

**Classics Revisited**

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**COMMENTS TO AN ARTICLE OF FRANK-KAMENETSKII ON  
THE QUASI-STEADY-STATE APPROXIMATION**

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Due to the growing need for the simulation of distributed parameter systems, the method of quasi-steady-state approximation (QSSA) has been revitalized. The wide-spread use of the QSSA is hindered because of the lack of a general condition for the application of the QSSA for kinetic systems of arbitrary size. An early article of Frank-Kamenetskii [3], gave such a condition but this work remained almost completely unknown. This paper is commented here in the light of recent results of chemical kinetics and of the theory of differential equations. The English translation of the complete original paper is also presented.

**Introduction**

Knowledge of reaction kinetics has grown considerably during recent decades. The determination of reaction rate constants and of product channels of elementary reactions has become possible using new experimental techniques. As a consequence of this process, large detailed mechanisms have been proposed, mainly in the fields of atmospheric chemistry, combustion chemistry and of the chemistry of pyrolysis and of exotic reactions. However, at the present time, simulation of spatially inhomogeneous systems (distributed parameter systems), where diffusion and convection also contribute to reaction dynamics, is not possible with chemical models of too many variables. Three branches of methods of special importance to chemical kinetics have been proposed for the lowering of the number of variables:

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(i) Based on the designation of important species and important reaction features, the redundant species can be found [1] and eliminated from the mechanism.

(ii) A general method to reduce the number of variables of ordinary differential equations is lumping. This technique has mainly been developed by chemists [2], although it is also known in other fields such as econometry, ecology and the theory of stochastic processes.

(iii) A third possible way is the separation of different time scales. A method for such separation is called quasi-steady-state approximation in chemistry.

The wide-spread use of the QSSA is hindered because there are only rules of thumb for the application of QSSA and well defined mathematical conditions are missing. It is not widely known that in the late thirties Frank-Kamenetskii [3] formulated conditions for the application of the QSSA, although he did not have computational facilities to test his theory. Since chemical kinetics and the theory of differential equations have developed considerably since that time, a possible question is if his ideas have remained applicable. In the main body of this paper the statements of the Frank-Kamenetskii article [3] are analyzed and criticized. The full text of the original paper is given in the Appendix.

### Ten comments to the Frank-Kamenetskii paper

The comments are addressed to specific statements of the original Frank-Kamenetskii article [3]. To locate these statements please refer to the original Russian paper or to the translation given in the Appendix. You will also find upper indices in the translation aimed at helping to locate the concerned text.

*Comment 1\** Although the Bodenstein method can be applied to significantly nonstationary processes, including autocatalysis, this fact is not strictly interrelated with the number of intermediates the QSSA has been applied to. However, in some cases the limitation of the number of QSSA species can really extend the applicability of the quasi-steady-state approximation.

*Comment 2* System (2) can be considered as an equation for the steady state of a reaction scheme, where the non-Bodensteinian species are considered as species of constant concentration (external species). Discussion of conditions for the existence and uniqueness of steady states of chemical reaction systems is found e.g., in Section 4.4 of ref. [4]. Shortly, a reversible mechanism always does have a

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\* See the sixth paragraph

nonnegative steady state, whereas even weakly reversible mechanisms and conservative mechanisms may have more than one. A generalized Wegscheider's condition [5] and the results of singularity theory [6] can also be applied here.

*Comment 3* The error  $\varepsilon$  of the Bodensteinian species (see Eq. (3)) also induces an error in the calculation of the concentration of the non-Bodensteinian species. Therefore the result of QSSA calculation is  $(X_k, A_l)$  instead of  $(X_k, a_l)$ . However, Frank-Kamenetskii assumes that if  $\varepsilon$  is small then this induced error is negligible and hence  $a_l = A_l$ .

*Comment 4* The reader is reminded that unindexed variables are vectors of the corresponding indexed variables. Letter  $x$  is simultaneously used for the designation of a species, of a vector valued concentration-time function and of a vector variable.

*Comment 5* The derivation of Eq. (7) requires that  $f_{ii} \neq 0$ . The unconsidered case  $f_{ii} = 0$  is equivalent to the case where the change in the concentration of  $X_i$  does not introduce any further change in the concentration of itself. As  $x_i$  is an intermediate and has at least one consuming reaction,  $f_{ii}$  contains at least one non zero additive term. Thus  $f_{ii}$  is zero if and only if the sum of positive terms, the result of direct autocatalytic reaction steps, is equal in absolute value to the sum of negative terms, originating from the consumption reactions, at the concentrations investigated. This situation practically never occurs.

*Comment 6* The sentence before Eq. (8) refers to Eqs (3) and (7) in the original Russian text, but it is clearly mistyped and is therefore corrected to Eqs (4) and (7) in the translation.

*Comment 7* In Eq. (12) obviously  $\psi_i$  is supposed to be non-negative.

*Comment 8* "...the quantity  $f_{ii}$  is characteristic for the ... degree of instability..." (see the third sentence after Eq. (12)). Instability has a chemical and a mathematical meaning. High rate of consumption is really associated with chemical instability of species. However, if Frank-Kamenetskii thought of the mathematical meaning of instability, he forecasted here the strong connections among a condition of the applicability of singular perturbation theory, of Ljapunov stability, and of the interpretation of  $|1/f_{ii}|$  as lifetime.

*Comment 9\** It is not true that the exact representation is of the product form in most cases, but based on a Taylor series expansion of  $\ln X_i$  as a function of  $\ln a_i$ 's, the given formula can always be derived as an approximation (see Ref. [7]).

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\* See the paragraph before Eq. (13)

*Comment 10\** Since then, a series of real oscillatory reactions have been discovered and it turned out that their periods are of several orders of magnitude larger than the lifetime of the species with the shortest lifetime.

### Conclusion

For a better evaluation of the article of Frank-Kamenskii we have to clarify which are the necessary conditions and which are the sufficient ones.

The relations among the statements expressed in the equations are as follows:

– Equation (4), together with the requirement of the existence of a positive real root to (2), makes up the definition of the applicability of the Bodenstein method.

– Equations (4) and (2) imply (6), up to the first order in  $\epsilon$ 's.

– Equation (6) (cf. comment 5) implies (7).

Thus (7) is a *necessary* condition of the applicability of the Bodenstein method.

Further analysis reveals *sufficient* conditions of the necessary condition (7):

– Equations (8), (9), and (10) imply (7).

– Equation (13), under further specialization, implies (11) which is equivalent to (8).

– Equation (14), together with (8) and (10), implies (9).

– Equation (16), under further specialization, implies (14).

– Equation (10) is fulfilled in special cases.

This complicated logical structure can be simplified this way: One faces the problem of checking the necessary condition (7) and it turns out that this will be fulfilled if (11) is fulfilled, at least under special conditions.

All these mean that the statements of the paper could serve as a guideline when developing a full mathematical theory or when the applicability of the Bodenstein method is tested numerically.

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\* See the paragraph where the Lotka article is cited

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## Appendix

# CONDITIONS FOR THE APPLICABILITY OF THE BODENSTEIN METHOD IN CHEMICAL KINETICS\*

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Conditions for the applicability of the Bodenstein method for reactions in case of any kinetics and any number of intermediates result in three inequalities. If the rate of elementary processes depends on the concentration of reactive species, as it is usual in chemical kinetics, only the first one is important, requiring that the lifetime of the intermediate be small compared to the time interval of the reaction.

In computation of the rate of chemical reactions, taking place in the presence of unstable intermediates, there is a basic importance of the Bodenstein method, which has been extended for autocatalytic reactions by Semenov.

Conditions for the use of this method have been cleared only for some most frequent cases. The task of this paper is a more general and more rigorous formulation of them.

In the chemical reaction investigated the number of intermediates is not restricted. All species which take part in the reaction and which influence the rate of the reaction (reactant species, intermediate species and product species) are divided into two groups.

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\* Translated from: *Zhurnal Fizicheskoy Himii*, **14**, 695-700 (1940)

The first group consists of species for which the Bodenstein method can not be applied. Reactant species and product species of the reaction belong to this group, but some intermediates, for which the conditions below are not fulfilled, also belong to this group. All these species will be called non-Bodensteinian and their concentrations will be denoted by the letter  $a$  with different indices.

Intermediates fulfilling the principles below, will be considered in the second group and hence the Bodenstein method will be applicable for them. Species belonging to the second group will be called Bodensteinian species and their concentrations will be denoted by the letter  $x$  with different indices.

The idea of applying the Bodenstein method to not all the intermediate species (as it was done previously) but only for some of them comes from Semenov [1]. This idea substantially increased the domain of applicability of the method as it became applicable for significantly non-stationary processes as well, including autocatalytic reactions<sup>1</sup>.

In a number of cases it turns out to be possible to select an intermediate from the numerous intermediates of the reaction, such that its concentration changes in a highly non-stationary way and the concentration of all the other intermediates can be calculated from the concentration of this non-Bodensteinian species and from the concentration of the reactants. This method of kinetic analysis, proposed by Semenov, is as important in the study of the kinetics of complex non-stationary reactions as the original Bodenstein method in case of stationary processes.

Let us suppose that the kinetic scheme of the reactions gives the equation of the form

$$\frac{dx_i}{dt} = F_i(x_k, a_l), \quad (1)$$

for the time dependence of the concentrations of the Bodensteinian species, where the index  $i$  is fixed and indices  $k$  and  $l$  can take on any possible values.

The Bodenstein method means that the system of equations

$$\begin{aligned} F_1(x_k, a_l) &= 0 \\ &\dots\dots\dots \\ &\dots\dots\dots \\ F_i(x_k, a_l) &= 0 \\ &\dots\dots\dots \\ &\dots\dots\dots \end{aligned} \quad (2)$$

is solved for the unknowns  $x_k$ . If this system of equations does not have positive real roots, the Bodenstein method is obviously not applicable<sup>2</sup>.

Let us assume, that the system of equations (2) has positive real roots for each  $x_k$  and let these roots be denoted by  $X_k$ . Values  $X_k$  are the Bodensteinian or quasistationary concentrations of the corresponding species. Assume that:

$$x_k = X_k + \varepsilon_k . \quad (3)$$

Assume that the  $\varepsilon$ 's are small

$$\varepsilon_k \ll X_k . \quad (4)$$

and look for conditions under which this assumption is fulfilled<sup>3</sup>.

These will just be the conditions of the applicability of the Bodenstein method.

Substituting expression (3) for  $x_k$  in equation (1) and assuming  $\varepsilon$  to be small<sup>4</sup>, function  $F$  can be expanded into a Taylor series near the value  $x=X$  and neglecting the higher orders of  $\varepsilon$ , one obtains:

$$\frac{dX_i}{dt} + \frac{d\varepsilon_i}{dt} = F_i(X_k, a_l) + \sum_k \left[ \frac{\partial F_i}{\partial x_k} \right]_{x=X} \varepsilon_k . \quad (5)$$

But as  $X_k$  is a root of the system (2), hence  $F_i(X_k, a_l) = 0$ . Furthermore, for brevity let us denote the values  $\partial F_i / \partial x_k$  for each  $x=X$  by  $f_{ik}$ :

$$f_{ik} = \left[ \frac{\partial F_i}{\partial x_k} \right]_{x=X} ;$$

then (5) is transformed into

$$\frac{dX_i}{dt} + \frac{d\varepsilon_i}{dt} = \sum_k f_{ik} \varepsilon_k . \quad (6)$$

Let us solve<sup>5</sup> this equation for:

$$\varepsilon_i = \frac{1}{f_{ii}} \left[ \frac{dX_i}{dt} + \frac{d\varepsilon_i}{dt} - \sum_{i \neq k} f_{ik} \varepsilon_k \right] . \quad (7)$$

Note, that the quantities of  $f_{ik}$  only depend on  $a_l$ , as the quantities  $X$ , which are the functions of  $a_l$ , are substituted for  $x$ .

Based on equations (4)<sup>6</sup> and (7), one can derive the conditions for the applicability of the Bodenstein method as three inequalities:

$$\left| \frac{1}{f_{ii}} \frac{dX_i}{dt} \right| \ll X_i ; \quad (8)$$

$$\left| \frac{1}{f_{ii}} \frac{d\varepsilon_i}{dt} \right| \ll X_i ; \quad (9)$$

$$\left| \frac{f_{ik}}{f_{ii}} \varepsilon_k \right| \ll X_i , \quad (10)$$

which have to be fulfilled for each value of  $i$  and  $k$ .

Inequality (8) has a very simple and clear physical meaning. For making it more visual, it will be rewritten into the form:

$$\left| \frac{d \ln X_i}{dt} \right| \ll |f_{ii}| . \quad (11)$$

Let us consider the simplest and most general case, when the quantity  $F_i$  can be expressed in the following form<sup>7</sup>:

$$F_i = \phi_i - \psi_i x_i^n , \quad (12)$$

where  $\phi_i$  and  $\psi_i$  do not depend on  $x_i$ , but they do depend upon all the other  $x$ 's and  $a$ 's. In this case one obtains the following expression for  $f_{ii}$ :

$$|f_{ii}| = n\psi_i X_i^{n-1} .$$

In particular, for  $n = 1$  we simply have:

$$|f_{ii}| = \psi_i .$$

This way in the case investigated the quantity  $f_{ii}$  is characteristic for the rate of consumption (degree of instability)<sup>8</sup> of an intermediate at its Bodensteinian concentration.

If the intermediates were not produced and only their consumption took place, i.e., the value of  $\phi_i$  became zero, then equation (12) would give us:

$$\frac{dx_i}{dt} = -\psi_i x_i^n$$

and we would have:

$$f_{ii} = \left[ \frac{n dx_i}{x_i dt} \right]_{x=X} = n \left[ \frac{d \ln x_i}{dt} \right]_{x=X} .$$



$$\left| \frac{1}{f_{ii}} \frac{dX_i}{dt} \right| \ll X_i ; \quad (8)$$

$$\left| \frac{1}{f_{ii}} \frac{d\epsilon_i}{dt} \right| \ll X_i ; \quad (9)$$

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and we would have:

$$f_{ii} = \left[ \frac{n dx_i}{x_i dt} \right]_{x=X} = n \left[ \frac{d \ln x_i}{dt} \right]_{x=X} .$$

Therefore, the order of the quantity  $f_{ii}$  is the reciprocal of the lifetime of the intermediate at its Bodensteinian concentration.

The physical meaning of inequalities (8) and (11) is that the lifetime of an intermediate must be small compared to the characteristic time of change of the quantity  $X$ . The latter is a function of the quantities  $a_i$  only.

Knowing the dependence of  $X_i$  on  $a_i$  one can rearrange inequality (11) in the following way:

$$\frac{d \ln X_i}{dt} = \sum_l \frac{\partial \ln X_i}{\partial a_l} \frac{da_l}{dt} = \sum_l \frac{\partial \ln X_i}{\partial \ln a_l} \frac{d \ln a_l}{dt}$$

Starting from the fact, that the reaction rate in kinetics is usually a power function of the concentrations of reacting species, the quantities  $X$  can in most<sup>9</sup> cases also be represented exactly, and in all cases approximately, in the form of  $X_i \sim \prod a_j^{\mu_j}$ , where the quantities of  $\mu$  are of the order of unity.

But then  $\partial \ln X_i / \partial \ln a_l = \mu_l$  and inequality (11) can be replaced by

$$\left| \frac{d \ln a_m}{dt} \right| \ll |f_{ii}|, \quad (13)$$

where  $a_m$  is changing in time the fastest of all the  $a_i$  quantities.

We can formulate the meaning of the inequality (13) in the following way: The lifetime of each Bodensteinian species has to be small compared to the characteristic time of change of the fastest changing concentration of the non-Bodensteinian species. This quantity can be called the characteristic time of the course of the reaction.

Let us search for conditions under which inequality (9) is fulfilled. If the other conditions for the applicability of the Bodenstein method are fulfilled, inequality (9) can be replaced with the following condition:

$$\left| \frac{1}{f_{ii}} \frac{d\varepsilon_i}{dt} \right| \gtrsim |\varepsilon_i|. \quad (14)$$

Let us select a time interval, during which  $d\varepsilon/dt$  does not become zero. Let us denote by  $M$  the maximum value of  $|d\varepsilon/dt|$  during this time interval, by  $N$  its minimum value, and by  $\varepsilon_0$  the value of  $|\varepsilon|$  at the beginning of the selected time interval. Then

$$\varepsilon = \varepsilon_0 + \int_0^t \frac{d\varepsilon}{dt} dt,$$

and as

$$\left| \int_0^t \frac{d\varepsilon}{dt} dt \right| \geq Nt ,$$

hence

$$|\varepsilon| \geq \varepsilon_0 + Nt ,$$

if at the starting time  $\varepsilon$  and  $d\varepsilon/dt$  are of the same signs, and

$$|\varepsilon| \geq |Nt - \varepsilon_0| ,$$

if they are of different signs, and therefore

$$|Nt \pm \varepsilon_0| > \left| \frac{1}{f_{ii}} M \right| , \quad (15)$$

where the positive sign relates the case when inequality  $\varepsilon$  and  $d\varepsilon/dt$  have the same signs and the negative sign relates the case when their signs are different.

If at the initial time  $x=0$  then  $\varepsilon_0=X$ . Hence if the time interval considered starts from the initial time of the reaction, inequality (15) can be replaced with the two inequalities below:

$$t > \left| \frac{1}{f_{ii}} \frac{M}{N} \right| , \quad (16)$$

$$t > \frac{X}{N} .$$

If there is a time interval, which is long enough compared to  $|1/f_{ii}|$  (i.e., to the lifetime of species  $x_i$ ) and during which  $d\varepsilon/dt$  will become neither zero nor infinite then having passed this time interval inequalities (16) are obviously fulfilled and the Bodenstein method will be applicable.

Thus the physical meaning of inequality (9) is that the concentration of a Bodensteinian species must not oscillate with a frequency of the order of  $|f_{ii}|$  or higher.

Besides, it expresses the striking fact, that the Bodenstein method can never be applied at the beginning of the reaction, but only after some time has elapsed, which is much longer than the lifetime of the intermediate.

Finally, the third condition of the applicability of the Bodenstein method expressed by inequality (10) is usually fulfilled automatically, as it is general in chemical kinetics that reaction rates are power functions of the concentrations of

reacting species and this inequality is usually fulfilled at least if the other conditions of the applicability of the Bodenstein method are fulfilled for each species  $x_k$ .

To show this, assume that  $F_i$  has the following form:

$$F_i = Ax_i^\mu x_k^\nu,$$

where  $A$  depends on each variables except for  $x_i$  and  $x_k$ . Then

$$f_{ik} = \nu AX_i^\mu X_k^{\nu-1},$$

$$f_{ii} = \mu AX_i^{\mu-1} X_k^\nu,$$

$$\frac{f_{ik}}{f_{ii}} = \frac{\nu X_i}{\mu X_k}$$

and inequality (10) leads to

$$\left| \frac{\nu \varepsilon_k}{\mu X_k} \right| \ll 1,$$

which is fulfilled automatically, as the species with index  $k$  is Bodensteinian according to the condition.

With functions  $F$  of the form ubiquitous in kinetics, inequality (9) can also be considered to be fulfilled automatically, at least if the time since the beginning of the reaction is much more than  $|1/f_{ii}|$ .

Thus, practically inequality (11) or (13) can be considered the unique and sufficiently general condition for the applicability of the Bodenstein method.

However, one has to consider that, as it was shown by Lotka [2] and the author [3], there is a possibility for an oscillating change<sup>10</sup> of the concentrations of intermediates in case of autocatalytic reactions having an autocatalysis involving two consecutive intermediates.

Based on the ideas presented, next we turn to the application of the Bodenstein method to an arbitrary kinetic scheme.

All species, taking part in the scheme, have to be divided into two groups: to species  $x$  for which we intend to apply the Bodenstein method and to species  $a$  for which the application of this method is not intended.

The following steps have to be done for obtaining conditions which allow the application of the Bodenstein method for species  $x$ .

First of all, the Bodensteinian system of equations (2) for these species has to be set up. If this system does not have positive real roots, then the Bodenstein method obviously can not be applied to the chosen species  $x$ .

If the system (2) has positive real roots  $X$ , then these roots can be substituted for concentrations  $x$  in kinetic equations, which describe the time dependence of the quantities  $a$ . Based on the equations obtained, one can estimate the value of the highest of  $|d \ln X/dt|$  or  $|d \ln a/dt|$ . This value must be smaller than the smallest of the values

$$|f_{ii}| = \left| \frac{\partial F_i}{\partial x_i} \right|_{x=X},$$

where the quantities  $F_i$  are determined by equation (1).

If this condition is fulfilled, then the Bodenstein method can be considered applicable to the ordinary forms of kinetics, except for the initial period of the reaction, duration of which is of the order equal to or greater than the greatest of the quantities  $|1/f_{ii}|$ .

In case of complex kinetic schemes having several autocatalytic species, the possibility of the oscillatory dependence of concentrations on any of the species  $x$  on time in any way has to be investigated, with a frequency of the order equal to or greater than any of the quantities  $|f_{ii}|$ . In the last case the Bodenstein method can not be applied even if the previous conditions are fulfilled.

Finally, with special forms of kinetics the necessity of the direct verification of inequality (10) may emerge, which leads to the requirement that none of the quantities  $|f_{ik}| X_k$  be too great compared to the smallest of the quantities  $|f_{ii}| X_i$ .

The set of these three conditions provide the perfect general criteria of the applicability of the Bodenstein method.

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