Geometry of Titration Systems
An Application of Horn's Theory to the Determination of p_K-Values

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(Z. Naturforsch. **31 a**, 408–413 [1976]; received March 5, 1976)

n-step tritration, Horn-equation, reaction simplex, rate constants, geometry of reaction systems

Following a brief summary of Horn's theory, the geometry of an n-step titration is presented. This suggests a simple and accurate method for the determination of p_K-values from concentration measurements. Mathematically, the affine invariance of barycentric coordinates is exploited. Formal analogies between titration process and kinetics are discussed.

1. Introduction

Recently the work by Horn, Jackson, and Feinberg [1–5] has led to a reformulation of polynomial kinetics under the name of general mass-action kinetics.

An essential step in this direction was an ingenious new notation which allowed to write down all differential equations in a certain matrix form, called the Horn-equation (by Müller-Herold [6]). The equation allows to discuss all chemical reaction systems of the well-stirred type, no matter whether closed or open, and whether exhibiting exotic phenomena or not. An important subnotion in Horn's theory is that of a reaction simplex, at first introduced into the theory of monomolecular reactions by Wei and Prater [7].

As an example for the practical applicability of the Horn-equation (and as a first step toward the solution of the problem of how to determine all rate constants in an arbitrary reaction network), the determination of p_K-values of an n-step titration may be chosen. This is a sequence of reactions which may be considered in isolation (so that the equilibrium point of each can be determined separately). Nonetheless, the potential use of Horn's theory for experimentalists in more general cases will become apparent.

At first, some of the results of Horn, Jackson, and Feinberg are to be reproduced for later use. Then we will briefly describe the titration process in terms of Horn's theory. The main part will be devoted to the description of a method for determining p_K-values of an n-step titration, followed by an application of the results to the spectrophotometrical determination of p_K-values. Finally, an analogy between titrations and more general reaction trajectories will be pointed out.

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2. The Horn-Equation

Consider a homogeneous chemical reaction system at constant temperature and volume, containing n different chemical species. We may build up a real vector space V, called species space, by assigning to each species, i, a natural basis vector $\boldsymbol{e}_i$, such that $\boldsymbol{e}_i = (0, \ldots, 0, 1, 0, \ldots, 0)^T$, with the i^{th} component equal to one, and all other components equal to zero.

The rates of change of the reacting species may then be written as

$$\dot{\boldsymbol{c}} = \boldsymbol{f}(\boldsymbol{c}) = \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij}(\boldsymbol{c}) \{\boldsymbol{y}^i - \boldsymbol{y}^j\}, \qquad (1)$$

where $\boldsymbol{c}(t) = [c_1(t), \ldots, c_n(t)]^T$ is the concentration vector at time t. In this equation, the y^i are called complexes. They correspond to the stoichiometric vectors on both the right-hand side and the left-hand side of the reaction scheme; i. e., they are linear combinations of the species vectors according to the stoichiometry of the reaction. The function $\boldsymbol{f}(\boldsymbol{c})$ is called the species formation vector. The $r_{ij}(\boldsymbol{c})$ are the elements of an $n \times n$-matrix $\mathbf{R}(\boldsymbol{c})$ - called the rate matrix. It is given by

$$\mathbf{R}(\boldsymbol{c}) = \mathbf{K}\, \mathrm{dg}\, \boldsymbol{c}^{\boldsymbol{y}}, \qquad (2)$$

where $\mathbf{K}$ is the matrix of rate constants and dg denotes the diagonal matrix built up by the next-following vector.

Defining now

$$\boldsymbol{c}^{\boldsymbol{y}} = \prod_{i=1}^{m} c_i^{y_i}, \quad \boldsymbol{c} \in \mathrm{V}^+, \boldsymbol{y} \in \mathrm{V}, \qquad (3)$$

and, if $\mathbf{Y}$ is an $n \times m$-matrix,

$$\boldsymbol{c}^{\mathbf{Y}} = (\boldsymbol{c}^{\boldsymbol{y}^1}, \boldsymbol{c}^{\boldsymbol{y}^2}, \ldots, \boldsymbol{c}^{\boldsymbol{y}^m})^{\mathrm{T}}, \tag{4}$$

we may, using a matrix $\mathbf{A}$ defined by

$$\mathbf{A} = \mathbf{K} - \mathrm{dg}\,\mathbf{K}^{\mathrm{T}} \boldsymbol{e}_{\mathrm{w}}, \quad \boldsymbol{e}_{\mathrm{w}} = (1, 1, \ldots, 1), \tag{5}$$

write Eq. (1) in the form

$$\boldsymbol{f}(\boldsymbol{c}) = \mathbf{Y}\mathbf{A}\,\boldsymbol{c}^{\mathbf{Y}}. \tag{6}$$

The i^{th} column of the $n \times m$-matrix of Y is equal to the i^{th} complex $\boldsymbol{y}^i$. By Y, a linear map from $\mathcal{W}$ into V is defined, where $\mathcal{W}$ is the complex space ($\mathcal{W} \subseteq \mathbb{R}^m$, m number of distinct complexes).

The reaction arrow defines a relation on the set of complexes. This relation is an equivalence relation in the presently considered class of reaction systems. For a more detailed definition of reaction arrows, see Horn [1, 2, 4, 5]. The stoichiometric subspace S of the whole reaction can now be built up by the subspaces spanned by each of these equivalence classes (termed linkage classes).

Stoichiometric subspace S is defined by

$$\mathrm{S} = [\{\boldsymbol{y}^j - \boldsymbol{y}^i \mid \boldsymbol{y}^i \rightarrow \boldsymbol{y}^j\}] \tag{7}$$

where the $\boldsymbol{y}^i, \boldsymbol{y}^j$ are the complexes of the reaction systems considered. $[\cdot]$ denotes the linear span built up by the vectors within the brackets.

If l is the number of linkage classes L_i, the stoichiometric subspace S can be computed by

$$\mathrm{S} = \sum_{i=1}^{l} S_i, \tag{8}$$

where the S_i are given by

$$S_i = [\{\boldsymbol{y}^j - \boldsymbol{y}^i \mid \boldsymbol{y}^i \rightarrow \boldsymbol{y}^j, \boldsymbol{y}^i, \boldsymbol{y}^j \in L_i\}]. \tag{9}$$

From the definition of S and Eq. (1) it follows that

$$\boldsymbol{f}(\boldsymbol{c}) \in \mathrm{S} \quad \text{for} \quad \boldsymbol{c} \in \overline{\mathrm{V}}^+, \tag{10}$$

or, taking into regard the initial concentration $\boldsymbol{c}_0$,

$$\boldsymbol{f}(\boldsymbol{c}) \in \overline{\mathrm{V}}^+ \cap (\boldsymbol{c}_0 + \mathrm{S}), \tag{11}$$

where $\boldsymbol{c}_0 + \mathrm{S}$ is the translation of S by the initial concentration $\boldsymbol{c}_0$. The intersection of $\boldsymbol{c}_0 + \mathrm{S}$ with the non-negative orthant of V, $\overline{\mathrm{V}}^+$, will be called reaction simplex σ. According to Eq. (11), all reaction paths [see Eq. (1)] are confined to σ.

3. The Titration Process

Consider now the following titration reaction scheme

$$\begin{array}{ccccccc} \mathrm{A}_n & \longleftrightarrow & \mathrm{A}_{n-1} & \mathrm{A}_{n-1} \longleftrightarrow \mathrm{A}_{n-2} \ldots \mathrm{A}_1 & \longleftrightarrow & \mathrm{A}_0 \\ & \searrow & & \searrow & & \searrow \\ & \mathrm{A}_{n+1} & & \mathrm{A}_{n+1} & & \mathrm{A}_{n+1} \end{array} \tag{12}$$

and let $\mathrm{A}_{n+1} := \mathrm{H}^+$. Then system (12) is an n-step protolysis reaction. (Hereby omission of the reaction $\mathrm{H}^+ + \mathrm{OH}^- \longleftrightarrow \mathrm{H_2O}$ is justified by the assumption that the concentration of $\mathrm{H_2O}$ is constant throughout the whole titration.)

The set of complexes $\mathscr{C}$ for this reaction is given by

$$\begin{aligned} \mathscr{C} &= \{\mathrm{A}_n, \ldots, \mathrm{A}_1, \mathrm{A}_{n-1} + \mathrm{A}_{n+1}, \ldots, \mathrm{A}_0 + \mathrm{A}_{n+1}\} \\ &= \bigcup_{i=1}^{n} \mathscr{C}_i \end{aligned} \tag{13}$$

where $\mathscr{C}_i = \{\mathrm{A}_i, \mathrm{A}_{i-1} + \mathrm{A}_{n+1}\}$ are the n linkage classes of the system. The stoichiometric subspace S is built up by the linear span of the stoichiometric subspaces S_i according to $\mathscr{C}_i$. That is to say,

$$\mathrm{S} = \sum_{i=1}^{n} \mathrm{S}_i \tag{14}$$

or, more precisely, because $S_i \cap S_{i+1} = \{\boldsymbol{O}\}$, $i = 1, \ldots, n$:

$$\begin{aligned} &\mathrm{S} = \bigoplus_{i=1}^{n} \mathrm{S}_i, \quad \text{where} \\ &S_i = [(0, \ldots, 0, -1, +1, 0, \ldots, 0, 1)^{\mathrm{T}}], \\ &\cdot i = 1, \ldots, n, \ \oplus \text{ denoting the direct sum.} \end{aligned} \tag{15}$$

Each stoichiometric subspace S_i is built up by a vector consisting of $n+2$ components, where the i^{th} component equals -1, the $(i-1)^{\text{th}}$ and the $(n+2)^{\text{th}}$ components equal 1, and all other components equal zero.

The initial concentration $\boldsymbol{c}_0$ then defines an n-simplex σ^n in $\overline{\mathrm{V}}^+ \subset \mathbb{R}^{n+2}$, given by

$$\sigma^n = \overline{\mathrm{V}}^+ \cap (\boldsymbol{c}_0 + \mathrm{S}). \tag{16}$$

This means that σ^n is restricted to the non-negative orthant of V.

If we now start the titration at $p_{\mathrm{H}} = 0$, then the initial concentration $\boldsymbol{c}_0{}^0$ is given by

$$\boldsymbol{c}_0{}^0 = (1, 0, \ldots, 0, 10^0)^{\mathrm{T}},$$

assuming that the total concentration of $A = \sum_{i=0}^{n} A_i$ is set equal to 1, without loss of generality. We find an equilibrium composition on $\sigma_0{}^n$ by virtue of

$$\boldsymbol{f}(\boldsymbol{c}) = \boldsymbol{O}.$$

We may now increase the p_{H}-value, so that $p_{\mathrm{H}} = 2$, say. The new initial concentration $\boldsymbol{c}_0{}^2$ on $\sigma_2{}^n$ is then given by

$$\boldsymbol{c}_0{}^2 = (1, 0, \ldots, 0, 10^{-2})^{\mathrm{T}},$$

and a new equilibrium point on $\sigma_2{}^n$ according to this initial composition is found as before.

The reason for the differing positions of $\sigma_0{}^n$ and $\sigma_2{}^n$ in $\overline{V}^+$ is that by changing the p_H-value, σ^n has been displaced in parallel to the p_H-axis according to the initial concentrations.

This process has been depicted in Fig. 1a for a one-step titration ($n=1$). Figure 1b shows the $\sigma_i{}^1$'s projected onto the AH, A^--plane in parallel to the p_H-axis.

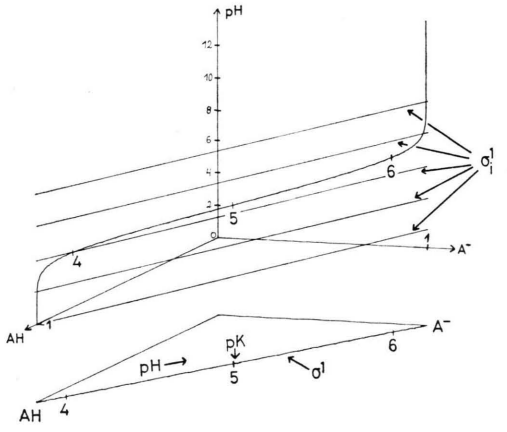

Fig. 1. 1-step titration ($AH \rightleftharpoons A^- + H^+$). a) Curve of equilibria in species space. Each equilibrium concentration lies on the corresponding 1-simplex $\sigma_i{}^1$ which is the state space for the assumed initial condition $\boldsymbol{c}_0{}^i$ (see text). The curve corresponds to Eq. (18) with $p_K=5$ inserted. Every point of the curve corresponds to a particular p_H-value (some of which have been indicated in the Figure). — b) Projection of the curve in parallel to the p_H-axis onto σ^1 in the AH, A^--plane. The p_K-value is given by the p_H-value of the midpoint (medidian) of the 1-simplex σ^1.

4. Determination of $\boldsymbol{p}_K$-Values

Now let us determine what the picture of the equilibrium points of an n-step titration looks like. Let $A=\sum_{i=0}^{n} A_i = 1$. We start the reaction from $\boldsymbol{c}_0 = (A_n, \ldots, p_H)$ and change the p_H-values continuously. Then we project the so obtained curve in $\overline{V}^+$ in parallel to the p_H-axis onto σ^n.

Setting $\boldsymbol{f}(\boldsymbol{c})$, taken from Eq. (12), equal to zero, we obtain the equilibrium concentrations λ_i as functions of the p_H-value:

$$\lambda\colon [10^{-14}, 10^q] \to \sigma^n, \qquad (17)$$
$$h \mapsto (\lambda_n(h), \ldots, \lambda_0(h))^T, \quad h \in [10^{-14}, 10^q], \; q \geqq 0,$$

with the coordinate functions (obtained by straightforward computation)

$$\lambda_i(h) = A \frac{\prod_{\nu=0}^{n-i} K_\nu h^i}{\sum_{j=0}^{n} \left(\prod_{\nu=0}^{n-j} K_\nu h^j \right)}, \qquad (18)$$

where $K_0 = 1$ by definition and $K_\nu = 10^{-p_{K\nu}}$.

When dealing with simplices, barycentric coordinates are the most convenient coordinates to use (cf. [8]). The components of $\lambda(h)$ can be represented within barycentric coordinates. The n-simplex σ^n has $n+1$ vertices, $\boldsymbol{p}_i$, $i=0,1,\ldots,n$. The $\boldsymbol{p}_i$ are the natural basis vectors in the species space V^+ in which the simplex is imbedded. Thus,

$$\lambda(h) = \lambda_n(h)\boldsymbol{p}_n + \lambda_{n-1}(h)\boldsymbol{p}_{n-1} + \ldots + \lambda_0(h)\boldsymbol{p}_0$$
$$\equiv \lambda_n(h) \begin{pmatrix} 1 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix} + \lambda_{n-1}(h) \begin{pmatrix} 0 \\ 1 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix} + \ldots + \lambda_0(h) \begin{pmatrix} 0 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 0 \\ 1 \end{pmatrix}. \qquad (19)$$

A point $\lambda(h)$, for which $A_i = A_{i-1}$ is valid, is then given by that particular h-concentration for which

$$\lambda(h) = \lambda_n(h)\boldsymbol{p}_n + \ldots + \lambda_{i+1}(h)\boldsymbol{p}_{i+1} + 2\,\lambda_i(h)\,(\boldsymbol{p}_i + \boldsymbol{p}_{i-1}) + \lambda_{i-2}(h)\boldsymbol{p}_{i-2} + \ldots + \lambda_0(h)\boldsymbol{p}_0. \qquad (20)$$

This means that, in order to determine p_K-values, we have to look for those parameter values h for which $\lambda(h)$ is also a point on $\sigma_i{}^{n-1}$, $i=1,\ldots,n$. The intersection of the curve $\lambda(h)$ with the simplex $\sigma_i{}^{n-1}$ gives us the p_K-values. In the case of a triangle (σ^2), the simplex σ^1 simply is a straigth line, namely one of the meridians. σ^{n-1} is generally given by

$$\sigma_i{}^{n-1} = \{(\lambda_n(h), \ldots, \lambda_0(h)) \mid \lambda_i(h) = \lambda_{i-1}(h), \quad i=1,\ldots,n \text{ and } \sum_{i=0}^{n} \lambda_i(h) = 1\}, \qquad (21)$$

In other words, when analyzing an n-step titration, we just have to determine n $(n-1)$-simplices and to look for those h-values for which

$$\lambda(h) \in \sigma_i{}^{n-1}. \qquad (22)$$

So, the p_K-values are given by

$$\{p_K\} = \{h \in [10^{-14}, 10^q] \mid \lambda(h) \in \sigma^n \text{ and } \lambda(h) \in \sigma_i{}^{n-1}, i=1,\ldots,n\}. \qquad (23)$$

For a two and a three step titration, this method to determine p_K-values is represented in Figure 2.

In the general case of an n-step titration, the corresponding n-simplex is impossible to visualize. Fortunately, it is sufficient to analyze the two-faces

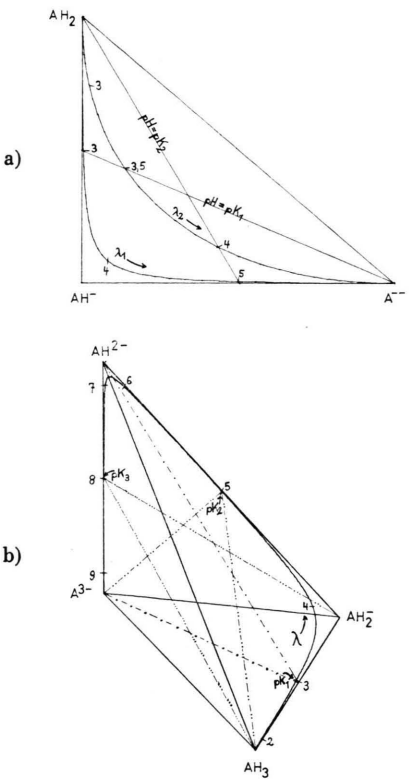

Fig. 2. Determination of p_K-values by the method of meridians. a) 2-step titration ($AH_2 \rightleftharpoons AH^- + H^+$, $AH^- \rightleftharpoons A^{--} + H^+$). The intersection points between the meridians (on which $p_H \equiv p_K$) and the titration curves λ_1 and λ_2 are the p_K-values. The two p_K-values obtained for λ_1 are $p_{K1}=3$ and $p_{K2}=5$, for λ_2: $p_{K1}=3.5$, $p_{K2}=4$. (λ_1, λ_2 have, in the present case, been computed, using Eq. (18) with $K_1=10^{-3}$, $K_2=10^{-5}$, and $K_1=10^{-3.5}$, $K_2=10^{-4}$, respectively.) — b) 3-step titration [Eq. (12), $n=3$]. In this case, the meridians are the dashed-line triangles (one of which is AH_3, A^{3-}, 5). The intersection points with the titration curve λ are indicated by p_{K1}, p_{K2}, p_{K3}. ($K_1=10^{-3}$, $K_2=10^{-5}$, $K_3=10^{-8}$ have been inserted into Equation (18).)

(2-simplices, that is, triangles) of the n-simplex in the following way. λ has to be projected onto these triangles, such that for each triangle the barycentric coordinates are given by $[\lambda_i(h), \lambda_{i-1}(h), 1-\lambda_i(h)+\lambda_{i-1}(h)]$, $i=1,\ldots,n$. Then the triangles may be strung together, and the p_K-values be determined as before. This procedure is illustrated in Figure 3. Notice that all p_K-values are represented at least twice. So each p_K-value may be determined (revised) in a multiple way. This enhances the experimental accuracy.

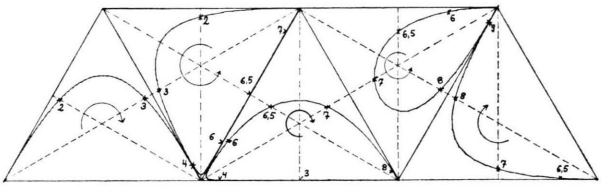

Fig. 3. Determination of p_K-values for a 5-step titration [Eq. (12), $n=5$]. — As indicated in the text, it suffices to consider the projections of the titration curve on the triangular faces of the 5-simplex. The p_K-values are again the intersection points with the meridians of the triangles (dashed lines). The circular arrows point in the direction of increasing p_H-values along the projected curves. [λ has been obtained, using Eq. (18) with $K_1=10^{-2}$, $K_2=10^{-3}$, $K_3=10^{-6.5}$, $K_4=10^{-7}$, $K_5=10^{-8}$]. Note that a repetitive determination of each of the p_K-values is possible. — As seen in the fourth triangle, the smaller the difference between two p_K-values, the nearer the titration curve is getting to the barycenter of the triangle. Such p_K-values are hard to determine by other methods.

5. Determination of p_K-Values from Spectrophotometric Data

The method of meridians is very useful also when we cannot directly measure the concentrations of the A_i. In a spectrophotometric titration [9–12], for example, we only can measure the absorbance E at various wavelengths in dependence on changing p_H. Formally, we get a linear combination of the equilibrium concentrations $\lambda_i(h)$, when measuring $E_a(h)$ (the subscript a denoting the wavelength):

$$E_a(h) = \varepsilon_{a0}\,\lambda_0(h) + \varepsilon_{a1}\,\lambda_1(h) + \ldots + \varepsilon_{an}\,\lambda_n(h)\,. \quad (24)$$

In order to analyze an n-step titration, we have to determine $E_a(h)$ at n different wavelengths.

Quite in general, the following equalities pertain:

$$\boldsymbol{E}(h) = \begin{pmatrix} E_1(h) \\ \cdot \\ \cdot \\ \cdot \\ E_n(h) \end{pmatrix}$$

$$= \boldsymbol{\epsilon} \cdot \boldsymbol{\lambda}(h) = \begin{pmatrix} \varepsilon_{10} & \varepsilon_{11} & \ldots & \varepsilon_{1n} \\ \varepsilon_{20} & \varepsilon_{21} & & \varepsilon_{2n} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \varepsilon_{n0} & \varepsilon_{n1} & \ldots & \varepsilon_{nn} \end{pmatrix} \begin{pmatrix} \lambda_0(h) \\ \cdot \\ \cdot \\ \cdot \\ \lambda_n(h) \end{pmatrix} \quad (25)$$

$$= \lambda_0(h) \begin{pmatrix} \varepsilon_{10} \\ \varepsilon_{20} \\ \cdot \\ \cdot \\ \varepsilon_{n0} \end{pmatrix} + \lambda_1(h) \begin{pmatrix} \varepsilon_{11} \\ \varepsilon_{21} \\ \cdot \\ \cdot \\ \varepsilon_{n1} \end{pmatrix} + \ldots + \lambda_n(h) \begin{pmatrix} \varepsilon_{1n} \\ \varepsilon_{2n} \\ \cdot \\ \cdot \\ \varepsilon_{nn} \end{pmatrix}.$$

ϵ is an $(n \times n+1)$-matrix of the extinction-coeffi- the barycentric coordinates λ_i have *not* changed ..., n the substances).

The r.h.s. of Eq. (25) is formally identical with Equation (19). Only the positions of the $n+1$ vertices $\boldsymbol{p}_i$ in $\mathbb{R}^{n+1}$ have now changed to the new positions $(\varepsilon_{1i}, \varepsilon_{2i}, \ldots, \varepsilon_{ni})^{\mathrm{T}}$. Going from Eq. (19) to Eq. (25) is nothing but generating an affine transformation of the simplex σ^n. The main point is that the barycentric coordinates λ_i have not changed under the affine transformation [8].

Therefore, supposing we know all of the ε_{ai}, the p_K-values can again be obtained directly by use of the meridians as described above. Instead of the λ_i, just the measured absorbances $E_a(h)$ have to be inserted. In Fig. 4, an example for the analysis of a 3-step titration according to this method is given. The data used stem from [9].

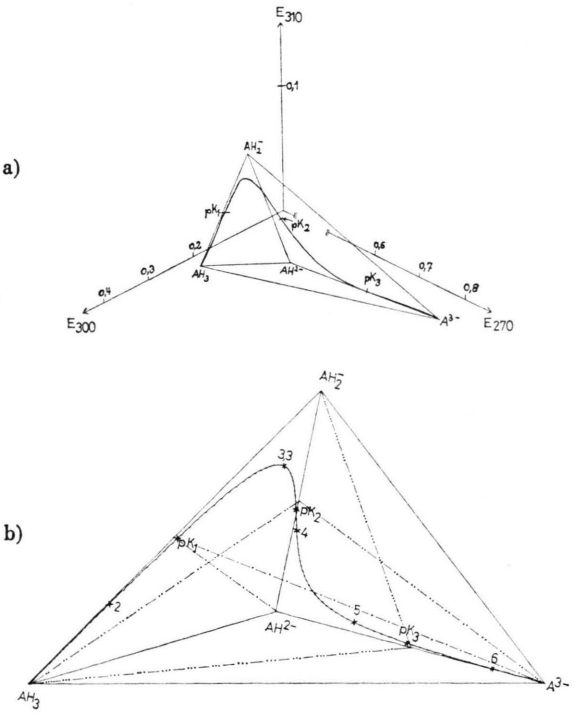

Fig. 4. Titration of (1,2,4)-benzenetricarbonylic acid [9]. — a) Titration curve in absorbance space, as measured [9]. The wavelengths are $a_1=270$ nm, $a_2=300$ nm, $a_3=310$ nm. The vertices of the tetrahedron AH_3, AH_2^-, AH^{2-}, A^{3-}, as indicated in the Figure, are given by the extinction coefficients as cited in reference [9]. — b) Reduction of both the tetrahedron and the titration curve to barycentric coordinates, as prescribed by Equation (25). The p_K-values are again obtained as the intersection points between the meridians (dashed-line triangles) and the titration curve. ($p_{K1}=2.427$, $p_{K2}=3.805$, $p_{K3}=5.383$.)

6. Analogy Between p_K-Value- and Rate Constant-Determination

The above described method of analyzing p_K-values by "meridians" may, by analogy, be useful also in determining rate constants in arbitrary kinetic systems. Comparing titration curves with solutions of systems of differential equations, the following juxtaposition can be made:

A titration curve, on the one hand, is a curve determined by equilibrium points of the kinetic system (12), given by

$$\begin{aligned} \lambda\colon\ & [10^{-14}, 10^{q}] \to \sigma^n\,, \\ & h \mapsto [\lambda_n(h), \ldots, \lambda_0(h)]^{\mathrm{T}}\,, \\ & h \in [10^{-14}, 10^{q}]\,. \end{aligned} \tag{26}$$

The solution of the differential equation $\boldsymbol{f}(\boldsymbol{c}) = \boldsymbol{Y}\boldsymbol{A}\boldsymbol{c}^{\boldsymbol{Y}}$, on the other hand, is a curve given by

$$\begin{aligned} C\colon\ & [0, \infty) \to \sigma^n\,, \\ & t \mapsto [c_1(t), c_2(t), \ldots, c_{n+1}(t)]^{\mathrm{T}}\,. \end{aligned} \tag{27}$$

That is to say, both curves lie on a simplex, given by $\boldsymbol{c}_0 + \mathrm{S}$. And, following from the linearity of S, each point can be uniquely represented by the basis $\{\boldsymbol{y}^j - \boldsymbol{y}^i \mid i \to j\}$ of S.

Obviously, the p_K-values (defined by $A_i = A_{i-1}$, $i = 1, \ldots, n$) can be compared to the reaction half-lives of ordinary chemical reactions. Considering the reaction $A \rightleftharpoons B$, which is the general case, a pseudo half-life (phl) may be defined by

$$t_{\mathrm{phl}}\colon \{t \in [0, \infty) \mid c_i(t) = c_i(\infty)/2, \quad i = 1, \ldots, m\}\,, \tag{28}$$

where $c_i(\infty)$ denotes the concentration of c_i at equilibrium. This is a measurable quantity. Using this information, it is possible to compute "backwards" for the underlying rate constants [13].

6. Discussion

Besides the potentiometric determination method, the determination of p_K-values by spectrophotometric methods is well-established [14, 8–11]. The method for analyzing titration curves on the basis of spectrophotometric data described in the present note allows to make optimum use of the available information. So far, due to the lack of a comprehensive theory of reaction networks, always only partial use could be made of the experimental data. The method has the further asset that the p_K-values are

determined, not in a "single shot", but by way of multiple checking (using the projections of the titration curve on the triangular faces of the reaction simplex). The underlying theoretical concepts are provided by the general theory of mass-action kinetics developed by Horn, Jackson, and Feinberg [1–5].

A second major advantage of the described method is its convenient applicability. For the notion of reaction simplices enables the use of barycentric coordinates. Due to the affine invariance of these coordinates, indirectly measured quantities (like absorbance) can be used in the same right as directly measured concentrations. This is because the geometric locus of distinguished points (such as intersection points, etc.) is not affected by such transformations. This equivalence is reflected in the structural identity of Eqs. (19) and (24). The same reasoning can apparently be extended to the determination of rate constants.

Acknowledgements

One of us (K.-D. W.) would like to thank the Friedrich-Ebert-Stiftung for support. We thank Professor F. F. Seelig for providing the necessary facilities and Drs. R. Blume, F. Göbber, H. Lachmann, and J. Polster for stimulating discussions and for kindly providing us with experimental data.

Thep lots were performed using the Calculator HP 9820 A.

[1] F. Horn and R. Jackson, Arch. Rat. Mech. Anal. **47**, 81 [1972].
[2] F. Horn, Arch. Rat. Mech. Anal. **49**, 172 [1972].
[3] M. Feinberg, Arch. Rat. Mech. Anal. **49**, 187 [1972].
[4] M. Feinberg and F. Horn, Chem. Eng. Sci. **29**, 775 [1974].
[5] F. Horn, Proc. R. Soc. London A **334**, 299, 313, 331 [1973].
[6] U. Müller-Herold, Chem. Phys. Letters **33**, 467 [1975].
[7] J. Wei and Ch. D. Prater, Adv. Cat. **13**, 204 [1962].
[8] G. Springer, Introduction to Riemann Surfaces, Addison-Wesly Publishing Co., Massachusetts 1957.
[9] R. Blume, H. Lachmann, H. Mauser, and F. Schneider, Z. Naturforsch. **29 b**, 500 [1974].
[10] R. Blume and J. Polster, Z. Naturforsch. **29 b**, 734 [1974].
[11] R. Blume, H. Lachmann, and J. Polster, Z. Naturforsch. **30 b**, 263 [1975].
[12] J. Polster, Z. Anal. Chem. **276**, 353 [1975].
[13] K.-D. Willamowski, in preparation [1976].
[14] E. J. King, Acid-Base Equilibria, Pergamon Press, Oxford 1965.