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24

Thermodynamics and Reaction Rates

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1. Introduction

Thermodynamics has established in chemistry principally as a science determining possibility and direction of chemical transformations and giving conditions for their final, equilibrium state. Thermodynamics is usually thought to tell nothing about rates of these processes, their velocity of approaching equilibrium. Rates of chemical reactions belong to the domain of chemical kinetics. However, as thermodynamics gives some restriction on the course of chemical reactions, similar restrictions on their rates are continuously looked for. Similarly, because thermodynamic potentials are often formulated as driving forces for various processes, a thermodynamic driving force for reactions rates is searched for.

Two such approaches will be discussed in this article. The first one are restrictions put by thermodynamics on values of rate constants in mass action rate equations. The second one is the use of the chemical potential as a general driving force for chemical reactions and also "directly" in rate equations. These two problems are in fact connected and are related to expressing reaction rate as a function of pertinent independent variables.

Relationships between chemical thermodynamics and kinetics traditionally emerge from the ways that both disciplines use to describe equilibrium state of chemical reactions (chemically reacting systems or mixtures in general). Equilibrium is the main domain of classical, equilibrium, thermodynamics that has elaborated elegant criteria (or, perhaps, definitions) of equilibria and has shown how they naturally lead to the well known equilibrium constant. On the other hand, kinetics describes the way to equilibrium, i.e. the nonequilibrium state of chemical reactions, but also gives a clear idea on reaction equilibrium. Combining these two views various results on compatibility between thermodynamics and kinetics, on thermodynamic restrictions to kinetics etc. were published. The main idea can be illustrated on the trivial example of decomposition reaction AB = A + B with rate (kinetic) equation $r = \vec{k}c_{\mathrm{AB}} - \overleftarrow{k}c_{\mathrm{A}}c_{\mathrm{B}}$ where r is the reaction rate, $\vec{k}, \overleftarrow{k}$ are the forward and reverse rate constants, and c_α are the concentrations. In equilibrium, the reaction rate is zero, consequently $\vec{k} / \overleftarrow{k} = \left(c_{\mathrm{A}}c_{\mathrm{B}} / c_{\mathrm{AB}}\right)_{\mathrm{eq}}$. Because the right hand side corresponds to the thermodynamic equilibrium constant (K) it is concluded that $K = \vec{k} / \overleftarrow{k}$. However, this is simplified approach not taking into account conceptual differences between the true thermodynamic equilibrium constant and the ratio of rate constants that is called here the kinetic equilibrium constant. This discrepancy is sometimes to be removed by restricting this approach to ideal systems of elementary reactions but even then some questions remain.

Chemical potential (μ) is introduced into chemical kinetics by similar straightforward way (Qian & Beard, 2005). If it is expressed by $\mu_\alpha = \mu_\alpha^\circ + RT\ln c_\alpha$, multiplied by stoichiometric coefficients, summed and compared with rate equation it is obtained for the given example that:

$$\Delta\mu \equiv -\mu_{\mathrm{AB}} + \mu_{\mathrm{A}} + \mu_{\mathrm{B}} = RT\ln\frac{c_{\mathrm{A}}c_{\mathrm{B}}}{Kc_{\mathrm{AB}}} = RT\ln\left(\overleftarrow{r}\,/\,\overrightarrow{r}\right) \tag{1}$$

(note that the equivalence of thermodynamic and kinetic equilibrium constants is supposed again; $\overrightarrow{r}, \overleftarrow{r}$ are the forward and reverse rates). Equation (1) used to be interpreted as determining the (stoichiometric) sum of chemical potentials (Δμ) to be some (thermodynamic) "driving force" for reaction rates. In fact, there is "no kinetics", no kinetic variables in the final expression $\Delta\mu = RT\ln\left(\overleftarrow{r}\,/\,\overrightarrow{r}\right)$ and reaction rates are directly determined by chemical potentials what is questionable and calls for experimental verification.

2. Restrictions put by thermodynamics on values of rate constants

2.1 Basic thermodynamic restrictions on rate constants coming from equilibrium

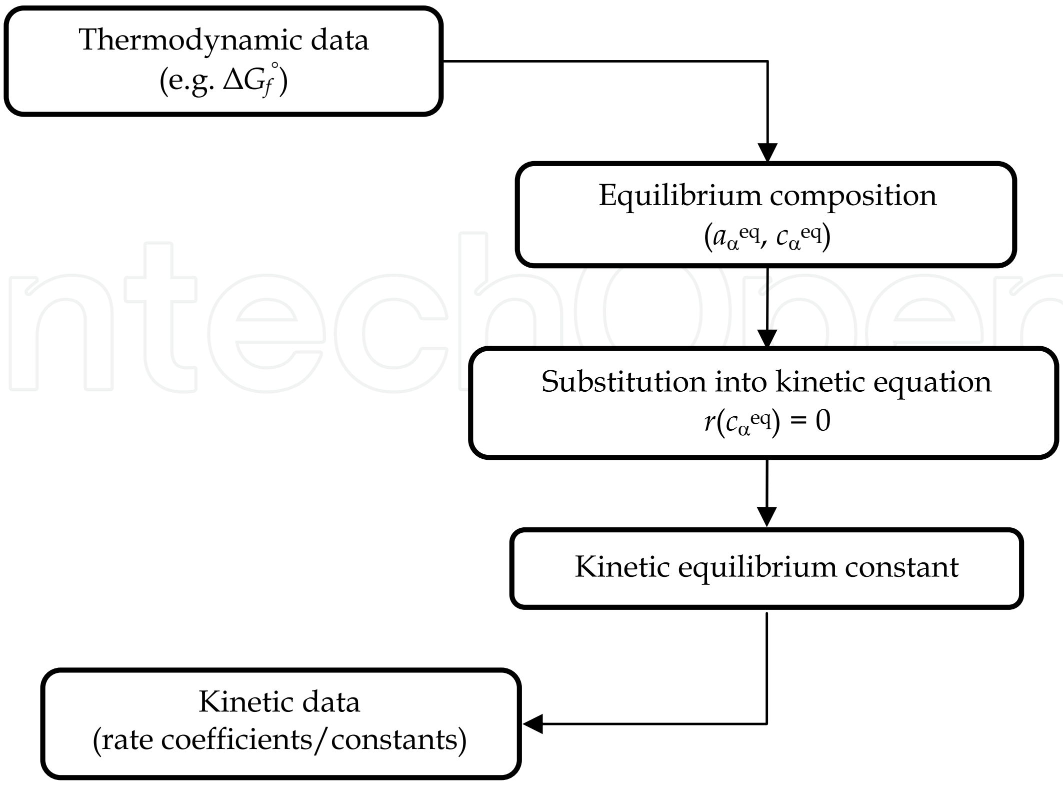
Perhaps the only one work which clearly distinguishes kinetic and thermodynamic equilibrium constant is the kinetic textbook by Eckert and coworkers (Eckert et al., 1986); the former is in it called the empirical equilibrium constant. This book stresses different approaches of thermodynamics and kinetics to equilibrium. In thermodynamics, equilibrium is defined as a state of minimum free energy (Gibbs energy) and its description is based on stoichiometric equation and thermodynamic equilibrium constant containing activities. Different stoichiometric equations of the same chemical equation can give different values of thermodynamic equilibrium constant, however, equilibrium composition is independent on selected stoichiometric equation. Kinetic description of equilibrium is based on zero overall reaction rate, on supposed reaction mechanism or network (reaction scheme) and corresponding kinetic (rate) equation. Kinetic equilibrium constant usually contains concentrations. According to that book, thermodynamic equilibrium data should be introduced into kinetic equations indirectly as shown in the Scheme 1.

Simple example reveals basic problems. Decomposition of carbon monoxide occurs (at the pressure p) according to the following stoichiometric equation:

$$2\,\mathrm{CO} = \mathrm{CO_2} + \mathrm{C} \tag{R1}$$

Standard state of gaseous components is selected as the ideal gas at 101 kPa and for solid component as the pure component at the actual pressure (due to negligible effects of pressure on behavior of solid components, the dependence of the standard state on pressure can be neglected here). Ideal behavior is supposed. Then $a_\alpha = p_\alpha/p^\circ = p_{\mathrm{rel}}\,n_\alpha/n_\Sigma$ for α = CO, CO_2, where $p_{\mathrm{rel}} = p/p^\circ$, and $a_{\mathrm{C}} = 1$; a_α is the activity, p_α is the partial pressure, p° the standard pressure, n_α is the number of moles, and n_Σ the total number of moles. Thermodynamic equilibrium constant is then given by

$$K = \left(\frac{n_\Sigma n_{\mathrm{CO_2}}}{p_{\mathrm{rel}} n_{\mathrm{CO}}^2}\right)_{\mathrm{eq}} = \left[\frac{(c_{\mathrm{CO}} + c_{\mathrm{CO_2}})c_{\mathrm{CO_2}}}{p_{\mathrm{rel}} c_{\mathrm{CO}}^2}\right]_{\mathrm{eq}} \tag{2}$$


Thermodynamic data
(e.g. ΔG_f°)
Equilibrium composition
(a_α^{eq}, c_α^{eq})
Substitution into kinetic equation
$r(c_\alpha^{eq}) = 0$
Kinetic equilibrium constant
Kinetic data
(rate coefficients/constants)

Scheme 1. Connecting thermodynamics and kinetics correctly (Eckert et al., 1986)

On contrary, the ratio of rate constants is given by

$$\left(\frac{\vec{k}}{\overleftarrow{k}}\right)_{\text{eq}} = \left(\frac{c_{\text{CO}_2} c_{\text{C}}}{c_{\text{CO}}^2}\right)_{\text{eq}} \tag{3}$$

It is clear that thermodynamic and kinetic equilibrium constants need not be equivalent even in ideal systems. For example, the former does not contain concentration of carbon and though this could be remedied by stating that carbon amount does not affect reaction rate and its concentration is included in the reverse rate constant, even then the kinetic equilibrium constant could depend on carbon amount in contrast to the thermodynamic equilibrium constant. Some discrepancies could not be remedied by restricting on elementary reactions only – in this example the presence of p_{rel} and of the total molar amount, generally, the presence of quantities transforming composition variables into standard state-related (activity-related) variables, and, of course, discrepancy in dimensionalities of the two equilibrium constants.

Let us use the same example to illustrate the procedure suggested by Eckert et al. (1986). At 1300 K and 202 kPa the molar standard Gibbs energies are (Novák et al., 1999): $G_m^\circ(\text{CO}) = -395.3\ \text{kJ/mol}$, $G_m^\circ(\text{CO}_2) = -712.7\ \text{kJ/mol}$, $G_m^\circ(\text{C}) = -20.97\ \text{kJ/mol}$ and from them the value of thermodynamic equilibrium constant is calculated: $K = 0.00515$. Equilibrium molar balance gives $(n_{\text{CO}_2})_{\text{eq}} = (n_{\text{C}})_{\text{eq}} = x$, $(n_{\text{CO}})_{\text{eq}} = 1 - 2x$, $n_\Sigma = 1 - x$. Then from (2) follows $x = 0.0107$ (Novák et al., 1999). Equilibrium composition is substituted into (3):

$$\left(\frac{\vec{k}}{\overleftarrow{k}}\right)_{\mathrm{eq}} = \frac{0.0107 \times 0.0107}{0.09786^2} = 0.012 \qquad (4)$$

and this is real and true result of thermodynamic restriction on values of rate constants valid at given temperature. More precisely, this is a restriction put on the ratio of rate constants, values of which are supposed to be independent on equilibrium, in other words, dependent on temperature (and perhaps on pressure) only and therefore this restriction is valid also out of equilibrium at given temperature. The numerical value of this restriction is dependent on temperature and should be recalculated at every temperature using the value of equilibrium constant at that temperature.

Thus, simple and safe way how to relate thermodynamics and kinetics, thermodynamic and kinetic equilibrium constants, and rate constants is that shown in Scheme 1. However, it gives no general equations and should be applied specifically for each specific reaction (reacting system) and reaction conditions (temperature, at least). There are also works that try to resolve relationship between the two types of equilibrium constant more generally and, in the same time, correctly and consistently. They were reviewed previously and only main results are presented here, in the next section. But before doing so, let us note that kinetic equilibrium constant can be used as a useful indicator of the distance of actual state of reacting mixture from equilibrium and to follow its approach to equilibrium. In the previous example, actual value of the fraction $c_{\mathrm{CO}_2} c_{\mathrm{C}} / c_{\mathrm{CO}}^2$ can be compared with the value of the ratio $\vec{k} / \overleftarrow{k}$ and relative distance from equilibrium calculated, for more details and other examples see our previous work (Pekař & Koubek, 1997, 1999, 2000).

2.2 General thermodynamic restrictions on rate constants

As noted in the preceding section there are several works that do not rely on simple identification of thermodynamic and kinetic equilibrium constants. Hollingsworth (1952a, 1952b) generalized restriction on the ratio of forward and reverse reaction rates (*f*) defined by

$$f(c_\alpha, T) = \vec{f}(c_\alpha, T) / \overleftarrow{f}(c_\alpha, T) \equiv \vec{r} / \overleftarrow{r} \qquad (5)$$

Hollingsworth showed that sufficient condition for consistent kinetic and thermodynamic description of equilibrium is

$$F(Q_r, T) = \Phi(Q_r/K) \text{ and } \Phi(1) = 1 \qquad (6)$$

where F is the function f with transformed variables, $F(Q_r, T) = f(c_\alpha, T)$, and Q_r is the well known reaction quotient. The first equality in (6) says that function F should be expressible as a function Φ of Q_r/K. This is too general condition saying explicitly nothing about rate constants. Identifying kinetic equilibrium constant with thermodynamic one, condition (6) is specialized to

$$\Phi(Q_r/K) = (Q_r/K)^{-z} \qquad (7)$$

where z is a positive constant. Equation (7) is a generalization of simple identity $K = \vec{k} / \overleftarrow{k}$ from introduction. Hollingsworth also derived the necessary consistency condition:

$$f - 1 = (Q_r/K - 1)\ \Psi(c_\alpha, T, u_j) \tag{8}$$

in the neighbourhood of $Q_r/K = 1$ (i.e., of equilibrium); u_j stands for a set of non-thermodynamic variables. Example of practical application of Hollingsworth's approach in an ideal system is given by Boyd (Boyd, 1977).

Blum (Blum & Luus, 1964) considered a general mass action rate law formulated as follows:

$$r = \vec{k}\phi\prod_{\alpha=1}^{m} a_\alpha^{\omega_\alpha} - \overleftarrow{k}\phi\prod_{\alpha=1}^{m} a_\alpha^{\omega'_\alpha} \tag{9}$$

where ϕ is some function of activities, a_α, of reacting species, ω_α and ω'_α are coefficients which may differ from the stoichiometric coefficients (ν_α), in fact, reaction orders. Supposing that both the equilibrium constant and the ratio of the rate constants are dependent only on temperature, they proved that

$$\vec{k} / \overleftarrow{k} = K^z \tag{10}$$

where

$$z = (\omega'_\alpha - \omega_\alpha) / \nu_\alpha ;\ \ \alpha = 1, \ldots, n \tag{11}$$

General law (9) is rarely used in chemical kinetics, in reactions of ions it probably does not work (Laidler, 1965; Boudart, 1968). It can be transformed, particularly simply in ideal systems, to concentrations. Samohýl (personal communication) pointed out that criteria (11) may be problematic, especially for practically irreversible reactions. For example, reaction orders for reaction 4 NH_3 + 6 NO = 5 N_2 + 6 H_2O were determined as follows: $\omega_{NH_3} = 1$, $\omega_{NO} = 0.5$, $\omega_{N_2} = \omega_{H_2O} = 0$. Orders for reversed direction are unknown, probably because of practically irreversible nature of the reaction. Natural selection could be, e.g., $\omega'_{NO} = 0$ (reaction is not inhibited by reactant), then $z = 1/12$ and from this follows $\omega'_{NH_3} = 2/3$ which seems to be improbable (rather strong inhibition by reactant).

2.3 Independence of reactions, Wegscheider conditions

Wegscheider conditions belong also among "thermodynamic restrictions" on rate constants and have been introduced more than one hundred years ago (Wegscheider, 1902). In fact, they are also based on equivalence between thermodynamic and kinetic equilibrium constants disputed in previous sections. Recently, matrix algebra approaches to find these conditions were described (Vlad & Ross, 2009). Essential part of them is to find (in)dependent chemical reactions. Problem of independent and dependent reactions is an interesting issue sometimes found also in studies on kinetics and thermodynamics of reacting mixtures. As a rule, a reaction scheme, i.e. a set of stoichiometric equations (whether elementary or nonelementary), is proposed, stoichiometric coefficients are arranged into stoichiometric matrix and linear (matrix) algebra is applied to find its rank which determines the number of linearly (stoichiometrically) independent reactions; all other reactions can be obtained as linear combinations of independent ones. This procedure can be viewed as an a posteriori analysis of the proposed reaction mechanism or network. Bowen has shown (Bowen, 1968) that using not only matrix but also vector algebra interesting results can be obtained on the basis of knowing only components of reacting mixture, i.e. with no reaction scheme. This is a priori type of analysis and is used in continuum nonequilibrium (rational) thermodynamics. Because Bowen's results are important for this article they are briefly reviewed now for reader's convenience.

Let a reacting mixture be composed from n components (compounds) which are formed by z different atoms. Atomic composition of each component is described by numbers $T_{\sigma\alpha}$ that indicate the number of atoms σ (= 1, 2,..., z) in component α (= 1, 2,..., n). Atomic masses M_{a}^{σ} in combination with these numbers determine the molar masses M_{α}:

$$M_{\alpha} = \sum_{\sigma=1}^{z} M_{\mathrm{a}}^{\sigma} T_{\sigma\alpha} \tag{12}$$

Although compounds are destroyed or created in chemical reactions the atoms are preserved. If J^{α} denotes the number of moles of the component α formed or reacted per unit time in unit volume, i.e. the reaction rate for the component α (component rate in short), then the persistence of atoms can be formulated in the form

$$\sum_{\alpha=1}^{n} T_{\sigma\alpha} J^{\alpha} = 0; \qquad \sigma = 1,2,\ldots,z \tag{13}$$

This result expresses, in other words, the mass conservation.

Atomic numbers can be arranged in matrix $\| T_{\sigma\alpha} \|$ of dimension $z \times n$. Chemical reactions are possible if its rank (h) is smaller than the number of components (n), otherwise the system (13) has only trivial solution, i.e. is valid only for zero component rates. If $h < z$ then a new $h \times n$ matrix $\| S_{\sigma\alpha} \|$ with rank h can be constructed from the original matrix $\| T_{\sigma\alpha} \|$ and used instead of it:

$$\sum_{\alpha=1}^{n} S_{\sigma\alpha} J^{\alpha} = 0; \qquad \sigma = 1,2,\ldots,h \tag{14}$$

In this way only linearly independent relations from (13) are retained and from the chemical point of view it means that instead of (some) atoms with masses M_{a}^{σ} only some their linear combinations with masses M_{e}^{σ} should be considered as elementary building units of components:

$$M_{\alpha} = \sum_{\sigma=1}^{h} M_{\mathrm{e}}^{\sigma} S_{\sigma\alpha} \tag{15}$$

Example. Mixture of NO_2 and N_2O_4 has the matrix $\| T_{\sigma\alpha} \|$ of dimension 2 × 2 and rank 1; the matrix $\| S_{\sigma\alpha} \|$ is of dimension 1 × 2 and can be selected as $(1 \quad 2)$ which means that the elementary building unit is NO_2 and $M_{\mathrm{e}}^{1} = M_{\mathrm{a}}^{1} + 2M_{\mathrm{a}}^{2} \equiv M_{\mathrm{a}}^{\mathrm{N}} + 2M_{\mathrm{a}}^{\mathrm{O}}$.

Multiplying each of the z relations (13) by corresponding M_{a}^{σ} and summing the results for all σ it follows that $\sum_{\alpha=1}^{n} M_{\alpha} J^{\alpha} = 0$. This fact can be much more effectively formulated in vector form because further important implications than follow. The last equality indicates that component molar masses and rates should form two perpendicular vectors, i.e. vectors with vanishing scalar product. Let us introduce n-dimensional vector space, called the component space and denoted by U, with base vectors $\mathbf{e}_\alpha$ and reciprocal base vectors $\mathbf{e}^\alpha$ (α = 1, 2,..., n). Then the vector of molar masses $\mathbf{M}$ and the vector of reaction rates $\mathbf{J}$ are defined in this space as follows:

$$\mathbf{M} = \sum_{\alpha=1}^{n} M_\alpha \mathbf{e}^\alpha, \quad \mathbf{J} = \sum_{\alpha=1}^{n} J^\alpha \mathbf{e}_\alpha \tag{16}$$

To proceed further we use relations (14) and (15) because in contrast to relations (12) and (13) the matrix $\|S_{\sigma\alpha}\|$ is of “full rank” (does not contain linearly dependent rows). The product of the two vectors can be then expressed in the following form:

$$\mathbf{M}.\mathbf{J} = \left(\sum_{\alpha=1}^{n} \sum_{\sigma=1}^{h} M_\mathrm{e}^\sigma S_{\sigma\alpha} \mathbf{e}^a \right) . \left(\sum_{\alpha=1}^{n} J^\alpha \mathbf{e}_\alpha \right) = \left(\sum_{\sigma=1}^{h} M_\mathrm{e}^\sigma \sum_{\alpha=1}^{n} S_{\sigma\alpha} \mathbf{e}^a \right) . \left(\sum_{\alpha=1}^{n} J^\alpha \mathbf{e}_\alpha \right) = 0 \tag{17}$$

where the latter equality follows using (14). Because the matrix $\|S_{\sigma\alpha}\|$ has rank h, the vectors

$$\mathbf{f}_\sigma = \sum_{\alpha=1}^{n} S_{\sigma\alpha} \mathbf{e}^a; \;\; \sigma = 1,2,\ldots,h \tag{18}$$

that appear in (17) are linearly independent and thus form a basis of a h-dimensional subspace W of the space U (remember that $h < n$). This subspace unambiguously determines complementary orthogonal subspace V (of dimension $n-h$), i.e. $\mathsf{U} = \mathsf{V} \oplus \mathsf{W}$, $\mathsf{V} \perp \mathsf{W}$. From (17) follows:

$$\mathbf{M} = \sum_{\sigma=1}^{h} M_\mathrm{e}^\sigma \mathbf{f}_\sigma \tag{19}$$

which shows that $\mathbf{M}$ can be expressed in the basis of the subspace W or $\mathbf{M} \in \mathsf{W}$. From (14) and $(16)_2$ follows:

$$\mathbf{J}.\mathbf{f}_\sigma = 0; \;\; \sigma = 1,2,\ldots,h \tag{20}$$

which means that $\mathbf{J}$ is perpendicular to all basis vectors of the subspace W, consequently, $\mathbf{J}$ lies in the complementary orthogonal subspace V, $\mathbf{J} \in \mathsf{V}$.

Let us now select basis vectors in the subspace V and denote them $\mathbf{d}^p$, p = 1, 2,..., $n-h$. Of course, these vectors lie also in the (original) space U and can be expressed using its basis vectors analogically to (16):

$$\mathbf{d}^p = \sum_{\alpha=1}^{n} P^{p\alpha} \mathbf{e}_\alpha \tag{21}$$

Because of orthogonality of subspaces V and W, their bases conform to equation

$$\mathbf{f}_\sigma.\mathbf{d}^p = \sum_{\alpha=1}^{n} S_{\sigma\alpha} P^{p\alpha} = 0 \tag{22}$$

which can be alternatively written in matrix form as

$$\left\| P^{p\alpha} \right\| \times \left\| S_{\sigma\alpha} \right\|^{\mathrm{T}} = \left\| 0 \right\| \tag{23}$$

Meaning of the matrix $\left\| P^{p\alpha} \right\|$ can be deduced from two consequences. First, because the reaction vector $\mathbf{J}$ lies in the subspace V, it can be expressed also using its basis vectors, $\mathbf{J} = \sum_{p=1}^{n-h} J_p \mathbf{d}^p$. Substituting for $\mathbf{J}$ from $(16)_2$ and for $\mathbf{d}^p$ from (21), it follows:

$$J^{\alpha} = \sum_{p=1}^{n-h} J_p P^{p\alpha};\ \ \alpha = 1, 2, \ldots, n \tag{24}$$

Second, because the vector of molar masses $\mathbf{M}$ is in the subspace W, it is perpendicular to all vectors $\mathbf{d}^p$ and thus

$$0 = \mathbf{d}^p . \mathbf{M} = \sum_{\alpha=1}^{n} P^{p\alpha} M_{\alpha};\ p = 1, 2, \ldots, n-h \tag{25}$$

as follows after substitution from (19), (21), (220. Eq. (25) shows that matrix $\left\| P^{p\alpha} \right\|$ enables to express component rates in n–h quantities J_p which are, in fact, rates of n–h independent reactions shown by (25) if instead of molar masses M_{α} the corresponding chemical symbols are used. In other words $\left\| P^{p\alpha} \right\|$ is the matrix of stoichiometric coefficients of component α in (independent) reaction *p*.

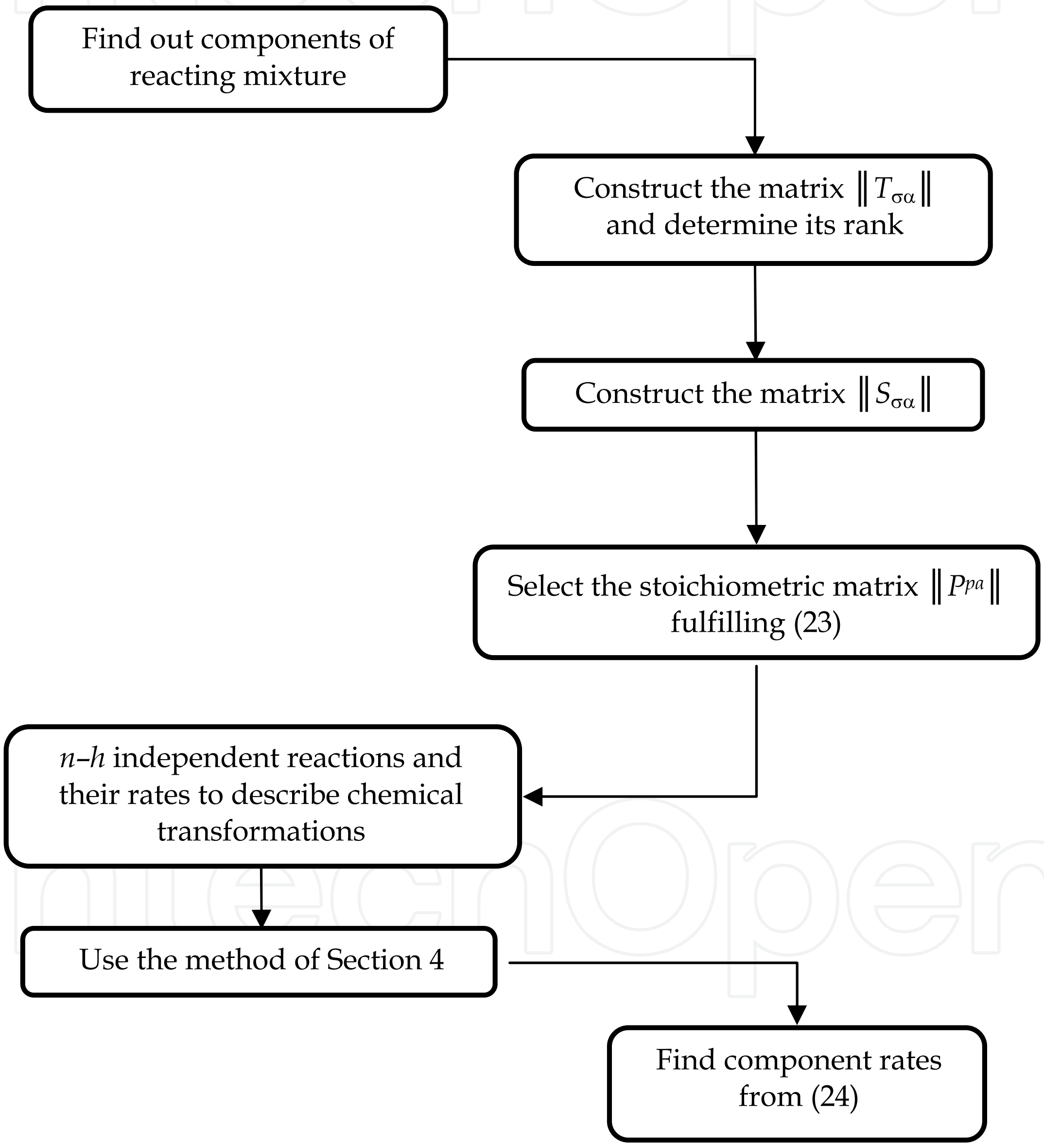
Vector algebra thus shows that chemical transformations fulfilling persistence of atoms (mass conservation) can be equivalently described either by component reaction rates or by rates of independent reactions. The number of the former is equal to the number of components (*n*) whereas the number of the latter is lower (*n*–*h*) which could decrease the dimensionality of the problem of description of reaction rates. In kinetic practice, however, changes in component concentrations (amounts) are measured, i.e. data on component rates and not on rates of individual reactions are collected. Reactions, in the form of reaction schemes, are suggested a posteriori on the basis of detected components, their concentrations changing in time and chemical insight. Then dependencies between reactions can be searched. Vector analysis offers rather different procedure outlined in Scheme 2. Dependencies are revealed at the beginning and then only independent reactions are included in the (kinetic) analysis. Vector analysis also shows how to transform (measured) component rates into (suggested, selected) rates of independent reactions. This transformation is made by standard procedure for interchange between vector bases or between vector coordinates in different bases. First, the contravariant metric tensor with components $d^{rp} = \mathbf{d}^r . \mathbf{d}^p$ is constructed and then its inversion (covariant metric tensor) with components d_{rp} is found. From $\mathbf{J} = \sum_{p=1}^{n-h} J_p \mathbf{d}^p$ it follows that $\mathbf{J}.\mathbf{d}_r = \sum_{p=1}^{n-h} J_p \mathbf{d}^p . \mathbf{d}_r \equiv J_r$. Using in the latter equation the well known relationship between metric tensors and corresponding base vectors and the definition of base vectors (21) it finally follows:

$$J_p = \sum_{\alpha=1}^{n} \left(J^{\alpha} \sum_{r=1}^{n-h} P^{r\alpha} d_{rp} \right);\ p = 1, 2, \ldots, n-h \tag{26}$$

Of course, so far we have seen only relationships between reaction rates and no explicit equations for them like, e.g., the kinetic mass action law. Analysis based only on permanence of atoms cannot give such equations – they belong to the domain of chemical kinetics although they can also be devised by thermodynamics, see Section 4.

Simple example on Wegscheider conditions was presented by Vlad and Ross (Vlad & Ross, 2009) – isomerization taking place in two ways:

$$\mathrm{A} = \mathrm{B},\ \ 2\mathrm{A} = \mathrm{A} + \mathrm{B} \tag{R2}$$


Find out components of reacting mixture
Construct the matrix $\|T_{\sigma\alpha}\|$ and determine its rank
Construct the matrix $\|S_{\sigma\alpha}\|$
Select the stoichiometric matrix $\|P^{\rho\alpha}\|$ fulfilling (23)
n–h independent reactions and their rates to describe chemical transformations
Use the method of Section 4
Find component rates from (24)

Scheme 2. Alternative procedure to find reaction rates

Vlad and Ross note that if the (thermodynamic) equilibrium constant is $K = \left(c_{\mathrm{B}} / c_{\mathrm{A}}\right)_{\mathrm{eq}}$ and if kinetic equations are expressed e.g. $r_1 = \vec{k}_1 c_{\mathrm{A}} - \overleftarrow{k}_1 c_{\mathrm{B}}$ then the consistency between thermodynamic and kinetic description of equilibrium is achieved only if the following (Wegscheider) condition holds:

$$\overrightarrow{k}_1 / \overleftarrow{k}_1 = \overrightarrow{k}_2 / \overleftarrow{k}_2 = K \tag{27}$$

It can be easily checked that in this mixture of one kind of atom and two components the rank of the matrix $\|T_{\sigma\alpha}\|$ (dimension 1×2) is 1 and there is only one independent reaction. The matrix $\|S_{\sigma\alpha}\|$ can be selected as equal to the matrix $\|T_{\sigma\alpha}\|$ and then the stoichiometric matrix can be selected as $\begin{pmatrix} -1 & 1 \end{pmatrix}$ which corresponds to the first reaction (A = B) selected as the independent reaction. There is one base vector $\mathbf{d}^1 = -\mathbf{e}_1 + \mathbf{e}_2$ giving one component contravariant tensor $d^{11} = 2$ and corresponding component of covariant tensor $d_{11} = 1/2$. Consequently, the rate of the independent reaction is related to component reaction rates by:

$$J^{\mathrm{A}} = J_1 P^{11} = -J_1, \quad J^{\mathrm{B}} = J_1 P^{12} = J_1 \tag{28}$$

and $J^{\mathrm{A}} = -J^{\mathrm{B}}$ which follows also from (14). Kinetics of transformations in a mixture of two isomers can be thus fully described by one reaction rate only – either from the two component rates can be measured and used for this purpose, the other component rate is then determined by it, can be calculated from it. At this stage of analysis there is no indication that two reactions should be considered and this should be viewed as some kind of "external" information coming perhaps from experiments. At the same time this analysis does not provide any explicit expression for reaction rate and its dependence on concentration – this is another type of external information coming usually from kinetics. Let us therefore suppose the two isomerization processes given above and their rates formulated in the form of kinetic mass action law:

$$r_1 = \overrightarrow{k}_1 c_{\mathrm{A}} - \overleftarrow{k}_1 c_{\mathrm{B}}, \quad r_2 = \overrightarrow{k}_2 c_{\mathrm{A}}^2 - \overleftarrow{k}_2 c_{\mathrm{A}} c_{\mathrm{B}} \tag{29}$$

Then the only one independent reaction rate is in the form $J_1 = r_1 + r_2$. Note, that although the first reaction has been selected as the independent reaction, the rate of independent reaction is not equal to (its mass action rate) r_1. This interesting finding has probably no specific practical implication. However, individual traditional rates (r_i) should not be independent. Let us suppose that r_2 is dependent on r_1, i.e. can be expressed through it: $r_2 = br_1$; then

$$\left(b\overrightarrow{k}_1 - \overrightarrow{k}_2 c_{\mathrm{A}}\right) c_{\mathrm{A}} - \left(b\overleftarrow{k}_1 - \overleftarrow{k}_2 c_{\mathrm{A}}\right) c_{\mathrm{B}} = 0 \tag{30}$$

should be valid for any concentrations. Sufficient conditions for this are $b = \overrightarrow{k}_2 c_{\mathrm{A}} / \overrightarrow{k}_1 = \overleftarrow{k}_2 c_{\mathrm{A}} / \overleftarrow{k}_1$ and from them follows:

$$\overrightarrow{k}_1 \overleftarrow{k}_2 = \overleftarrow{k}_1 \overrightarrow{k}_2 \tag{31}$$

i.e. "kinetic part" of Wegscheider condition (27). Substituting derived expressions for b into br_1 it can be easily checked that r_2 really results. Although the derivation is rather straightforward and is not based on linear dependency with constant coefficients it points to assumption that Wegscheider conditions are not conditions for consistency of kinetics with thermodynamics but results of dependencies among reaction rates. Moreover, this derivation need not suppose equality of thermodynamic and kinetic equilibrium constant.

There is a thermodynamic method giving kinetic description in terms of independent reactions as noted in Scheme 2, see Section 4.

More complex reaction mixture and scheme was discussed by Ederer and Gilles (Ederer & Gilles, 2007). Their mixture was composed from six formal components (A, B, C, AB, BC, ABC) formed by three atoms (A, B, C). Three independent reactions are possible in this mixture while four reactions were considered by Ederer and Gilles (Ederer & Gilles, 2007) $r_4 = b_1r_1 + b_2r_2 + b_3r_3$ with following mass action rate equations:

$$r_1 = \overrightarrow{k}_1 c_\mathrm{A} c_\mathrm{B} - \overleftarrow{k}_1 c_\mathrm{AB}, \quad r_2 = \overrightarrow{k}_2 c_\mathrm{AB} c_\mathrm{C} - \overleftarrow{k}_2 c_\mathrm{ABC}, \quad r_3 = \overrightarrow{k}_3 c_\mathrm{B} c_\mathrm{C} - \overleftarrow{k}_3 c_\mathrm{BC}, \quad r_4 = \overrightarrow{k}_4 c_\mathrm{A} c_\mathrm{BC} - \overleftarrow{k}_4 c_\mathrm{ABC} \tag{32}$$

Let us suppose that the fourth reaction rate can be expressed through the other three rates: $b_1r_1 + b_2r_2 + b_3r_3$. By similar procedure as in the preceding example we arrive at conditions $b_2 = \overleftarrow{k}_4 / \overleftarrow{k}_2$, $b_3 = -\overrightarrow{k}_4 c_\mathrm{A} / \overleftarrow{k}_3$, and $b_1 = b_2 \overrightarrow{k}_2 c_\mathrm{C} / \overleftarrow{k}_1 = -b_3 \overrightarrow{k}_3 c_\mathrm{C} / \overrightarrow{k}_1 c_\mathrm{A}$ from which it follows that

$$\frac{\overleftarrow{k}_1 \overleftarrow{k}_2 \overrightarrow{k}_3 \overrightarrow{k}_4}{\overrightarrow{k}_1 \overrightarrow{k}_2 \overleftarrow{k}_3 \overleftarrow{k}_4} = 1 \tag{33}$$

i.e., Wegscheider condition derived in (Ederer & Gilles, 2007) from equilibrium considerations. Thus also here Wegscheider condition seems to be a result of mutual dependence of reaction rates and not a necessary consistency condition between thermodynamics and kinetics.

If reactions A + B = AB, AB + C = ABC, and B + C = BC are selected as independent ones then (24) gives

$$J^\mathrm{A} = -J_1, \ J^\mathrm{B} = -J_1 - J_3, \ J^\mathrm{C} = -J_2 - J_3, \ J^\mathrm{AB} = J_1 - J_2, \ J^\mathrm{BC} = J_3, \ J^\mathrm{ABC} = J_2 \tag{34}$$

Remember that, e.g., $J_1 \neq r_1$ but that the relationships between rates of independent reactions and mass action rates (32) follow from (34):

$$J_1 = r_1 + r_4, \ J_2 = r_2 + r_4, \ J_3 = r_3 - r_4 \tag{35}$$

Eq. (26) gives more complex expressions for independent rates, e.g. $J_1 = -J^\mathrm{A}/2 - J^\mathrm{B}/4 + J^\mathrm{AB}/4 - J^\mathrm{BC}/4 + J^\mathrm{ABC}/4$, whereas from (24), i.e. (34), simply follow: $J_1 = -J^\mathrm{A}$, $J_2 = J^\mathrm{ABC}$, $J_3 = J^\mathrm{BC}$. This is because the rates are considered as vector components – components J^α of six dimensional space are transformed to components J_i in three dimensional subspace. Consequently, in practical applications (24) should be preferred in favor of (26) also to express J_i in terms of J^α.

Message from the analysis of independence of reactions in this example is that it is sufficient to measure three component rates only (J^A, J^ABC, J^BC); the remaining three component rates are determined by them. Although concentrations, i.e. component rates, are measured in kinetic experiments, results are finally expressed in reaction rates, rates of reactions occurring in suggested reaction scheme. Component rates are simply not sufficient in kinetic analysis and they are (perhaps always) translated into rates of reaction steps. However, from the three independent rates there cannot be unambiguously determined rates of four reactions in suggested reaction schemes as (35) demonstrates (three equations for four unknown r_i). One equation more is needed and this is the above equation relating r_4 to the remaining three rates. Equations containing r_i are too general and in practice are replaced by mass action expressions shown in (32) – eight parameters (rate constants) are thus introduced in this example. They can be in principle determined from three equations (35) with the three measured independent reactions, four equations relating equilibrium composition (or thermodynamic equilibrium constant) and kinetic equilibrium constant and one Wegscheider condition (33), i.e. eight equations in total. Alternative thermodynamic method is described in Section 4.

Algebraically more rigorous is this analysis in the case of first order reactions as was illustrated on a mixture of three isomers and their triangular reaction scheme which is traditional example used to discuss consistency between thermodynamics and kinetics. Here, Wegscheider relations are consequences of linear dependence of traditional mass action reaction rates (Pekař, 2007).

2.4 Note on standard states

Preceding sections demonstrated that one of the main problems to be solved when relating thermodynamics and kinetics is the transformation between activities and concentration variables. This is closely related to the selection of standard state (important and often overlooked aspect of relating thermodynamic and kinetic equilibrium constants) and to chemical potential. Standard states are therefore briefly reviewed in this section and chemical potential is subject of the following section.

Rates of chemical reactions are mostly expressed in terms of concentrations. Among standard states introduced and commonly used in thermodynamics there is only one based on concentration – the standard state of nonelectrolyte solute on concentration basis. Only this standard state can be directly used in kinetic equations. Standard state in gaseous phase or mixture is defined through (partial) pressure or fugacity. As shown above even in mixture of ideal gases it is impossible to simply use this standard state in concentration based kinetic equations. Although kinetic equations could be reformulated into partial pressures there still remains problem with the fact that standard pressure is fixed (at 1 atm or, nowadays, at 10^5 Pa) and its recalculation to actual pressure in reacting mixture may cause incompatibility of thermodynamic and kinetic equilibrium constants (see the factor p_{rel} in the example above in Section 2.1). This opens another problem – the very selection of standard state, particularly in relation to activity discussed in subsequent section. In principle, it can be selected arbitrarily, as dependent only on temperature or on temperature and pressure. Standard states strictly based on the (fixed) standard pressure are of the former type and only such will be considered in this article. All other states, including states dependent also on pressure, will be called the reference state; the same approach is used, e.g. by de Voe (de Voe, 2001).

The value of thermodynamic equilibrium constant and its dependence or independence on pressure is thus dependent on the selected standard (or reference) state. This is quite uncommon in chemical kinetics where the dependence of rate constants is not a matter of selection of standard states but result of experimental evidence or some theory of reaction rates. As a rule, rate constant is always function of temperature. Sometimes also the dependence on pressure is considered but this is usually the case of nonelementary reactions. Consequently, attempts to relate thermodynamic and kinetic equilibrium constants should select standard state consistently with functional dependence of rate constants. On the other hand, the method of Scheme 1 is self-consistent in this aspect because equilibrium composition is independent of the selection of standard state.

3. Chemical potential and activity revise

Chemical potential is used in discussions on thermodynamic implications on reaction rates, particularly in the form of (stoichiometric) difference between chemical potentials of reaction products and reactants and through its explicit relationship to concentrations (activities, in general). Before going into this type of analysis basic information is recapitulated.

Chemical potential is in classical, equilibrium thermodynamics defined as a partial derivative of Gibbs energy (*G*):

$$\mu_\alpha = \left(\partial G / \partial n_\alpha\right)_{T,p,n_{j\neq\alpha}} \tag{36}$$

Although another definitions through another thermodynamic quantities are possible (and equivalent with this one), the definition using the Gibbs energy is the most useful for chemical thermodynamics. Chemical potential expresses the effect of composition and this effect is also essential in chemical kinetics. To make the mathematical definition of the chemical potential applicable in practice its relationship to composition (concentration) should be stated explicitly. Practical chemical thermodynamics suggests that this is an easy task but we must be very careful and bear all (tacit) presumptions in mind to arrive at proper conclusions. Generally the explicit relationship between chemical composition and chemical potential is stated defining the activity of a component α:

$$a_\alpha = \exp\left(\frac{\mu_\alpha - \mu_\alpha^\circ}{RT}\right) \tag{37}$$

which can be transformed to

$$\mu_\alpha = \mu_\alpha^\circ + RT \ln a_\alpha \tag{38}$$

but this still lacks direct interconnection/linkage to measurable concentrations. Just this is the main problem of applying chemical potential (and activities) in rate equations which systematically use molar concentrations. Even when reaction rates would be expressed using activities in place of concentrations the activities should be properly calculated from the measured concentrations, in other words, the concentrations should be correctly transformed to the activities. Activity is very easily related to measurable composition variable in the case of mixture of ideal gases. Providing that Gibbs energy is a function of temperature, pressure and molar amounts, following relation is well known from thermodynamics for the partial molar volume: $\bar{V}_\alpha = \left(\partial \mu_\alpha / \partial p\right)_{T,n_{j\neq\alpha}}$. In a mixture of ideal gases partial molar volumes are equal to the molar volume of the mixture, V_m (Silbey et al., 2005). Because $V_m = RT/p$ we can write:

$$RT / p = \left(\partial \mu_{\alpha,\mathrm{g}} / \partial p_\alpha\right)\left(\partial p_\alpha / \partial p\right) = x_\alpha \left(\partial \mu_{\alpha,\mathrm{g}} / \partial p_\alpha\right) \tag{39}$$

and

$$RT / p_\alpha = \left(\partial \mu_{\alpha,\mathrm{g}} / \partial p_\alpha\right) \tag{40}$$

Integration from the standard state to some actual state then yields

$$\mu_{\alpha,\mathrm{g}} = \mu^{\circ}_{\alpha,\mathrm{g}} + RT\ln\left(p_\alpha / p^{\circ}\right) \tag{41}$$

Comparing with the definition of activity it follows

$$a_\alpha = p_\alpha / p^{\circ} \ \text{(mixture of ideal gases)} \tag{42}$$

Application of this relationship was illustrated in the example given above. Note that (42) was not derived from the definition of activity but comparing the properties of chemical potential in the ideal gas mixture (41) with the definition of activity. Note also that the partial derivative in the original definition of chemical potential is in general a function of molar amounts (contents) of all components but eq. (42) states that the chemical potential of a component α is a function only of the content of that component.

In a real gas mixture, non-idealities should be taken into account, usually by substituting fugacity (f_α) for the partial pressure:

$$\mu_{\alpha,\mathrm{g}} = \mu^{\circ}_{\alpha,\mathrm{g}} + RT\ln\left(f_\alpha / p^{\circ}\right) \tag{43}$$

The fugacity can be eliminated in favor of directly measurable quantities using the fugacity coefficient ϕ_α

$$f_\alpha = \phi_\alpha p_\alpha \tag{44}$$

and its relationship to the partial molar volume and the total pressure (de Voe, 2001):

$$\mu_{\alpha,\mathrm{g}} = \mu^{\circ}_{\alpha,\mathrm{g}} + RT\ln\left(p_\alpha / p^{\circ}\right) + \int_0^p \left(\bar{V}_\alpha - RT / p\right)\mathrm{d}p \tag{45}$$

It should be stressed that in derivation of the expression for the fugacity coefficient it was assumed that the Gibbs energy is a function of (only) temperature, pressure, and molar amounts of all components. Comparing with the definition of activity we have

$$a_\alpha = f_\alpha / p^{\circ} \ \text{(mixture of gases)} \tag{46}$$

If kinetic equations for mixture of real gases are written in partial pressures then thermodynamic and kinetic equilibrium constants are incompatible due to the presence of fugacity coefficient or the integral in eq. (45). Kinetic equations for mixture of real gases could be formulated in terms of fugacities instead of concentrations (or partial pressures) to achieve compatibility between thermodynamic and kinetic equilibrium constants but even than the same problem remains with the presence of the standard pressure in thermodynamic relations. Kinetic equations formulated in fugacities are really rare – some success in this way was demonstrated by Eckert and Boudart (Eckert & Boudart, 1963) while Mason (Mason, 1965) showed, using the same data, that fugacities need not remedy the whole situation.

Similar derivation for liquid state (solutions) has different basis. It stems from the equilibrium between liquid and gaseous phase in which the following identity holds: $\mu_{\alpha,\mathrm{g}} = \mu_{\alpha,\mathrm{l}}$. Introducing expression (41) or (43) and using either Raoult's or Henry's law for the relationship between compositions of equilibrated liquid and gaseous phases final form of $\mu_{\alpha,l}$ dependence on the composition of liquid is obtained. For example, with Raoult's law $p_\alpha = x_\alpha p_\alpha^*$ and ideal gas phase we have this equation

$$\mu_{\alpha,1} = \mu^\circ_{\alpha,g} + RT\ln\left(x_\alpha p^*_\alpha / p^\circ\right) \equiv \mu^{\text{ref}}_\alpha + RT\ln x_\alpha \tag{47}$$

which has, in fact, inspired the definition of an ideal (liquid, solid, or gas) mixture as a mixture with the chemical potential defined, at a given T and p, as $\mu_\alpha = \mu^{\text{ref}}_\alpha + RT\ln x_\alpha$ where μ_α^{ref} is a function of both T and p. This definition, as well as the identity in (47), can be simply related to the definition of activity only if the standard state is selected consistently with the reference state, i.e. if the former is a function of both T and p. If the standard state is selected as dependent on temperature, as it should be, than the pressure factor (Γ_α) should be introduced (see, e.g., de Voe, 2001)

$$\Gamma_\alpha = \exp\left(\frac{\mu^{\text{ref}}_\alpha - \mu^\circ_\alpha}{RT}\right) \tag{48}$$

Then the activity of a (non-electrolyte) component in real solution is written as $a_\alpha = \Gamma_\alpha \gamma_\alpha x_\alpha$ where γ_α is the activity coefficient introduced by the equation $\mu_\alpha = \mu^{\text{ref}}_\alpha + RT\ln\left(\gamma_\alpha x_\alpha\right)$. Introducing activities in place of concentrations means in this case to know the pressure factor and to transform molar fractions into molar concentrations to be consistent with thermodynamics.

The main problems with using activities defined for liquid systems can be summarized as follows. Activity is based on molar fractions whereas kinetic uses concentrations. Although there are formulas for the conversion of these variables they do not allow direct substitution, they introduce other variables (e.g., solution density) and lead to rather complex expression of thermodynamic equilibrium constant in concentrations. Whereas concentrations of all species are independent (variables) this is not true for molar fractions – value of one from them is unambiguously determined by values of remaining ones. Chemical potential in liquid and activity based on it are introduced on the basis of (liquid-gas) equilibrium while kinetics essentially works with reactions out of equilibrium. Applicability of equilibrium-based formulated in fugacities are really rare in nonequilibrium states deserves further study. The problem with molar fractions can be resolved by the use of molar concentration based Henry's law giving for ideal-dilute solution $\mu_{\alpha,1} = \mu^{\text{ref}}_{\alpha,c} + RT\ln c_\alpha / c^\circ$, however, rate equations should be formulated with the standard concentration. Sometimes following relationship is used: $\mu_{\alpha,1} = \mu^{\text{ref}}_{\alpha,c} + RT\ln c_\alpha / c_\Sigma$ (Ederer & Gilles, 2007) where c_Σ is the sum of all concentrations. In this case, the invertibility for c_α is problematic because it is included in c_Σ; reaction rates should be then formulated in c_α/c_Σ instead of concentrations that is quite unusual. Of course, the value of activity is dependent on the selected standard state, anyway. All attempts to relate thermodynamic and kinetic equilibrium constants should pay great attention to the selection of standard state and its consequences to be really rigorous and correct.

It is clear from this basic overview that chemical potential, activity and their interrelation are in principle equilibrium quantities which, in kinetic applications, are to be used for non-equilibrium situations. Let us now trace one relatively simple non-equilibrium approach to description of chemically reacting systems and its results regarding the chemical potential. Samohýl has developed rational thermodynamic approach for chemically reacting fluids with linear transport properties (henceforth called briefly linear fluids) and these fluids seem to include many (non-electrolyte) systems encountered in chemistry (Samohýl & Malijevský, 1976; Samohýl, 1982, 1987). This is a continuum mechanics based approach working with densities of quantities and specific quantities (considered locally, in other words, as fields but this is not crucial for the present text) therefore it primarily uses densities of components (more precisely, the density of component mass) instead of their molar concentrations or fractions that are common in chemistry. This density, in fact, is known in chemistry as a mass concentration with dimension of mass per (unit) volume and can be thus easily recalculated to concentration quantities more common in chemistry. Chemical potential of a reacting component α is defined in this theory as follows:

$$g_\alpha = \partial\left(\rho \overline{f}\right) / \partial \rho_\alpha \tag{49}$$

Here ρ is the density of mixture, i.e. the sum of all component densities ρ_α, and $\overline{f}$ is the specific free energy of (reacting) mixture as a function of relevant independent variables (the value of this function is denoted by *f*). Inspiration for this definition came from the entropic inequality (the "second law" of thermodynamics) as formulated in rational thermodynamics generally for mixtures and from the fact that this definition enabled to derive classical (equilibrium) thermodynamic relations in the special case that is covered by classical theory. The chemical potential g_α thus has the dimensions of energy per mass. The product $\rho\overline{f}$ essentially transforms the specific quantity to its density and the definition (49) can be viewed as a generalization of the classical definition (36) – partial derivative of mixture free energy (as a function) with respect to an independent variable expressing the amount of a component.

The specific free energy $\overline{f}$ is function of various (mostly kinematic and thermal) variables but here it is sufficient to note that component densities are among them, of course.

In the case of linear fluids it can be proved that free energy is function of densities and temperature only, $f = \overline{f}\left(\rho_1, \rho_2, \ldots, \rho_n, T\right)$. The same result is proved also for chemical potentials g_α and also for reaction rates expressed as component mass created or destroyed by chemical reactions at a given place and time in unit volume, $r_\alpha = \overline{r}_\alpha\left(\rho_1, \rho_2, \ldots, \rho_n, T\right)$. These rates can be easily transformed to molar basis much more common in chemistry using the molar mass M_α: $J^\alpha = r_\alpha / M_\alpha$. Component densities are directly related to molar concentration by a similar equation: $c_\alpha = \rho_\alpha / M_\alpha$. In this way, the well known kinetic empirical law – the law of mass action – is derived theoretically in the form: $J^\alpha = \overline{J}^\alpha\left(c_1, c_2, \ldots, c_n, T\right)$. Apparently, activities could be introduced into this function as independent variables controlling reaction rates by means of relations as $a_\alpha = \Gamma_\alpha \gamma_\alpha c_\alpha / c^\circ$ but this is not rigorous because these relations are consequences of chemical potential and its explicit dependence on mixture composition and not definitions per se. Therefore, chemical potentials should be introduced as independent variables at first. This could be done providing that component densities can be expressed as functions of chemical potential, i.e. providing that functions $g_\alpha = \overline{g}_\alpha\left(\rho_1, \rho_2, \ldots, \rho_n, T\right)$ are invertible (with respect to densities). This invertibility is not self-evident and the best way would be to prove it. Samohýl has proved (Samohýl, 1982, 1987) that if mixture of linear fluids fulfils Gibbs' stability conditions then the matrix with elements $\partial\overline{g}_\alpha / \partial\rho_\gamma$ (α, γ = 1,..., n) is regular which ensures the invertibility. This stability is a standard requirement for reasonable behavior of many reacting systems of chemist's interest, consequently the invertibility can be considered to be guaranteed and we can transform the rate functions as follows:

$$J^\alpha = \overline{J}^\alpha\left(\rho_1, \rho_2, \ldots, \rho_n, T\right) = \hat{J}^\alpha\left(g_1, g_2, \ldots, g_n, T\right) = \breve{J}^\alpha\left(\mu_1, \mu_2, \ldots, \mu_n, T\right) \tag{50}$$

where the last transformation was made using the following transformation of (specific) chemical potential into the traditional chemical potential (which will be called the molar chemical potential henceforth): $\mu_\alpha = g_\alpha M_\alpha$. Using the definition of activity (37) another transformation, to activities, can be made providing that the standard state is a function of temperature only:

$$\breve{J}^\alpha\left(\mu_1, \mu_2, \ldots, \mu_n, T\right) = \tilde{J}^\alpha\left(a_1, a_2, \ldots, a_n, T\right) \tag{51}$$

It should be stressed that chemical potential of component α as defined by (49) is a function of densities of all components, i.e. of ρ_γ, γ = 1,..., n, therefore also the molar chemical potential is following function of composition: $\mu_\alpha = \overline{\mu}_\alpha\left(c_1, c_2, \ldots, c_n, T\right)$. Note that generally any rate of formation or destruction (J^α) is a function of densities, or chemical potentials, or activities, etc. of all components.

Although the functions (dependencies) given above were derived for specific case of linear fluids they are still too general. Yet simpler fluid model is the simple mixture of fluids which is defined as mixture of linear fluids constitutive (state) equations of which are independent on density gradients. Then it can be shown (Samohýl, 1982, 1987) that

$$\partial\overline{f}_\alpha / \partial\rho_\gamma = 0 \quad \text{for } \alpha \neq \gamma;\ \alpha, \gamma = 1, \ldots, n \tag{52}$$

and, consequently, also that $g_\alpha = \overline{g}_\alpha\left(\rho_\alpha, T\right)$, i.e. the chemical potential of any component is a function of density of this component only (and of temperature). Mixture of ideal gases is defined as a simple mixture with additional requirement that partial internal energy and enthalpy are dependent on temperature only. Then it can be proved (Samohýl, 1982, 1987) that chemical potential is given by

$$g_\alpha = g_\alpha^\circ(T) + R_\alpha T \ln\left(p_\alpha / p^\circ\right) \tag{53}$$

that is slightly more general than the common model of ideal gas for which $R_\alpha = R/M_\alpha$. Thus the expression (41) is proved also at nonequilibrium conditions and this is probably only one mixture model for which explicit expression for the dependence of chemical potential on composition out of equilibrium is derived. There is no indication for other cases while the function $g_\alpha = \overline{g}_\alpha\left(\rho_\alpha, T\right)$ should be just of the logarithmic form like (47). Let us check conformity of the traditional ideal mixture model with the definition of simple mixture. For solute in an ideal-dilute solution following concentration-based expression is used:

$$\mu_\alpha = \mu_\alpha^{\mathrm{ref}} + RT\ln\left(c_\alpha / c^\circ\right) \tag{54}$$

where $\mu_\alpha^{\mathrm{ref}}$ includes (among other) the gas standard state and concentration-based Henry's constant. Changing to specific quantities and densities we obtain:

$$g_\alpha = \mu_\alpha^{\mathrm{ref}} / M_\alpha + \left(RT / M_\alpha\right)\ln\left(\rho_\alpha / M_\alpha c^\circ\right) \tag{54}$$

which looks like a function of ρ_α and T only, i.e. the simple mixture function $g_\alpha = \overline{g}_\alpha\left(\rho_\alpha, T\right)$. However, the referential state is a function of pressure so this is not such function rigorously. Except ideal gases there is probably no proof of applicability of classical expressions for dependence of chemical potential on composition out of equilibrium and no proof of its logarithmic point. There are probably also no experimental data that could help in resolving this problem.

4. Solution offered by rational thermodynamics

Rational thermodynamics offers certain solution to problems presented so far. It should be stressed that this is by no means totally general theory resolving all possible cases. But it clearly states assumptions and models, i. e. scope of its potential application.

The first assumption, besides standard balances and entropic inequality (see, e.g., Samohýl, 1982, 1987), or model is the mixture of linear fluids in which the functional form of reaction rates was proved: $J^\alpha = \overline{J}^\alpha\left(c_1, c_2, \ldots, c_n, T\right)$ (Samohýl & Malijevský, 1976; Samohýl, 1982, 1987). Only independent reaction rates are sufficient that can be easily obtained from component rates, cf. (26) from which further follows that they are function of the same variables. This function, $J_i = \overline{J}_i\left(c_1, c_2, \ldots, c_n, T\right)$, is approximated by a polynomial of suitable degree (Samohýl & Malijevský, 1976; Samohýl, 1982, 1987). Equilibrium constant is defined for each independent reaction as follows:

$$-RT\ln K_p = \sum_{\alpha=1}^{n} \mu_\alpha^\circ P^{p\alpha};\ \ p = 1, 2, \ldots, n-h \tag{55}$$

Activity (37) is supposed to be equal to molar concentrations (divided by unit standard concentration), which is possible for ideal gases, at least (Samohýl, 1982, 1987). Combining this definition of activity with the proved fact that in equilibrium $\sum_{\alpha=1}^{n} (\mu_\alpha)_{\mathrm{eq}} P^{p\alpha} = 0$ (Samohýl, 1982, 1987) it follows

$$K_p = \prod_{\alpha=1}^{n}\left[(c_\alpha)_{\mathrm{eq}}\right]^{P^{p\alpha}} \tag{56}$$

Some equilibrium concentrations can be thus expressed using the others and (56) and substituted in the approximating polynomial that equals zero in equilibrium. Equilibrium polynomial should vanish for any concentrations what leads to vanishing of some of its coefficients. Because the coefficients are independent of equilibrium these results are valid also out of it and the final simplified approximating polynomial, called thermodynamic polynomial, follows and represents rate equation of mass action type. More details on this method can be found elsewhere (Samohýl & Malijevský, 1976; Pekař, 2009, 2010). Here it is illustrated on two examples relevant for this article.

First example is the mixture of two isomers discussed in Section 2. 3. Rate of the only one independent reaction, selected as A = B, is approximated by a polynomial of the second degree:

$$J_1 = k_{00} + k_{10}c_{\mathrm{A}} + k_{01}c_{\mathrm{B}} + k_{20}c_{\mathrm{A}}^2 + k_{02}c_{\mathrm{B}}^2 + k_{11}c_{\mathrm{A}}c_{\mathrm{B}} \tag{57}$$

The concentration of B is expressed from the equilibrium constant, $(c_{\mathrm{B}})_{\mathrm{eq}} = K(c_{\mathrm{A}})_{\mathrm{eq}}$ and substituted into (57) with $J_1 = 0$. Following form of the polynomial in equilibrium is obtained:

$$0 = k_{00} + \left(k_{10} + K\,k_{01}\right)(c_{\mathrm{A}})_{\mathrm{eq}} + \left(k_{20} + K^2k_{02} + K\,k_{11}\right)(c_{\mathrm{A}})_{\mathrm{eq}}^2 \tag{58}$$

Eq. (58) should be valid for any values of equilibrium concentrations, consequently

$$k_{00} = 0; \quad k_{10} = -K\,k_{01}; \quad k_{20} = -K^2k_{02} - K\,k_{11} \tag{59}$$

Substituting (59) into (57) the final thermodynamic polynomial (of the second degree) results:

$$J_1 = k_{10}\left(-Kc_{\mathrm{A}} + c_{\mathrm{B}}\right) + k_{02}\left(-K^2c_{\mathrm{A}}^2 + c_{\mathrm{B}}^2\right) + k_{11}\left(-Kc_{\mathrm{A}}^2 + c_{\mathrm{A}}c_{\mathrm{B}}\right) \tag{60}$$

Note, that coefficients k_{ij} are functions of temperature only and can be interpreted as mass action rate constants (there is no condition on their sign, if some k_{ij} is negative then traditional rate constant is k_{ij} with opposite sign). Although only the reaction A = B has been selected as the independent reaction, its rate as given by (60) contains more than just traditional mass action term for this reaction. Remember that component rates are given by (28). Selecting $k_{02} = 0$ two terms remain in (60) and they correspond to the traditional mass action terms just for the two reactions supposed in (R2). Although only one reaction has been selected to describe kinetics, eq. (60) shows that thermodynamic polynomial does not exclude other (dependent) reactions from kinetic effects and relationship very close to $J_1 = r_1 + r_2$, see also (29), naturally follows. No Wegscheider conditions are necessary because there are no reverse rate constants. On contrary, thermodynamic equilibrium constant is directly involved in rate equation; it should be stressed that because no reverse constant are considered this is not achieved by simple substitution of K for $\overleftarrow{k}_j$ from (27). Eq. (60) also extends the scheme (R2) and includes also bimolecular isomerization path: 2A = 2B.

This example illustrated how thermodynamics can be consistently connected to kinetics considering only independent reactions and results of nonequilibrium thermodynamics with no need of additional consistency conditions.

Example of simple combination reaction A + B = AB will illustrate the use of molar chemical potential in rate equations. In this mixture of three components composed from two atoms only one independent reaction is possible. Just the given reaction can be selected with equilibrium constant defined by (55): $\ln K = \left(-\mu_{\mathrm{A}}^{\circ} - \mu_{\mathrm{B}}^{\circ} + \mu_{\mathrm{AB}}^{\circ}\right)/(-RT)$ and equal to

$K = \left(c_{\mathrm{AB}} / c_{\mathrm{A}} c_{\mathrm{B}}\right)_{\mathrm{eq}}$, cf. (56). The second degree thermodynamic polynomial results in this case in following rate equation:

$$J_1 = k_{110}(c_{\mathrm{A}} c_{\mathrm{B}} - K^{-1} c_{\mathrm{AB}}) \tag{61}$$

that represents the function $J_1 = \overline{J}_1(T, c_{\mathrm{A}}, c_{\mathrm{B}}, c_{\mathrm{AB}})$. Its transformation to the function $J_1 = \breve{J}_1(T, \mu_{\mathrm{A}}, \mu_{\mathrm{B}}, \mu_{\mathrm{AB}})$ gives:

$$J_1 = k_{110} \exp\left(\frac{-\mu_{\mathrm{A}}^{\circ} - \mu_{\mathrm{B}}^{\circ}}{RT}\right)\left[\exp\left(\frac{\mu_{\mathrm{A}} + \mu_{\mathrm{B}}}{RT}\right) - \exp\frac{\mu_{\mathrm{AB}}}{RT}\right] \tag{62}$$

This is thermodynamically correct expression (for the supposed thermodynamic model) of the function $\breve{J}$ discussed in Section 3 and in contrast to (1). It is clear that proper "thermodynamic driving force" for reaction rate is not simple (stoichiometric) difference in molar chemical potentials of products and reactants. The expression in square brackets can be considered as this driving force. Equation (62) also lucidly shows that high molar chemical potential of reactants in combination with low molar chemical potential of products can naturally lead to high reaction rate as could be expected. On the other hand, this is achieved in other approaches, based on $\sum \nu_i \mu_i$, due to arbitrary selection of signs of stoichiometric coefficients. In contrast to this straightforward approach illustrated in introduction, also kinetic variable (k_{110}) is still present in eq. (62), explaining why some "thermodynamically highly forced" reactions may not practically occur due to very low reaction rate. Equation (62) includes also explicit dependence of reaction rate on standard state selection (cf. the presence of standard chemical potentials). This is inevitable consequence of using thermodynamic variables in kinetic equations. Because also the molar chemical potential is dependent on standard state selection, it can be perhaps assumed that these dependences are cancelled in the final value of reaction rate.

Rational thermodynamics thus provides efficient connection to reaction kinetics. However, even this is not totally universal theory; on the other hand, presumptions are clearly stated. First, the procedure applies to linear fluids only. Second, as presented here it is restricted to mixtures of ideal gases. This restriction can be easily removed, if activities are used instead of concentrations, i.e. if functions $\tilde{J}$ are used in place of functions $\overline{J}$ – all equations remain unchanged except the symbol a_α replacing the symbol c_α. But then still remains the problem how to find explicit relationship between activities and concentrations valid at non equilibrium conditions. Nevertheless, this method seems to be the most carefully elaborated thermodynamic approach to chemical kinetics.

5. Conclusion

Two approaches relating thermodynamics and chemical kinetics were discussed in this article. The first one were restrictions put by thermodynamics on the values of rate constants in mass action rate equations. This can be also formulated as a problem of relation, or even equivalence, between the true thermodynamic equilibrium constant and the ratio of forward and reversed rate constants. The second discussed approach was the use of chemical potential as a general driving force for chemical reaction and "directly" in rate equations.

Both approaches are closely connected through the question of using activities, that are common in thermodynamics, in place of concentrations in kinetic equations and the problem of expressing activities as function of concentrations.

Thermodynamic equilibrium constant and the ratio of forward and reversed rate constants are conceptually different and cannot be identified. Restrictions following from the former on values of rate constants should be found indirectly as shown in Scheme 1.

Direct introduction of chemical potential into traditional mass action rate equations is incorrect due to incompatibility of concentrations and activities and is problematic even in ideal systems.

Rational thermodynamic treatment of chemically reacting mixtures of fluids with linear transport properties offers some solution to these problems whenever its clearly stated assumptions are met in real reacting systems of interest. No compatibility conditions, no Wegscheider relations (that have been shown to be results of dependence among reactions) are then necessary, thermodynamic equilibrium constants appear in rate equations, thermodynamics and kinetics are connected quite naturally. The role of ("thermodynamically") independent reactions in formulating rate equations and in kinetics in general is clarified.

Future research should focus attention on the applicability of dependences of chemical potential on concentrations known from equilibrium thermodynamics in nonequilibrium states, or on the related problem of consistent use of activities and corresponding standard states in rate equations.

Though practical chemical kinetics has been successfully surviving without special incorporation of thermodynamic requirements, except perhaps equilibrium results, tighter connection of kinetics with thermodynamics is desirable not only from the theoretical point of view but may be of practical importance considering increasing interest in analyzing of complex biochemical network or increasing computational capabilities for correct modeling of complex reaction systems. The latter when combined with proper thermodynamic requirements might contribute to more effective practical, industrial exploitation of chemical processes.

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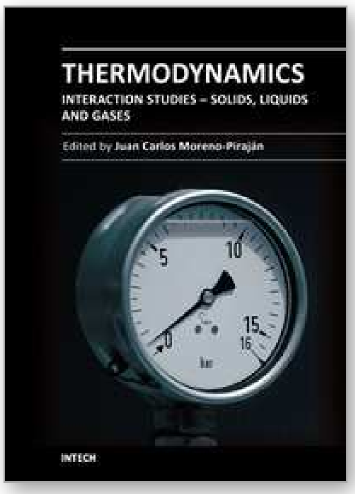

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