# MACROSCOPIC DERIVATION OF THE KINETIC MASS ACTION LAW

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Using several reaction examples with experimentally determined rate equations, traditional mass action rate equations are shown to be simplified forms of polynomial approximation to a general rate function derived by non-equilibrium thermodynamics for a mixture of fluids with linear transport properties. The mass action kinetic law is thus proved also on the macroscopic level and limited to this type of fluids.

**INTRODUCTION**

The mass action law is a well established instrument of chemical kinetics for formulating reaction rate equations. According to this law, the forward or backward reaction rate is written as a product of the rate constant and concentrations of reacting species raised to reaction orders; the overall rate of a reversible reaction is then given by the difference between the forward and backward rates. On the macroscopic level, this law is viewed as a result of experimental experience and not of some theoretical derivation, cf. any textbook on physical chemistry or chemical kinetics, e.g. [1-4]. Explanations come only from microscopic approaches – collision or statistical theories. Indeed, several phenomenological theoretical (thermodynamic) approaches to mass action kinetics have been published; they were reviewed in details in ref. [5]. Briefly, some of them only tested the mass action rate equations for thermodynamic consistency, i.e. used the mass action a priori [6-12]. In a paper by García-Colín et al. [13] it is claimed that the kinetic mass-action law was derived from extended irreversible thermodynamics. In fact, an equation for the time derivative of reaction rate was derived, which is determined by the affinity, heat and diffusion fluxes and some undetermined function. Resulting equation is thus not in the form of traditional mass action law. Lebon et al. [14] postulated that the time evolution of difference of the degree of advancement and the equilibrium degree of advancement is a function of temperature, pressure and this difference. They derived an equation relating the time evolution of this difference to the affinity and some undetermined function of temperature, pressure and this difference, which is claimed to be the standard law of mass-action. However, no explicit mass-action rate equation was derived. Lengyel in a series of papers [15-18] introduced the mass-action law into the non-equilibrium thermodynamics based on Gyarmati's variational approach and reformulated it into a form containing affinities in the forward and reverse reaction directions. Similar approach was used by Oláh [19-24] who prefers chemical potentials instead of affinities. Continuum thermodynamics [25-31] provides only very general statements on the functional form of reaction rate, e.g., reaction rate is a function of densities (i.e., mass concentrations) of components present in a reacting mixture, temperature, and gradients of density, temperature and deformations. No particular form of the function is derived.

There is, however, a result of macroscopic theory that can be considered as a derivation of the mass action law. Samohýl and Malijevský [32] *proved*, using phenomenological non-

equilibrium (rational) thermodynamics, that in a reacting mixture of linear fluids, reaction rates are functions of temperature and concentration only, $r = f(T, c_1, c_2,…, c_n)$. This is a general statement of what the mass action law says specifically. Moreover, this general proof limits its validity to the linear fluids only; in more complex material systems, reaction rates may be functions of additional variables, e.g. density, temperature or deformation gradients. Briefly, linear fluids are a class of fluid materials with (general) Newtonian flow behavior, with heat transfer and mass transport, i.e., material model covering a broad spectrum of systems encountered in practical chemistry.

The general rate function will be analyzed here for several examples to find conditions under which the function is really transformed into traditional mass action reaction rates that can be thus derived on the basis of a purely macroscopic approach. It should be noted that this approach works with independent reactions only because they are sufficient for mathematical description of transformations in chemically reacting systems and their kinetics. Independent reactions are defined by linear algebra as a set of reactions which cannot be obtained as a linear combination of other reactions occurring in the system; for more details see Bowen [33]. The number of independent reactions is determined by the number of components in reacting mixture and by the number of atoms from which they are formed.

**THEORY**

Samohýl [32, 34, 35] (see also [5]) suggested to approximate the general rate function $r = f(T, c_1, c_2,…, c_n)$, resulting from non-equilibrium thermodynamics of linear fluids, by a polynomial of suitable degree ($M$) in concentrations ($c_\alpha$):

$$\mathbf{r} = \sum_{\beta=1}^{Z} \mathbf{k}_{\mathbf{v}_\beta} \prod_{\alpha=1}^{n} c_\alpha^{v_{\beta\alpha}}, \quad \sum_{\alpha=1}^{n} v_{\beta\alpha} \leq M \tag{1}$$

where $\mathbf{r}$ is the vector containing rates of independent reactions. The vector $\mathbf{k}_{\mathbf{v}_\beta}$ contains polynomial coefficients dependent on temperature only, the vectors $\mathbf{v}_\beta = (v_{\beta 1}, v_{\beta 2},…, v_{\beta n})$ contain the polynomial powers (exponents) and are used also as subscripts to index vectors of the polynomial coefficients ($\mathbf{k}_{\mathbf{v}_\beta}$). When used in the subscripts of vectors $\mathbf{k}_{\mathbf{v}_\beta}$, the components of vectors $\mathbf{v}_\beta$ are written without commas and parenthesis. Note that the vector component $v_{\beta\alpha}$ determines the power of concentration of component $\alpha$ in the corresponding polynomial term

β. $Z$, the number of polynomial terms, is determined by the number of reacting components ($n$) and the polynomial degree [34, 35]. The polynomial approximation should satisfy also equilibrium conditions which, after introducing the equilibrium constants of independent reactions (assumption of ideal behavior is sufficient in this work), put restrictions on some of the polynomial coefficients – some of them turn out to be zero, some can be expressed through others [34, 35]; see also the first example below. Because the coefficients are dependent on temperature only, these restrictions are valid also out of equilibrium and the approximating polynomial is greatly simplified. Resulting polynomial, expressing the reaction rate equation, is called here the thermodynamic polynomial.

To formulate the approximating polynomial (1) and to transform it to final rate equation, the thermodynamic polynomial, only the list of all components detected in a reacting mixture is needed as a starting point. The polynomial approximation directly uses equilibrium constants, i.e. it does not need the backward rate constants; thus also detailed balancing (microscopic reversibility) is automatically satisfied.

To make discussion clear, textbook reaction examples were selected but such that were published with experimentally determined rate equation.


**RESULTS AND DISCUSSION**

The first example is NOBr decomposition:

$$2\,NOBr \rightarrow 2\,NO + Br_2 \tag{R1}$$

with a simple second order rate equation, $r = k(c_{NOBr})^2$ [36]. In this case of three atoms and three components, only one independent reaction is possible [33]. Let us select just the stoichiometric reaction R1. The equilibrium condition in the case of the first and second degree approximating polynomial leads to a conclusion that these polynomials are identically zero. Consequently, the general rate function $r = f(T, c_1, c_2,\ldots, c_n)$ should be approximated by a polynomial of degree not smaller than three. The third degree approximating polynomial is as follows:

$$
\begin{aligned}
r = {} & k_{000} + k_{100}c_1 + k_{010}c_2 + k_{001}c_3 + k_{200}c_1^2 + k_{020}c_2^2 + k_{002}c_3^2 + k_{110}c_1c_2 + k_{101}c_1c_3 + k_{011}c_2c_3 + \\
& k_{300}c_1^3 + k_{030}c_2^3 + k_{003}c_3^3 + k_{111}c_1c_2c_3 + k_{120}c_1c_2^2 + k_{210}c_1^2c_2 + k_{012}c_2c_3^2 + k_{021}c_2^2c_3 + \\
& k_{102}c_1c_3^2 + k_{201}c_1^2c_3
\end{aligned}
\tag{2}
$$

(1 = NOBr, 2 = NO, 3 = Br$_2$). To apply the equilibrium condition, the concentration of bromine is expressed from the equation for the equilibrium constant of R1 ($K$),

$(c_3)_{eq} = K(c_1^2 c_2^{-2})_{eq}$, and substituted into the equilibrium polynomial ($r_{eq} = 0$). Two terms of resulting polynomial can be then merged, viz. the terms with $c_1^2$, and the coupled term reads $(k_{200} + k_{021}K)(c_1^2)_{eq}$. Because the equilibrium polynomial should be zero for any equilibrium concentrations, it follows that all coefficients in the equilibrium polynomial are zero [34, 35]. Consequently, most coefficients $k_{ijl}$ are zero and only from the coupled term follows that $k_{021} = -k_{200}K^{-1}$. These conclusions are valid also outside the equilibrium because the coefficients are functions of temperature only. The resulting thermodynamic polynomial then is:

$$r = k_{200}(c_1^2 - K^{-1}c_2^2 c_3) \tag{3}$$

The experimental mass action rate equations is recovered if $k \equiv k_{200}$ and $K^{-1} \rightarrow 0$. The latter condition is a result of reaction irreversibility expressed by the experimental rate equation. In this example, the traditional and experimentally determined mass action law is thus a simplified form of the third degree thermodynamic polynomial.

The second example is the reaction between nitrogen dioxide and carbon monoxide:

$$NO_2 + CO \rightarrow NO + CO_2 \tag{R2}$$

In experiments, another component of the reacting mixture was detected – NO$_3$. In this mixture of five components formed from three atoms two independent reactions are possible [33]. They can be selected as the two steps of experimentally confirmed mechanism [36]:

$$2\,NO_2 \rightarrow NO + NO_3 \tag{R2-1}$$

$$NO_3 + CO \rightarrow NO_2 + CO_2 \tag{R2-2}$$

Thermodynamic polynomial resulting from the first degree approximating polynomial is identically zero. The second degree thermodynamic polynomial is as follows:

$$r_i = k_{20000}^i(c_1^2 - K_1^{-1}c_3 c_5) + k_{11000}^i(c_1 c_2 - K_1^{-1}K_2^{-1}c_3 c_4) + k_{01001}^i(c_2 c_5 - K_2^{-1}c_1 c_4) \tag{4}$$

(1 = NO$_2$, 2 = CO, 3 = NO, 4 = CO$_2$, 5 = NO$_3$) where $r_i$ is the rate of $i$-th independent reaction and $K_i$ its equilibrium constant. The experimental rate law is $r = kc_1^2$ [36] and represents the reaction rate for NO$_2$ (consumption). From stoichiometry of the two independent reactions follows: $r_{NO_2} = -2r_1 + r_2$. The experimental rate law is obtained selecting $k = -2k_{20000}^1 + k_{20000}^2$

and $k_{11000}^i = k_{01001}^i = 0$, and if $K_1^{-1} \to 0$ (irreversibility of R2-1) or if the concentration of $NO_3$ is very low (reactive intermediate). In this example, the mass action law has been shown to be a simplified form of the second degree thermodynamic polynomial. It should be stressed that the rate equations (4) contain three mass-action terms in total, corresponding either to the independent reactions or to the (dependent) stoichiometric equation R2. Thus, rate of any independent reaction can be generally influenced also by other reactions and even thermodynamically dependent reactions are not excluded from effects on kinetics.

The last example is the following reaction

$$2\,N_2O_5 \to 4\,NO_2 + O_2 \tag{R3}$$

The reacting mixture contains also $NO_3$ and $NO$ as intermediates [36]. In this reacting mixture of five components formed from two atoms three independent reactions are possible. They can be selected as the three steps of proposed mechanism [36]:

$$N_2O_5 \to NO_2 + NO_3 \tag{R3-1}$$

$$NO_3 \to O_2 + NO \tag{R3-2}$$

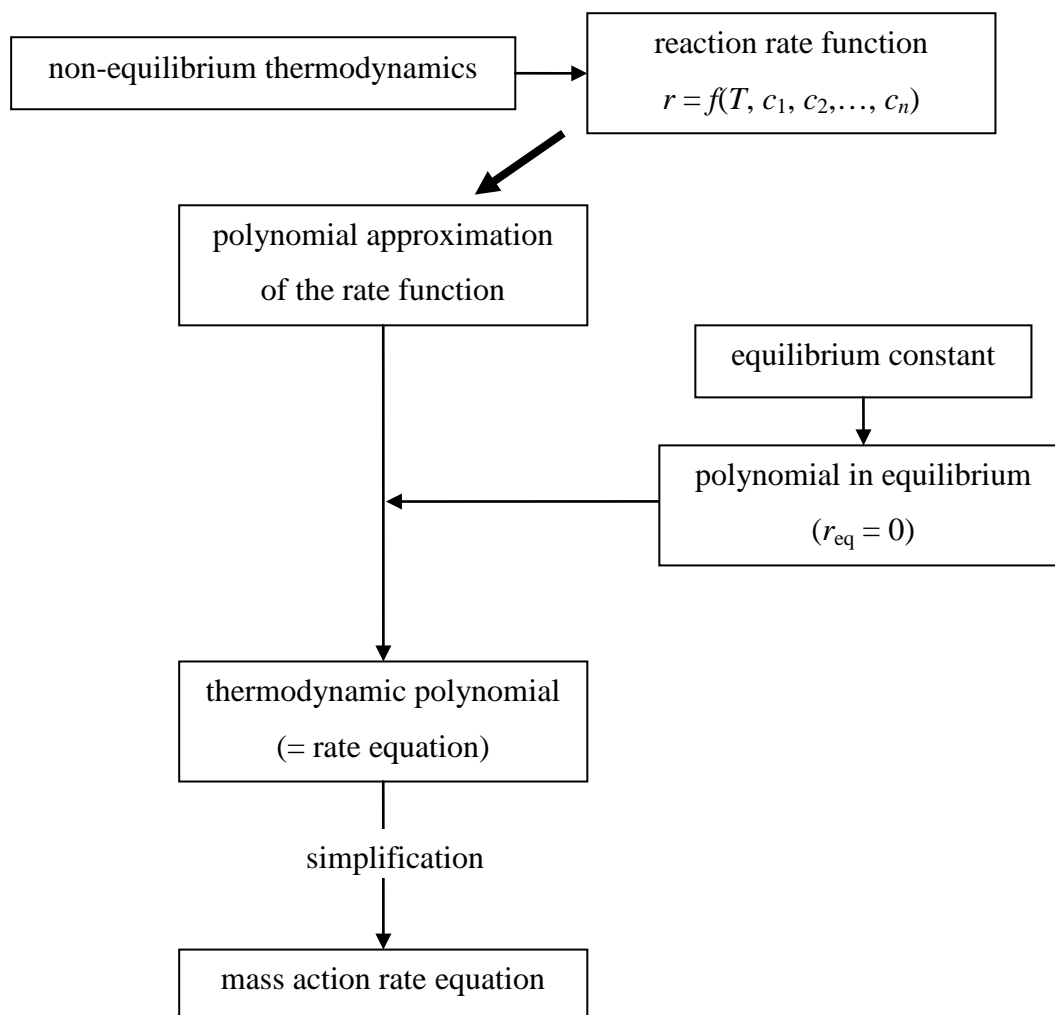$$NO_3 + NO \to 2\,NO_2 \tag{R3-3}$$

Thermodynamic polynomial resulting from the first degree approximating polynomial is identically zero. The second degree thermodynamic polynomial is as follows:

$$r_i = k_{10000}^i (c_1 - K_1^{-1} c_2 c_4) + k_{00010}^i (c_4 - K_2^{-1} c_3 c_5) + k_{00011}^i (c_4 c_5 - K_3^{-1} c_2^2) \tag{5}$$

($1 = N_2O_5$, $2 = NO_2$, $3 = O_2$, $4 = NO_3$, $5 = NO$). The experimentally determined mass action rate law concerns the oxygen production: $r \equiv dc_{O_2} / dt = kc_1$. Because $r_{O_2} = r_2$ the experimental law is recovered selecting $k_{00010}^2 = k_{00011}^2 = 0$ and when $K_1^{-1} \to 0$ or the concentration of $NO_3$ is very low (irreversibility of R3-1 or very low concentration of the reactive intermediate, respectively), and identifying $k = k_{10000}^2$. The mass action law is thus proved to be a special form of the second degree thermodynamic polynomial. Note that the original thermodynamic polynomial (5) contains all three mass action terms corresponding to individual independent reactions in any rate of any independent reaction, i.e. rate of an independent reaction can be generally influenced also by other (independent) reactions.

In summary, traditional kinetic mass action laws were shown to be simplified forms of the thermodynamic polynomial which itself is a result of polynomial approximation of general

reaction rate function proved by non-equilibrium continuum thermodynamics. The whole procedure is resumed in the following scheme:

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┌─────────────────────────────────┐        ┌─────────────────────────────┐
│ non-equilibrium thermodynamics  │───────▶│   reaction rate function    │
└─────────────────────────────────┘        │  r = f(T, c₁, c₂,…, cₙ)     │
                                            └─────────────────────────────┘
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The whole procedure is resumed in the following scheme:



non-equilibrium thermodynamics → reaction rate function $r = f(T, c_1, c_2, \ldots, c_n)$ → polynomial approximation of the rate function → thermodynamic polynomial (= rate equation) → simplification → mass action rate equation

equilibrium constant → polynomial in equilibrium ($r_{\mathrm{eq}} = 0$) → [into polynomial approximation / thermodynamic polynomial]

The starting polynomial is transformed into the thermodynamic polynomial to ensure zero reaction rate in equilibrium; this equilibrium condition leads to vanishing many terms in the starting polynomial. Polynomial basis of the kinetic mass action law is quite natural because polynomial powers represent, in fact, stoichiometric coefficients in independent reactions or in their linear combinations. The further simplification just means that only those terms are retained in thermodynamic polynomial, expressing the rate of particular step in reaction network, which contain concentrations of species directly participating in this step, as is usual in the traditional mass action approach. Actually, the thermodynamic polynomial in its non-simplified version allows also more complex rate equations as noted at the second and third

examples. Detailed analysis of this feature is beyond the scope of this letter and will be subject of future work. It should be added that selecting different independent reactions, different thermodynamic polynomials are obtained; however, they are easily transformable to each other [34, 35].

**CONCLUSIONS**

Three simple examples showed that traditional mass action rate laws are, in fact, simplified forms of polynomial approximation of the general reaction rate function that was derived in non-equilibrium continuum thermodynamics of linear fluids. Mass action rate laws are usually weaker approximations than polynomial of degree equal to the highest kinetic order (or molecularity) of independent reactions in reacting mixture. This way, the mass action kinetic law is derived also on the phenomenological, macroscopic level. The original thermodynamic proof further shows that the law is limited to mixtures of ideal linear fluids.

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