments; an example is displayed in *Fig. 1*. The experiments thus confirmed the linear temperature effect on the reaction rate for each initial composition and not the linearity of the reaction rate – affinity relationship.

What is the cause of this linear dependence? Could it be a linear effect of the affinity on the rate and the rate – affinity linearity proved, after all? Clearly, the revealed linear dependence of the rate of (reversible) reaction on temperature should be rooted in the *Arrhenius* equation. Generally, we can write:

$$v' = \vec{A}\exp(-\vec{E}/RT)\vec{f}(P_i) - \overleftarrow{A}\exp(-\overleftarrow{E}/RT)\overleftarrow{f}(P_i) \tag{2.4}$$

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1) All original data are reproduced here in *Fig. 6,a* and in the *Appendix*.

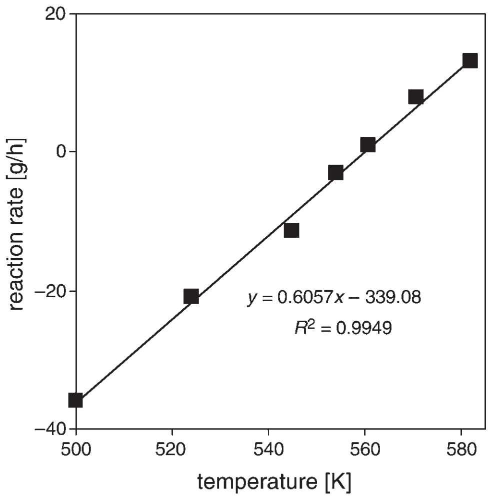

Fig. 1. *Example of linear dependence of measured reaction rate on temperature.* Based on data from Table 1 in [1].

Without loss of generality, we can continue our discussion considering both concentration (partial pressure) functions equal to one. Because of its appearance in exponential, the value of the activation energy determines the shape and magnitude of the reaction rate dependence on the temperature. Two cases are possible – activation energies in both directions are comparable, or one of them is several times higher. In the first case, it can be easily imagined that an increase of partial rates in both directions by elevated temperature results, after the subtraction of the partial rates, in the linear change of the overall rate. An example is shown in *Fig. 2* for the following specific form of *Eqn. 2.4*:

$$4.5 \times 10^{11} \exp(-60000/RT) - 1.5 \times 10^{11} \exp(-54000/RT) \tag{2.5}$$

Herbo [25] gives for this reaction a value of some activation energy of *ca.* 54 kJ · mol^{-1}.

If both activation energies in *Eqn. 2.4* have incomparable values, the term with the lower value outweighs, again due to the exponential. Within the used temperature range (*ca.* 480–580 K), an acceptable value of the activation energy can be found, which gives sufficiently linear approximation to the *Arrhenius* exponential. Thus, 30 kJ · mol^{-1} gives the squared correlation coefficient of the linear approximation equal to 0.983, whereas 40 kJ · mol^{-1} gives 0.965.

To summarize, the revealed linear rate–temperature dependence can be readily explained as an approximation of the *Arrhenius* exponential in some domain with no need to suppose linear effect of the affinity on the rate. Experimentally observed linear dependence of the rate on temperature leads also to the linear relationship between the rate and affinity. The experiments cannot be considered as a proof of the latter.

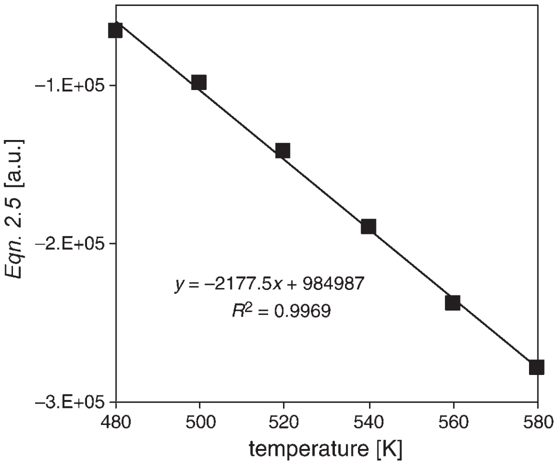

Fig. 2. *Linear dependence of difference from* Eqn. 2.5 *on temperature*

Table 2 in the original work [1], the second main table with experimental results, gives the results obtained with varying initial compositions at two different temperatures. Again, linear plots of the reaction rate against the affinity are reported. Because the affinity was *calculated* (*cf. Eqn. 2.1*) from the partial pressures at the reactor inlet, *i.e.*, from the composition of the prepared initial reacting mixture, and the temperature was constant in these experiments, the affinity is determined solely by the initial composition. It means that the affinity *was prepared* in advance. Further, the reaction rate *was determined* from the initial and exit concentration of hydrogen as explained above. Specifically, according to *Prigogine et al.* [1], the reaction rate (v') is given by:

$$v' = F_b^o - F_b^i \tag{2.6}$$

where F is the flow rate in g/h, symbol 'b' states for benzene, 'o' for the reactor outlet, and 'i' for the inlet. As the flow rate is constant ('very high' giving a 'maximum' yield [1][24][25]), the reaction rate can be considered to be proportional to the benzene partial pressure. It follows that the only one *outright* result of experimentation is that the concentration change of benzene, determined from *Eqn. 2.6*, is linearly proportional to the following expression, hidden in the *Eqn. 2.1*:

$$Q = \log[P_c/(P_b P_h^3)] \tag{2.7}$$

which is, in fact, the logarithm of the well-known reaction quotient $Q_r = P_c/(P_b P_h^3)$ (originally, it is defined with natural logarithm, *cf. Eqn. 1.2*). Is this experimental outcome really a consequence of just linear dependence of the reaction rate on affinity?

Supposition on the proportionality between the *determined* reaction rate and the benzene partial pressure made above can be explicitly written as

$$v' = k'(P_{\mathrm{b}}^{\mathrm{o}} - P_{\mathrm{b}}) \qquad (2.8)$$

where ‘o’ again means reactor outlet and k' is some proportionality coefficient. Because both partial pressures are in a differential reactor very close, it can be further supposed that the outlet partial pressure is directly proportional (coefficient k'') to the inlet partial pressure:

$$v' = k'(k''P_{\mathrm{b}} - P_{\mathrm{b}}) = k'P_{\mathrm{b}}(k'' - 1) \equiv kP_{\mathrm{b}} \qquad (2.9)$$

Thus, the *determined* rate can be finally supposed to be linearly dependent on the inlet partial pressure of benzene. This is really confirmed by the experimental data, for an example see *Fig. 3*. The linear dependence can be easily understood if we realize that just the initial rates were measured, and the hydrogen initial pressure has only little effect on the reaction rate (hydrogen is in excess): $v' \cong \vec{k}P_{\mathrm{b}} - \overleftarrow{k}P_{\mathrm{c}}$, and the cyclohexane pressure is proportional to the benzene pressure.

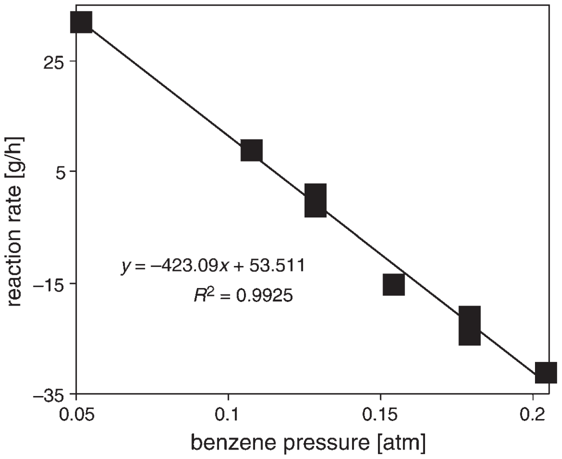

Fig. 3. *Example of linear dependence of measured reaction rate on inlet partial pressure of benzene.* Based on data for 548 K from Table 2 in [1].

It can be easily verified that also the logarithm of the reaction quotient for the data by *Prigogine et al.* [1] is a linear function of the benzene (and even also cyclohexane) partial pressure; an example is shown in *Fig. 4*. Consequently, also the dependence between the logarithm of reaction quotient (*cf. Eqn. 2.7*) or the affinity calculated from it, and the reaction rate should be linear:

$$(v' = kP_{\mathrm{b}} \wedge \log Q = k'''P_{\mathrm{b}} + C') \Rightarrow v' = \bar{k}\log Q + C \Rightarrow v' \propto A/R \qquad (2.10)$$

The linear dependence between the reaction rate and affinity (as well as linearities like in the *Fig. 4*), therefore, resulted from the *preparation* of the initial reacting mixture.

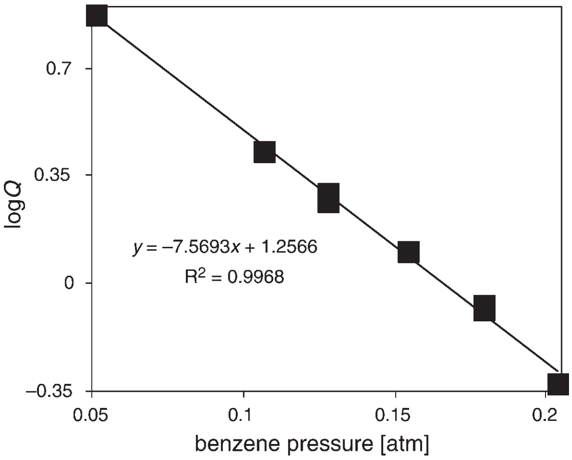

Fig. 4. *Example of linear dependence of logarithm of reaction quotient on inlet partial pressure of benzene*. Based on data for 548 K from Table 2 in [1].

Argumentation just given may be further supported by another one, which is based more on mathematic considerations. Differences in the affinity, which should force the reaction to different rates, are rooted in the reaction quotient given by *Eqn. 2.7.* Expanding it we obtain:

$$Q = 2[(P_c - P_b P_h^3)/(P_c + P_b P_h^3) + (1/3)(P_c - P_b P_h^3)^3/(P_c + P_b P_h^3)^3 + \cdots]/\ln 10 \quad (2.11)$$

Introducing the following abbreviation

$$Z = (P_c - P_b P_h^3)/(P_c + P_b P_h^3) \quad (2.12)$$

it is found that the (decadic) logarithm of the reaction quotient can be at the reported experimental conditions successfully approximated by the first term of *Eqn. 2.11*, linear in Z. For the two examples by *Prigogine et al.* [1], the slopes of these approximations are 1.187 and 1.139, and squared correlation coefficients 0.984 and 0.995, respectively. Further, the initial composition was selected in such a way that the fraction Z is again a linear function of the (initial) benzene partial pressure as is illustrated by the example in *Fig. 5*. Thus, the affinity was in fact determined by the fraction Z, which in turn depended linearly on P_b. Combining with *Eqn. 2.9*, the linear relation between the affinity and reaction rate follows, once more.

On the basis of analysis hitherto presented, it can be competently assumed that published linear relationship between the affinity and reaction rate [1] is much more a matter of particular experimental arrangement than of the true thermodynamic principle. Definitive confirmation of the linear relationship should be made with yet different compositions of the reacting mixture and probably also using a non-differential, non-stationary reactor. Experimental results presented in [1] seem to confirm 'only' the linear relationship in *Eqn. 2.9*.

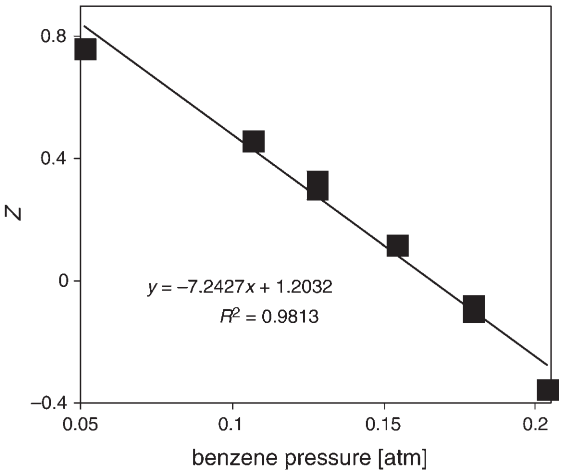

Fig. 5. *Example of linear dependence of fraction* Z *from* Eqn. 2.12 *on inlet partial pressure of benzene.* Based on data for 548 K from Table 2 in [1].

Eqn. 2.1 contains influence of both temperature and composition on the affinity. Ignoring possible pressure effect, this equation should thus comprise all variables affecting the affinity. There is thus no reason to consider experimental data given by *Prigogine et al.* [1] separately for each experimental run. Collecting all the data into one plot, it is seen that the linear dependence is not very satisfactory (see *Fig. 6*). *Fig. 6,a* indicates some linear relationship close equilibrium, but *Fig. 6,b* shows that it is only slightly better. Really very close to the equilibrium, the plot is yet worse and fouled perhaps by insufficient accuracy of experiments (*cf. Fig. 6,c*).

Summarizing, all particular linear plots given in [1] and reproduced in [23] are probably due to the particular experimental arrangement and not due to general validity of the linear relationship between the reaction rate and affinity.

3. Reconsideration of Data by *Nebeker* and *Pings*. – *Nebeker* and *Pings* [2] tried to test the thermodynamic coupling of the two reactions:

1) $2\ NO + Cl_2 = 2\ NOCl$
2) $2\ NOCl + I_2 = 2\ NO + 2\ ICl$

and also to confirm experimentally the linear relationship between the affinity and reaction rate. They measured concentrations of all components in the reacting mixture²). Of course, the affinities were not measured but calculated from the reaction isotherm and concentration profiles. The rates of reactions were taken as the time derivatives of the Cl_2 and I_2 concentrations. It was found that, for some portions of a run of the reacting system, the linear relationship is valid. In general, however, this was not verified as well as the so-called *Onsager*'s reciprocity relations, which are not discussed here. Further, it was revealed that the second reaction runs with negative affinity.

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²) Original data are reconstructed here in *Fig. 8*.

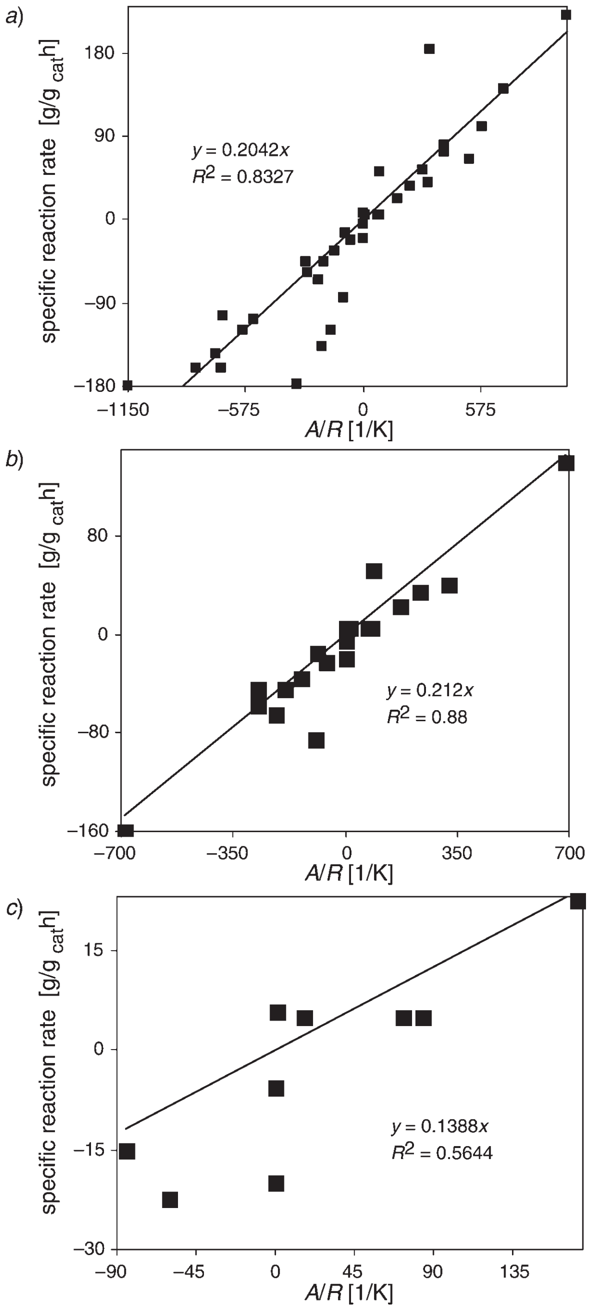

Fig. 6. *Plot of all data given in* [1] *which should give linear relationship between reaction rate and affinity.* Reaction rate was recalculated per unit catalyst weight. *a*) Overall view; *b*) details close to equilibrium; *c*) very close to equilibrium.

What does negative value of reaction affinity really mean in this case? *Nebeker* and *Pings calculated* the affinity from the *Eqn. 3.1* [2]:

$$A_j = RT \ln K_j - RT \ln \prod_i (c_i RT f_i^0 / P)^{\nu_i} \tag{3.1}$$

where A_j is the affinity of reaction j, K_j its equilibrium constant, c_i the concentration of i-th component, f_i^0 the fugacity of the pure component i, P is the total pressure, and ν_i the stoichiometric coefficient. Thus, the affinity in fact *measures* (not *determines*) the distance from equilibrium [26–28], and compares the equilibrium constant to the actual value of the reaction quotient (Q):

$$A_j = RT \ln(K_j / Q_j) \tag{3.2}$$

The negative affinity value means that the actual value of the reaction quotient is higher than that of the equilibrium constant, *i.e.*, the composition of reacting mixture is 'shifted to the right' in comparison with the equilibrium state. The affinity should be considered more as an indicator of the actual state than its cause and the driving force for kinetics. It is clear that any reaction which begins from the mixture of reactants only possesses at the start always infinite and positive value of the affinity. Introducing also the products into the initial mixture, the affinity sign can be changed, and its finite value can be set.

Are the positive value of the rate and the negative value of the affinity of step *2* so unexpectable? The initial reaction mixture contained one of the reactants (I_2) and one of the products (NO) for this step, the latter being in a high excess (in molar concentration values: almost 38 times higher). However, for the step *2* to go in the reverse direction (negative rate), it *has to proceed* in the forward direction (positive rate) at first, because this is the only way how the other product (ICl, *i.e.*, the second reactant in the reverse direction) can be formed. But the second reactant for the forward direction of this step (NOCl) was not present in the initial mixture and could be formed only in the first step. The reaction rate of the second step was thus inevitably positive in the very beginning. During the next course of the reaction, when more and more of ICl developed, the reverse rate rose, as the data measured by *Nebeker* and *Pings* – rapid decrease of the overall rate – show. Their data also reveal that the reverse rate never exceeded the forward one. The cause is much higher overall rate of the first step (in about one order of magnitude during the whole reported run) which supplies the second reactant for the second step (NOCl). This results in a continuous and nearly linear increase of NOCl concentration over the whole run.

The initial reaction mixture contained a high excess of both reactants for the first step (NO and Cl_2) comparing to the concentration of the only one initially present reactant for the second step (I_2). In the time 600 s, which is the last reported instant where A_2 is claimed to be almost zero, *ca.* 90% of initial I_2 amount has reacted (in step *2*), but only 50% of Cl_2 (in the step *1*) and 69% of NO (however, NO is re-formed in step *2*). The negative values of A_2 are a consequence just of the high NO concentration and lower and lower I_2 concentration.

To sum up, the sign of affinity of the second step was determined by the composition of the initial mixture. The positive overall rate of this step is a result of its forcing by the much faster first step. In this sense, the two steps are coupled. Additional experiments with a greater variability of concentration *proportions* in the initial mixture would be desirable to better analyze the affinity – rate relationships. The experiments seem even to confirm that a reaction can proceed *regardless* of its affinity sign. Statement by *Nebeker* and *Pings* that the reaction *2* is running in a direction which is not spontaneous is not appropriate, as they proved in their experiments that the reaction is running spontaneously – of course, on cooperation with reaction *1*. The single affinity just is not suitable criterion of 'spontaneity' in a system of reactions.

The existence of some relation between the measured reaction rates and affinities found by *Nebeker* and *Pings* is a logical consequence of their data gathering and treatment. Only concentration profiles were measured, and both rates and affinities were calculated from them. The rates (v_i) were calculated by differentiation:

$$v_1 = -dc_{\mathrm{Cl_2}}/dt, \quad v_2 = -dc_{\mathrm{I_2}}/dt \tag{3.3}$$

and the affinities by combining the concentrations as stated in *Eqn. 3.1*. From stoichiometry, it follows that only two concentrations are independent, *i.e.*, both affinities can be unambiguously expressed using only $c_{\mathrm{Cl_2}}$ and $c_{\mathrm{I_2}}$. The reaction rates, as they were determined, are some functions of time: $v_i = F_i[c_i(t)] \equiv f_i(t)$ as well as the affinities determined from the same source: $A_j = G_j[c_i(t)] \equiv g_j(t)$. Assuming invertibility of the latter function, relationship $v_i = h_i(A_j)$ naturally follows. From the scarce data given by *Nebeker* and *Pings*, it further follows that the affinities are changing for the major portion of the whole run slowly and almost linearly: $A_j = \mathrm{const.} + \alpha_j t$, where α_j is the proportionality constant. The inversion is thus very simple and possible, and, for those parts of the whole run where also the reaction rate changes almost linearly with time, *i.e.*, where the concentration time derivative is a linear function of time, linear relationships between the rate and affinities are inevitable.

The relationships between rates and affinities, found by *Nebeker* and *Pings*, being linear or nonlinear are thus rather matter of two various data (concentration) fitting procedures than of some general thermodynamic cause. They are a direct consequence of concentration evolutions in time, because they were arrived at by two different operations on the same curves – the concentration – time profiles.

To gain deeper insight into the behavior of *Nebeker* and *Ping*'s reaction system and to test the above reasoning, we tried to do some model calculations. However, discrepancies were immediately revealed. The evolution of the value of A_2 during the course of the reaction under constant temperature and pressure should be determined by the value of Q_2 only (*cf. Eqn. 3.2*). Because the original paper reports on the negative and continuously increasing A_2, Q_2 should be smoothly decreasing. However, with the concentration data published in it, we have found no systematic change in the value of Q_2 (see *Fig. 7*). On contrary, the figure indicates that step *2* roughly maintains its state not far from equilibrium. Of course, our estimation of concentrations from the published figure is not exact, but errors in orders of magnitude are quite improbable unless there are some misprints in the original.

Further, there are no explicit data or information on the equilibrium constants in the original paper [2]. We have, therefore, used the standard *Gibbs* energies of formation from a common handbook [29] to make the model calculations (see the

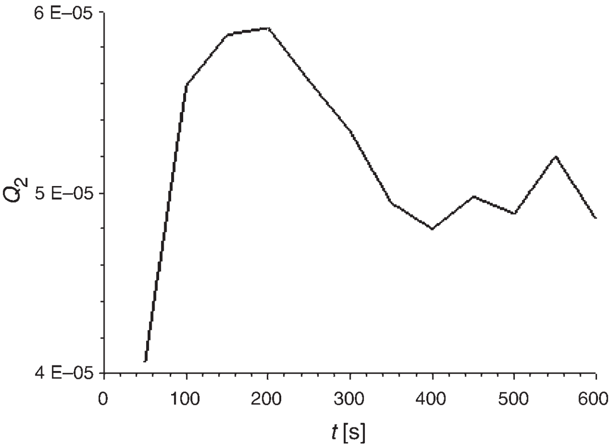

Fig. 7. *Sketch of time profile of reaction quotient for 2 NOCl + I_2 = 2 NO + 2 ICl as calculated from data given by* Nebeker *and* Pings [2]

Table). Standard state for the gaseous substances is in this source taken as a (hypothetical) state of ideal gas under the standard pressure (P°) of 100 kPa. Thus, the activities (a_i) should be calculated from the following relation:

$$a_i = c_i RT/P^\circ \tag{3.4}$$

Table. *Standard* Gibbs *Energy of Formation at 298.15 K* [29]

Substance	ΔG_f° [kJ/mol]
ICl	– 5.5
NO	87.6
NOCl	66.1
I_2	19.3

From these data, values of the equilibrium constants for the two above reactions were calculated as follows: $K_1 = 3.447 \times 10^7$, $K_2 = 5.940 \times 10^{-3}$ (at 298.15 K). Note the difference of several orders of magnitude. *Eqn. 3.4* shows that an ideal system was considered. *Nebeker* and *Pings* report [2] that they made corrections for *small* deviations from the perfect gas law with no explicit details. Because their activity *Eqn. 3.1* does not contain any activity coefficients, they probably considered the whole mixture as ideal (*i.e.*, with unit activity coefficients), and the small non-ideality corrections were made only with respect to the fugacities of pure components (*cf.* also *Eqn. 3.5* below). It was not possible to reproduce *Nebeker* and *Pings* concentration profiles with the equilibrium constants calculated from data in the *Table*. Another problem in modeling arose due to the fact that, in systems with reaction orders equal to the stoichiometric coefficients and with unity activity coefficients, it is not possible to have positive reaction rate and negative affinity at the same time, as can be easily found from *Eqn. 1.4* or *1.5*. There is no information on the reaction orders in the original reference [2].

We have, therefore, used computers only as a substitute for an experimental facility, *i.e.*, only to obtain concentration profiles as close as possible to the published ones, with reaction orders equal to the stoichiometric coefficients. Respective values of the rate constants giving reaction rates in $\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$ were as follows: $\overrightarrow{k}_1 = 6500$, $\overleftarrow{k}_1 = 1.886 \times 10^{-4}$, $\overrightarrow{k}_2 = 5 \times 10^8$, $\overleftarrow{k}_2 = 2577 \times 10^8$. The initial concentrations read from the figure published in the original paper [2] in $\mathrm{mol \cdot dm^{-3}}$: 5.1×10^{-4} for NO, 1.95×10^{-4} for Cl_2, 1.35×10^{-5} for I_2 (and zero for the remaining two components). From the data given by *Nebeker* and *Pings* [2], we have estimated the values of equilibrium constants as 8.43×10^9 (K_1) and 4.33×10^{-5} (K_2). These values were used to calculate the affinities from the calculated concentrations using *Eqn. 3.4*.

Comparison of calculated and experimental (read from published figures) concentration profiles is shown on an example in *Fig. 8*. The affinities calculated for the same example are given in *Fig. 9*; A_1 at least qualitatively imitates the published profile, A_2, on the contrary, does not approach zero but is mostly negative as in the original source which gives the first value for *ca.* 40 s (explained by the authors by initial affinities scattering due to high sensitivity to small fluctuations of the concentrations).

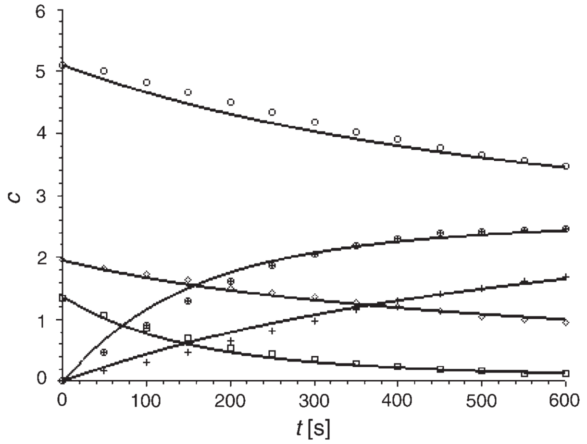

Fig. 8. *Calculated* (lines) *and experimental* [2] (symbols) *time profiles of concentration of components of reacting mixture.* NO: ○, Cl_2: ◇, NOCl: +, I_2: □, ICl: ⊕. Concentration units: 10^{-4} mol/l (NO, Cl_2, NOCl), 10^{-5} mol/l (I_2, ICl).

Computation revealed that, in the very beginning, A_2 is positive and, only during the reaction run, is, due to the action of the first step, forced to the negative values regardless of the positive value of the reaction rate. Although the calculated profiles are not exactly the same as the published ones, both simulated and experimental results point to the high care which should be taken when calculating any quantity, *e.g.*, affinity, from measured data, especially using such functions as logarithm [20]. This is exemplified in *Fig. 10* where calculated values of Q_2 for the I_2 and Cl_2 concentration ranges published by *Nebeker* and *Pings* are plotted. *Fig. 10,a* gives an overall view, *Fig. 10,b* shows points with smaller Q_2 values than K_2 (calculated from the

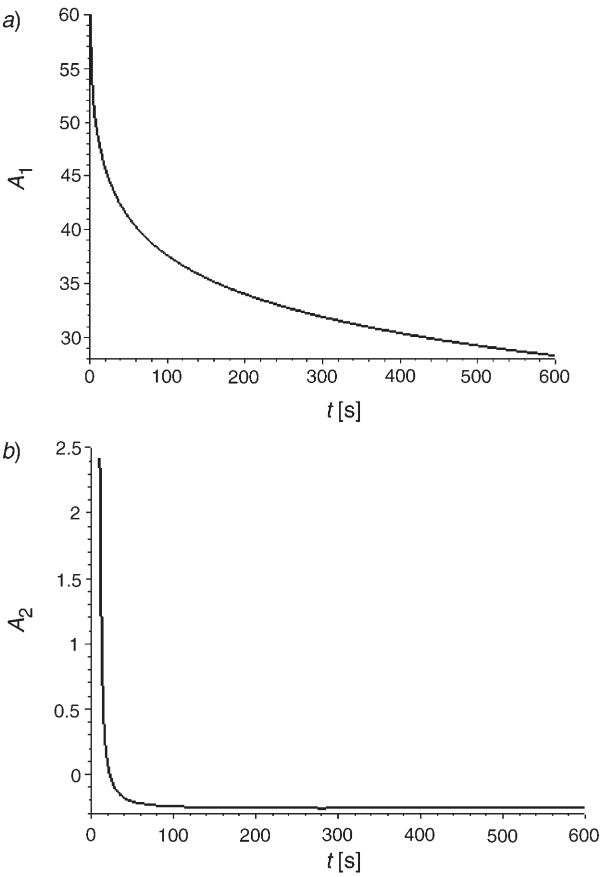

Fig. 9. *Calculated affinity time profiles for* Nebeker *and* Pings' *reaction system* [2]

thermodynamic data), whereas *Fig. 10,c* plots points of higher Q_2 values than K_2. Family of points leading to negative values of A_2 spreads over much more restricted area. The figure also shows small areas of high sensitivity of the reaction quotient to the values of concentrations.

Decreasing the initial concentration of NO led to a delay of changing the values A_2 from positive to negative (see *Figs. 11* and *12*). Making all the initial concentrations equal to that of NO speeds up attaining the negative affinity values (*Fig. 13*). Profile of A_1 for all these three examples resembles that in *Fig. 9,a*. These small examples support speculations that the affinity sign is controlled by the initial (and actual) concentrations and is not a result of some independent, external 'thermodynamic force'. Concentrations are the (independent) quantities which determine the value of both the reaction rate and affinity.

Measuring or calculating concentration profiles, the affinity values and signs are determined by the procedure used to calculate the affinity, *viz.* by the (standard) state and the value of the equilibrium constant. As shown above, with profiles very close to

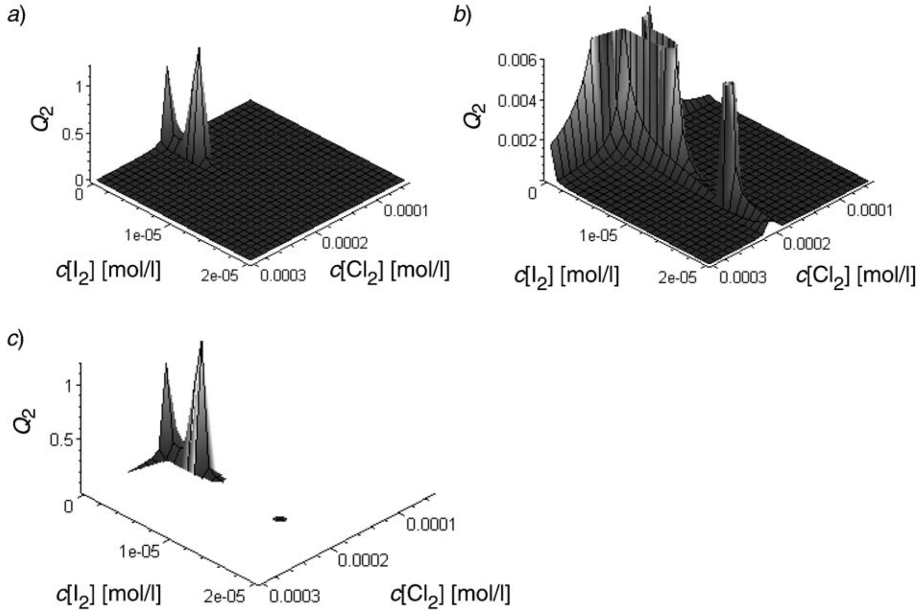

Fig. 10. *Reaction quotient for 2 NOCl + I_2 = 2 NO + 2 ICl as function of Cl_2 and I_2 concentrations within ranges reported by* Nebeker *and* Pings [2]

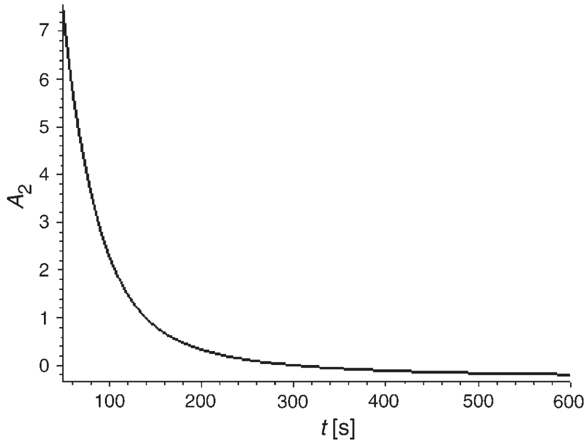

Fig. 11. *Calculated affinity – time profiles for 2 NOCl + I_2 = 2 NO + 2 ICl and initial concentration of NO 1.1×10^{-4} mol dm^{-3}*

published ones and with the standard state and thermodynamic data used in the present days, it was impossible to reproduce reported negative affinity values. Unfortunately, *Nebeker* and *Pings* gave explicitly no values of the equilibrium constants used in their calculations, and no information on the source of thermodynamic data they used, which complicates evaluation of their contribution. Moreover, they used rather unusual state

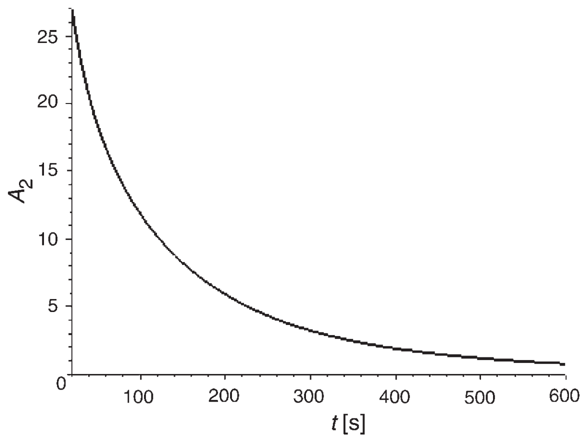

Fig. 12. *Calculated affinity – time profiles for* $2\ NOCl + I_2 = 2\ NO + 2\ ICl$ *and initial concentration of NO* 5.1×10^{-5} *mol* dm^{-3}

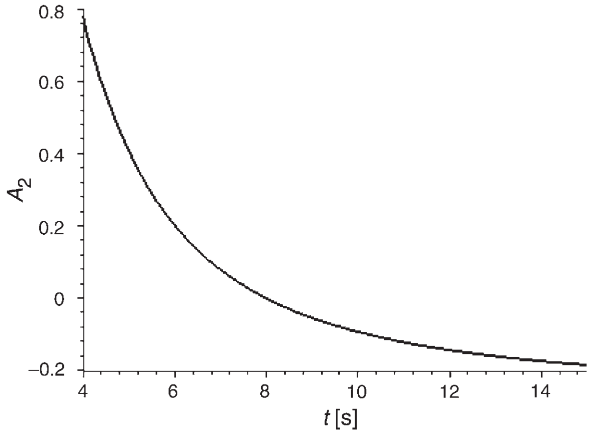

Fig. 13. *Calculated affinity – time profiles for* $2\ NOCl + I_2 = 2\ NO + 2\ ICl$. Initial concentrations of NO, Cl_2, and I_2 all equal to 5.1×10^{-4} mol dm^{-3}.

to calculate the affinities (*cf. Eqn. 3.1*). They mention that the standard state (denoted by '°') of unit fugacity was employed. Analyzing the latter equation, the following conclusions are obtained:

$$c_iRTf_i^0/P = P_if_i^0/P = x_if_i^0 \equiv a_i = f_i/f_i^\circ = f_i \tag{3.5}$$

i.e., the generalized *Raoult* law for the gas phase, $f_i = f_i^0x_i$, is used as a reference state. Perhaps then, the reported negative affinity may be true only for this specific model. Moreover, there is no information in the original source that this state is consistent with the value of equilibrium constant employed in calculations.

4. Conclusions. – Careful analysis of published experimental data shows that they obviously do not prove either the linear relationship between the reaction rate and affinity or the thermodynamic coupling. In fact, the affinity is used as an alternative for the interpretation and description of measured concentration profiles. It is a measure of a distance from equilibrium and not independent variable which fully determines the value of the reaction rate. The linear affinity–rate dependence, reported to be experimentally confirmed, is a result of particular experimental arrangement. The affinity sign in a complex reaction is controlled by the initial and actual concentrations of reacting species and is not a result of some independent, external 'thermodynamic force'. The value and sign of both the reaction rate and affinity are determined by concentrations which are the proper independent quantities (besides temperature).

Rigorous irreversible thermodynamics treatments show that, even in simple (close to 'ideal') material systems and close to equilibrium, relationships between the reaction rate and affinity are not simple and unambiguous [16–19]. By no means is the affinity the only one quantity which determines the reaction rate [17–20]. This is clearly seen even from the 'classical' *Eqn. 1.7.* This equation does not state the reaction rate as a function of its affinity but, at most, the reaction rate as a function of the affinity *and* the forward rate. The right message of the classical equation is that the affinity expresses some potential, but its manifestation in the reaction rate is controlled by the very kinetics. The affinity itself is not sufficient to tell anything about the reaction rate. That is why kinetics is needed besides the thermodynamics.

Value of affinity in practice of chemical kinetics is also not clear. The affinity is not measured. It is only calculated from the measured concentrations similarly, as also the reaction rates are calculated. There is no clear evidence for advantage of calculating and using the affinities instead of the rates. Of course, the affinity is a useful measure of how far is the actual composition from the equilibrium one. Exploring affinity–reaction rate relationships, we should remember that affinity is a thermodynamic quantity, the value of which is dependent on the selected standard state, analogously, as is the value of equilibrium constant. On the contrary, reaction rate or rate constants expressed in common concentration mass-action kinetic law do not refer to or depend on the standard state. We have to check very carefully if the standard state 'hidden' in the affinity (or equilibrium constant) accords to our reacting system and the rate expression used to describe its kinetics.

The affinity is not the (only one) cause of the reaction rate. Concentration–time profiles are not results of some effect of the affinity. On the contrary, the affinity–time profiles are calculated and thus *determined from* the concentration profiles. Statements on the cause and effect should be made very carefully using rigorous mathematical reasoning and not impressions evoked by some equations. Thus, the affinity should be viewed as a consequence of the concentration profiles and underlying kinetics, and not as the cause of the reaction speed.

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Appendix

Table A1. *Data Reported by* Prigogine et al. (Table 1 in [1]) *for Constant Initial Composition*

P_b [atm]	P_c [atm]	P_h [atm]	v' [g/h]	T [K]
0.0242	0.104	0.899	–29	488
			–21.5	498
			9	509
			1	523
			7	533
			16	546
0.0172	0.252	0.771	–9	501
			1	513
			10.5	523.5
			20	535
0.0487	0.0784	0.912	–32	497
			–13	522
			–4.5	533
			4.5	544
			14.5	555
			–7	529
			–24	510
			–33.5	497
0.0977	0.0262	0.925	–36	500
			–21	524
			–11.5	545
			–3	554
			1	561
			8	571
			13	582

Table A2. *Data Reported by* Prigogine et al. (Table 2 in [1]) *for Constant Temperature*

T [K]	P_b [atm]	P_c [atm]	P_h [atm]	v' [g/h]
548a)	0.179	0.073	0.792	–24
	0.204	0.048	0.790	–31
	0.051	0.195	0.799	32
	0.107	0.145	0.796	9
	0.154	0.097	0.792	–15
	0.128	0.121	0.797	–1
	0.077c)	0.017	0.786	29
	0.179	0.073	0.781	–21
	0.128	0.121	0.782	1
563b)	0.294	0.024	0.714	–8
	0.225	0.042	0.765	–1
	0.100	0.075	0.859	11
	0.146	0.063	0.825	7

a) Catalyst weight: 175 mg. b) Catalyst weight: 50 mg. c) There is some error in data published for this run, because the composition does not correspond to the affinity value given in the original paper.

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