The Determination of Molecular Quantities from Measurements on Macroscopic Systems

IV. Phases with Chemical Reactions

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Z. Naturforsch. **37a**, 1416–1426 (1982); received June 29, 1982

A general method for the determination of molecular quantities from measurements in dense phases without chemical reactions has been presented in a previous paper [1]. The method is extended to phases where chemical reactions may occur. The intimate relationship between the investigation of chemical equilibria and the determination of model molar quantities is shown. Some particular reactions have to be assumed as hypothesis. A scheme is developed, by which in favorable cases it is possible to falsify the assumed hypothesis or to estimate corresponding equilibrium constants and model molar quantities. Some special chemical reactions are treated, where observable quantities are insensitive to any variation of the concentrations of solutions and therefore such methods cannot contribute to the investigation of the systems.

1. Introduction

For a macroscopic phase meeting a few general requirements it is possible to define measurable quantities corresponding to certain bulk properties without introducing any assumption relating to the particular molecular structure of the considered phase [1]. Of special interest are extensive quantities and their adjoint densities, defined by (I.22) *, since originally measured quantities, as determined with suitable instruments, are either bulk quantities of one or the other type or such quantities can easily be calculated from them. Knowledge of their values for varying composition of the phase allows the determination of corresponding partial molar quantities (PMQ's), methods for appropriate evaluations have been discussed previously [1]. The set of generalized densities or the set of all PMQ's, obtainable with a given set of measured data, includes all information known, particularly that about any chemical reaction occurring in the phase. To relate the generalized densities or the PMQ's to molecular quantities necessitates the introduction of an appropriate molecular model. For systems with chemical reactions there are actually two independent models needed. The one model serves for the description of the chemical reactions taking place in the phase, and the other model has to allow some representation of the model molar quantities (MMQ's) for all substances present. In the model about chemical reactions all thinkable ones should be taken into consideration, but this is never possible. The choice of only one or a few of such reactions leads to a particular model which may be considered as a hypothesis about the investigated system. The comparison of the hypothesis and its consequences with the experimental data can falsify the hypothesis or not. As a consequence therefrom many reaction models can be discarded, but not any one can be proved. Usually an investigator is not as alert of this fact when systems in equilibrium states are analyzed as when similar work in reaction kinetics is performed.

In paper I of this series the determination of PMQ's from extensive quantities or densities has been discussed. In systems without chemical reactions the PMQ's are related only to the MMQ's of the substances used to generate the mixture. The further evaluation, based on a molecular model, allows the determination of molecular quantities; examples have been presented in papers II and III [2, 3]. In systems with chemical reactions the PMQ's are related as well to the MMQ's, naturally now of all substances present in the phase, but additionally they are intimately related to the chemical reactions taking place. These connections will be discussed in this paper, and an application will be presented in the following one [4].

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* The abbreviation Eq. (I....) denotes equations of paper I of this series [1].

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2. The Composition of a Phase

A one-phase system can usually be generated by mixing a number E of pure substances A_J (initial substances, $J = 1, \ldots, E$). The amount of the phase and its composition in a stationary state is completely described by the values of the initial masses m_{0J} or of the initial amounts of substances $n_{0J} = m_{0J}/M_J$, where M_J is the molar mass of A_J. If we consider a solution, we assume $A_1, \ldots, A_S$ to constitute the mixed solvent and $A_{S+1}, \ldots, A_E$ the solutes.

A chemical reaction causes a change of the amounts of some of the substances initially present and possibly generates additional substances. The number of substances present in the phase after termination of the reaction processes shall be K, the mass and amount of substance A_I in the thermodynamical equilibrium state shall be m_I and n_I, respectively. To define a relation between the n_{0J} ($J = 1, \ldots, E$) and the n_I ($I = 1, \ldots, K$), we have to describe the chemical reactions by formulas as

$$\sum_{J=1}^{K} \nu_{RJ} A_J = 0, \quad R = 1, \ldots, U, \tag{1}$$

where ν_{RJ} is the stoichiometric coefficient of substance A_J in the reaction R. If one or more of the molecules A_J take part in two or more reactions, then the set of coupled reactions can be represented equivalently by different sets of formulas of the type of eq. (1). It is always possible, but usually not unique, to select from all those formulas a set of mutually independent ones, so that their number is the minimal one covering all reactions occurring in the phase. This minimal number shall be U. Introducing ξ_R, the extent of the reaction R in units of amount of substance, the amount of substance A_J present in the phase is given by the equation

$$n_J = n_{0J} + \sum_{R=1}^{U} \nu_{RJ} \xi_R, \quad J = 1, \ldots, K. \tag{2}$$

If chemical reactions occur, usually it is $K > E$; it can be $K = E$ if either there is no chemical reaction or if the amounts of substance of all educts and all products participating in any of the reactions are chosen as primitive variables. This can be realized if all substances A_J, $J = 1, \ldots, K$, can be prepared as pure substances. This is not the case, for example, if dissociation reactions leading to ions are considered, since the balance equation for electrical charges always has to be satisfied,

$$\sum_{J=1}^{K} z_J n_J = 0, \tag{3}$$

where z_J is the charge number of substance A_J.

In a stationary state the quantities ξ_R are homogeneous functions of first degree of $n_{01}, \ldots, n_{0E}$, and they depend on further variables wherefore we choose the intensive quantities temperature $T = \vartheta_1$, pressure $p = \vartheta_2$, and, if necessary, $\vartheta_3, \ldots, \vartheta_\varepsilon$, that is $\xi_R = \xi_R(n_{0I}, \vartheta_\iota)$. In many cases it is advantageous to substitute one or some of the extensive variables n_{0I} by intensive variables ψ_{0I} defined as in (I.14) by

$$\psi_{0I} = n_{0I}/\chi_I \Psi, \tag{4}$$

where Ψ is an extensive quantity, and χ_I is a constant quantity possibly different for different substances. Examples of ψ_{0I} have been listed in Table 1 of paper I. Using the same extensive quantity Ψ, one can define an extent of reaction $\xi_{\psi R}$ in a unit equal to that of the corresponding $\chi_I \psi_{0I}$ by

$$\xi_{\psi R} = \frac{\xi_R}{\Psi}. \tag{5}$$

$\xi_{\psi R} = \xi_{\psi R}(n_{0I}, \vartheta_\iota)$ is a function homogeneous of zeroth degree of $n_{01}, \ldots, n_{0E}$, hence it can as well be represented by the concentration variables ψ_{0I}, that is $\xi_{\psi R} = \xi_{\psi R}(\psi_{0I}, \vartheta_\iota)$. Using (2), (5), (4) and (I.71), $\psi_I = n_I/\chi_I \Psi$, the following relations result *

$$\psi_J = \psi_{0J} + \chi_J^{-1} \sum_{R=1}^{U} \nu_{RJ} \xi_{\psi R}, \quad J = 1, \ldots, K. \tag{6}$$

3. The Relation of Partial Molar Quantities to Model Molar quantities in Phases with Chemical Reactions

To any extensive bulk quantity Φ of a phase there are adjoint a common density $D_\Phi = \Phi/V$ and a generalized density

$$\mathsf{P}_{\psi\Phi} = \frac{\Phi}{\Psi} = \frac{D_\Phi m_0}{\varrho \Psi} \tag{7}$$

as defined by (I.21) and (I.57), respectively.

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* Choosing $\psi_J = x_J$ we take $\Psi = n_0 = \sum_{I=1}^{E} n_{0I}$ as defined in Table 1 [1]. Then $\sum_{J=1}^{K} x_J = \sum_{J=1}^{K} n_J/n_0$, which is not necessarily equal to one.

$m_0 = \sum_{J=1}^{E} m_{0J}$ is the total mass of the phase, ϱ its density and Ψ is the quantity used in (4) for the definition of the concentration variable ψ_{0J}. Corresponding to each Φ and each substance A_J there are partial molar quantities Φ_{0J} defined by (I.22). With the PMQ's the generalized densities can be represented as

$$\mathsf{P}_{\psi\Phi} = \sum_{J=1}^{E} \chi_J \, \Phi_{0J} \, \psi_{0J} \, . \tag{8}$$

Choosing $\Psi = 1$, $\chi_J = 1$ leads to $\psi_{0J} = n_{0J}$ and $\mathsf{P}_{\psi\Phi}$ is reduced to Φ (i.e. $\mathsf{P}_{n\Phi} = \Phi$); choosing $\Psi = V$, $\chi_J = 1$ leads to $\psi_{0J} = c_{0J} = n_{0J}/V$ and $\mathsf{P}_{\psi\Phi}$ is reduced to D_Φ (i.e. $\mathsf{P}_{c\Phi} = D_\Phi$).

To relate the bulk quantities Φ, D_Φ, $\mathsf{P}_{\psi\Phi}$ or Φ_{0J} to molecular quantities, an appropriate molecular model has to be introduced. In such models it is generally assumed that Φ can be represented as

$$\Phi = \sum_{J=1}^{K} \varphi_J \, n_J \, , \tag{9}$$

where φ_J is the model molar quantity (MMQ) of the substance A_J present in the phase as introduced by (I.68), or equivalently

$$\mathsf{P}_{\psi\Phi} = \sum_{J=1}^{K} \chi_J \, \varphi_J \, \psi_J \, . \tag{10}$$

The sum in (8) includes only the initial substances $A_1, \ldots, A_E$, whereas the sums in (9) and (10) have to include all substances $A_1, \ldots, A_K$ present in the phase in the thermodynamical equilibrium state. With (6) and (10) follows

$$\mathsf{P}_{\psi\Phi} = \sum_{J=1}^{E} \psi_{0J} \, \chi_J \, \varphi_J + \sum_{R=1}^{U} \xi_{\psi R} \, \Delta_R \, \varphi \, , \tag{11}$$

where the abbreviation

$$\Delta_R \, \varphi = \sum_{J=1}^{K} \nu_{RJ} \, \varphi_J \tag{12}$$

has been introduced. The second term on the right-hand side of eq. (11) describes the effects of any chemical reaction on any generalized density $\mathsf{P}_{\psi\Phi}$. It can be recognized that a chemical reaction contributes only to $\mathsf{P}_{\psi\Phi}$ if $\Delta_R \varphi \neq 0$. In investigating chemical reactions it is therefore necessary to find some quantity Φ, where the value of the corresponding change $\Delta_R \varphi$ is sufficiently different from zero, otherwise it is impossible to gain any information about occurring chemical reactions. Usually neither $\xi_{\psi R}$ nor $\Delta_R \varphi$ are known a priori, and the values of both quantities have to be determined from an analysis of the available data. For this purpose the PMQ's Φ_{0J} are well suited.

The relation of the PMQ's Φ_{0J} to the MMQ's φ_J follows from (I.76). If $\Phi = \Phi(n_{0I}, \vartheta_\iota)$ is differentiable at $(n_{0I}, \vartheta_\iota) \in \mathrm{d_d}$, it becomes with (2) and (12)

$$\begin{aligned} \Phi_{0J} = \varphi_J &+ \sum_{I=1}^{E} n_{0I} \left(\frac{\partial \varphi_I}{\partial n_{0J}} \right)_{n_{0J'}, \vartheta_\iota} \\ &+ \sum_{R=1}^{U} \left[\left(\frac{\partial \xi_R}{\partial n_{0J}} \right)_{n_{0J'}, \vartheta_\iota} \Delta_R \varphi + \xi_R \left(\frac{\partial \Delta_R \varphi}{\partial n_{0J}} \right)_{n_{0J'}, \vartheta_\iota} \right] . \end{aligned} \tag{13}$$

The subscripts of the derivatives are explained at (I.6). According to (13) there are four contributions to the PMQ Φ_{0J}, the first and second ones occurring also in phases without any chemical reaction, as has been discussed at (I.77). The first contribution is the MMQ φ_J of the initial substance A_J. The second contribution is caused by the dependences of the MMQ's φ_I of all initial substances A_I ($I = 1, \ldots, E$) on the composition of the phase. The third and fourth term represent the contributions specific for the chemical reactions. Usually the derivative $(\partial \Delta_R \varphi / \partial n_{0J})_{n_{0J'}, \vartheta_\iota}$ is a rather small quantity, hence the main contribution is due to $(\partial \xi_R / \partial n_{0J})_{n_{0J'}, \vartheta_\iota} \Delta_R \varphi$. From this term it can be recognized that the contribution of a chemical reaction to Φ_{0J} is determined essentially by the derivative $(\partial \xi_R / \partial n_{0J})_{n_{0J'}, \vartheta_\iota}$ and not by the magnitude of ξ_R*. Equation (13) as well as (11) shows, that the MMQ's φ_P ($P = E + 1, \ldots, K$) of those substances, which are not used as initial substances, i.e. generally of the products generated by the chemical reactions, cannot be obtained directly by any measurement but only the quantities $\Delta_R \varphi$. If there is only one product generated in a chemical reaction, (12) can be solved for the MMQ φ_P of this product, if the MMQ's φ_J of the educts have been determined independently. If there are two or more products generated, only the weighted sum of their MMQ's can be obtained in this way, the values of individual MMQ's being obtainable only if other information can be gained, as for example, if one or the other of the products can be investigated separately.

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* A specialized case was considered by Person [5] who recognized that the most accurate value of the formation constant of an 1 : 1 complex can be obtained when the concentration of the complex is approximately the same as the equilibrium concentration of the most dilute initial substance, i.e. where $(\partial \xi_R / \partial n_{0J})_{n_{0J'}, \vartheta_\iota}$ is maximal.

The PMQ's Φ_{0J}, the MMQ's φ_J and the extents of reaction $\xi_{\psi R}$ can also be considered as functions of the set $n_{01}, \ldots, n_{0J-1}, \psi_{0J}, n_{0J+1}, \ldots, n_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon$. Application of (I.18) on (13) and usage of (5) lead to

$$\begin{aligned}\Phi_{0J} = \varphi_J &+ \frac{1-\chi_J\,\psi_{0J}\,\Psi_{0J}}{\chi_J}\sum_{I=1}^{U}\chi_I\,\psi_{0I}\left(\frac{\partial\varphi_I}{\partial\psi_{0J}}\right)_{n_{0J}',\,\vartheta_\iota}\\ &+ \Psi_{0J}\sum_{R=1}^{U}\xi_{\psi R}\,\Delta_R\varphi + \frac{1-\chi_J\,\psi_{0J}\,\Psi_{0J}}{\chi_J}\\ &\cdot\sum_{R=1}^{U}\left[\left(\frac{\partial\xi_{\psi R}}{\partial\psi_{0J}}\right)_{n_{0J}',\,\vartheta_\iota}\Delta_R\varphi\right.\\ &\left.+\,\xi_{\psi R}\left(\frac{\partial\Delta_R\varphi}{\partial\psi_{0J}}\right)_{n_{0J}',\,\vartheta_\iota}\right]. \qquad (14)\end{aligned}$$

Ψ_{0J} is the PMQ of the quantity Ψ used in (4). If the quantities φ_J are considered as functions of some parameters $\alpha_1, \ldots, \alpha_\varrho$, as has been discussed at (I.73), the derivatives $(\partial\varphi_I/\partial\psi_{0J})_{n_{0J}',\,\vartheta_\iota}$ and $(\partial\Delta_R\varphi/\partial\psi_{0J})_{n_{0J}',\,\vartheta_\iota}$ can be developed similar to (I.79). This is necessary if molecular quantities, as electric dipole moments, for example, are desired [2]. In the course of the further evaluation it is sometimes advantageous to use the set $\psi_{02}, \ldots, \psi_{0E}, \vartheta_\iota$ for the representation of the φ_J's and $\xi_{\psi R}$'s; the proper transformation of (13) follows by application of (I.19).

For solutions sufficiently dilute in any one of the initial substances, let us say A_G, the generalized densities $\mathsf{P}_{\psi\Phi}$ are linear functions of the properly chosen concentration variables, as has been discussed at eqs. (I.62) and (I.63). From measurements in such concentration intervals the limit $\Phi^{+}_{0G(G)}$ of the PMQ Φ_{0G} for $\psi_{0G}\to 0$ can be estimated*. The relation of $\Phi^{+}_{0G(G)}$ to the MMQ's φ_J and the $\xi_{\psi R}$'s (and their limits) follows easily from eq. (14).

4. The Change of an Extensive Quantity Near an Equilibrium State

In a thermodynamic equilibrium state the values of bulk quantities and of other quantities meeting requirements (1) and (2) of section 1, paper I [1], are usually uniquely determined by the values of the variables of the set $(n_{0I}, \vartheta_\iota)$. For some systems there are non-equilibrium states, where requirements (1) and (2) are still satisfied for macroscopic quantities of interest. In such cases one or a few further parameters β_p besides the set $(n_{0I}, \vartheta_\iota)$ are necessary for a unique description of bulk quantities, i.e. any bulk quantity can be considered as a function $\gamma_{hk}=\gamma_{hk}(n_{0I}, \vartheta_\iota, \beta_p)$, where β_p is a function of time.

During a time interval, when chemical processes occur, the extent of the chemical reactions usually can also be defined, i.e. there are quantities $\xi_R^{(\mathrm{n})}$ so that equations (2) are satisfied (with $\xi_R=\xi_R^{(\mathrm{n})}$). For many chemical reactions at least in states sufficiently close to the thermodynamic equilibrium state, the conditions for the processes can be chosen so that the system is in a thermodynamic equilibrium state with respect to all processes except to the chemical processes. In such cases the quantities $\xi_R^{(\mathrm{n})}$ can be considered as an additional set of mutually independent parameters which can be substituted for the β_p's in the above equation, i.e. any bulk quantity can be considered as a function $\gamma_{hk}=\gamma_{hk}(n_{0I}, \vartheta_\iota, \xi_R^{(\mathrm{n})})$. This is also true for other quantities satisfying requirements (1) and (2) of section 1, paper I.

Consequently in such chemical non-equilibrium state we may consider $\Phi=\Phi(n_{0I}, \vartheta_\iota, \xi_R^{(\mathrm{n})})$, $n_J=n_J(n_{0I}, \vartheta_\iota, \xi_R^{(\mathrm{n})})$ and $\varphi_J=\varphi_J(n_{0I}, \vartheta_\iota, \xi_R^{(\mathrm{n})})$. From eq. (9) follows correctly in linear order for any arbitrary variation Δn_{0I}, $\Delta\vartheta_\iota$, $\Delta\xi_R=\xi_R^{(\mathrm{n})}-\xi_R$ (where ξ_R is the value of the extent of reaction in the equilibrium state)

$$\begin{aligned}\Phi(n_{0I}+\Delta n_{0I}, \vartheta_\iota+\Delta\vartheta_\iota, \Delta\xi_R) &= \Phi(n_{0I}, \vartheta_\iota)\\ &+\sum_{I=1}^{E}\left[\varphi_I+\sum_{J=1}^{E}n_{0J}\left(\frac{\partial\varphi_J}{\partial n_{0I}}\right)_{n_{0I}',\,\vartheta_\iota,\,\xi_R}\right.\\ &\quad\left.+\sum_{S=1}^{U}\xi_S\left(\frac{\partial\Delta_S\varphi}{\partial n_{0I}}\right)_{n_{0I}',\,\vartheta_\iota,\,\xi_R}\right]\Delta n_{0I}\\ &+\sum_{\iota=1}^{\varepsilon}\left[\sum_{J=1}^{E}n_{0J}\left(\frac{\partial\varphi_J}{\partial\vartheta_\iota}\right)_{n_{0I},\,\vartheta_\iota',\,\xi_R}\right.\\ &\quad\left.+\sum_{S=1}^{U}\xi_S\left(\frac{\partial\Delta_S\varphi}{\partial\vartheta_\iota}\right)_{n_{0I},\,\vartheta_\iota',\,\xi_R}\right]\Delta\vartheta_\iota\\ &+\sum_{R=1}^{U}\left[\Delta_R\varphi+\sum_{J=1}^{E}n_{0J}\left(\frac{\partial\varphi_J}{\partial\xi_R^{(\mathrm{n})}}\right)_{n_{0I},\,\vartheta_\iota,\,\xi_R'}\right.\\ &\quad\left.+\sum_{S=1}^{U}\xi_S\left(\frac{\partial\Delta_S\varphi}{\partial\xi_R^{(\mathrm{n})}}\right)_{n_{0I},\,\vartheta_\iota,\,\xi_R'}\right]\Delta\xi_R, \qquad (15)\end{aligned}$$

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* All quantities denoted with a cross as a superscript and a capital letter in brackets as a subscript ((G) for the above example) are the limits of these quantities for vanishing concentration of one substance ($\psi_{0G}\to 0$, for example), as defined by eq. (I.38). Quantities denoted with a star as a superscript are their limits for the pure mixed solvent as defined by eq. (I.37), i.e. for $n_0\to n_0^*$, where $n_0=\sum_{J=1}^{E}n_{0J}$ is the total amount of all initial substances.

whenever $(n_{0I}+\Delta n_{0I}, \vartheta_\iota+\Delta\vartheta_\iota, \Delta\xi_R) \in \mathrm{d_d}$, and consequently

$$\left(\frac{\partial\Phi}{\partial\xi_R^{(\mathrm{n})}}\right)_{n_{0I},\vartheta_\iota,\xi_{R'}} = \Delta_R\varphi + \sum_{J=1}^{E} n_{0J}\left(\frac{\partial\varphi_J}{\partial\xi_R^{(\mathrm{n})}}\right)_{n_{0I},\vartheta_\iota,\xi_{R'}} + \sum_{S=1}^{U}\xi_S\left(\frac{\partial\Delta_S\varphi}{\partial\xi_R^{(\mathrm{n})}}\right)_{n_{0I},\vartheta_\iota,\xi_{R'}}, \tag{16}$$

or with (2) and (12)

$$\left(\frac{\partial\Phi}{\partial\xi_R^{(\mathrm{n})}}\right)_{n_{0I},\vartheta_\iota,\xi_{R'}} = \Delta_R\varphi + \sum_{J=1}^{K}\sum_{I=1}^{K}\nu_{RI}\, n_J\left(\frac{\partial\varphi_J}{\partial n_I}\right)_{n_{I'},\vartheta_\iota}, \tag{17}$$
$$R = 1,\dots,U.$$

The derivative $(\partial\Phi/\partial\xi_R^{(\mathrm{n})})_{n_{0I},\vartheta_\iota,\xi_{R'}}$ represents the change of the quantity Φ due to the reaction R described by formula (1) per unit extent of reaction in units of amount of substance. Equation (17) is based on the molecular model introduced in (9). In this model there are two contributions to $(\partial\Phi/\partial\xi_R^{(\mathrm{n})})_{n_{0I},\vartheta_\iota,\xi_{R'}}$. The first contribution is, as can be recognized from (17) and (12), the difference of the sum of the MMQ's of the products and the educts weighted by their stoichiometric coefficients. The second contribution is due to the dependences of the MMQ's φ_J of all substances A_J present in the phase on its composition.

If the molecular model is chosen so that

$$\left(\frac{\partial\varphi_J}{\partial n_I}\right)_{n_{I'},\vartheta_\iota} = \left(\frac{\partial\varphi_I}{\partial n_J}\right)_{n_{J'},\vartheta_\iota}, \tag{18}$$
$$J,\ I = 1,\dots,K,$$

for all I, J, then the second term on the right-hand side of (17) vanishes. Only under this peculiar circumstance is the change of the quantity Φ per unit extent of reaction equal to the quantity $\Delta_R\varphi$.

5. The Equilibrium Constant and the Thermodynamic Standard Reaction Quantities

The Gibbs energy G of a phase in a stationary state can be represented by

$$G = \sum_{J=1}^{E} G_{0J}\, n_{0J}, \tag{19}$$

where G_{0J} is the partial molar Gibbs energy of substance A_J defined as

$$G_{0J} = \left(\frac{\partial G}{\partial n_{0J}}\right)_{n_{I'},\vartheta_\iota}, \quad (\vartheta_1 = T,\ \vartheta_2 = p),$$
$$J = 1,\dots,E. \tag{20}$$

A representation of the Gibbs energy based on some molecular model is according to (9)

$$G = \sum_{J=1}^{K} g_J\, n_J, \tag{21}$$

where the g_J are MMQ's corresponding to the Gibbs energy.

In a stationary state it is necessarily

$$G = \mathrm{Min}!, \tag{22}$$

if processes are restricted to those where all n_{0I} and ϑ_ι are kept constant. Choosing the sets n_{0J}, ϑ_ι and $\xi_R^{(\mathrm{n})}$ as primitive variables for the description of a chemical non-equlibrium state, then (22) together with (15) and (17) lead to the following condition for the chemical equilibrium state:

$$\left(\frac{\partial G}{\partial\xi_R^{(\mathrm{n})}}\right)_{n_{0J},\vartheta_\iota,\xi_{R'}} = \Delta_R g + \sum_{J=1}^{K}\sum_{I=1}^{K}\nu_{RI}\, n_J\left(\frac{\partial g_J}{\partial n_I}\right)_{n_{I'},\vartheta_\iota} = 0, \tag{23}$$
$$R = 1,\dots,U.$$

If the molecular model is based on a complete molecular model (CMM) or on a separate molecular model (SMM) [1] which is so chosen that (18) is satisfied for all MMQ's g_J, $J = 1,\dots,K$, and all n_I, $I = 1,\dots,K$, then the second term of (23) vanishes and the equilibrium condition becomes

$$\Delta_R g = \sum_{J=1}^{K}\nu_{RJ}\, g_J = 0, \quad R = 1,\dots,U. \tag{24}$$

Also, according to (21), (2), (19) and because of (24) it is in the equilibrium state

$$G_{0I} = \left(\frac{\partial G}{\partial n_{0I}}\right)_{n_{0I'},\vartheta_\iota} = \left(\frac{\partial G}{\partial n_I}\right)_{n_{I'},\vartheta_\iota} = g_I, \tag{25}$$
$$I = 1,\dots,E.$$

Based on a separate molecular model MMQ's g_J satisfying eq. (18) for all I and J have been introduced in Sect. 9.2 of paper I [1]. For a solution of substances $\mathrm{A}_{S+1},\dots,\mathrm{A}_E$ in a mixed solvent consisting of the substances $\mathrm{A}_1,\dots,\mathrm{A}_S$, the MMQ g_G of any solute as defined by (I.126) is according to eq. (I.132)

$$g_G = g_{\psi G}^{*} + RT\ln\left(\frac{\psi_G\,\check{f}_{\psi G}}{\psi^{\ominus}}\right), \tag{26}$$
$$G = S+1,\dots,K,$$

and the MMQ g_L of any solvent becomes similar to (I.128)

$$g_L = g_L^* + RT \ln \frac{\psi_L f_{\psi L}}{\psi_L^*}, \quad L = 1, \ldots, S, \tag{27}$$

where the standard MMQ's $g_{\psi G}^*$ and g_L^* are defined as

$$g_{\psi G}^* = \lim_{n_0 \to n_0^*} (g_G - RT \ln (\psi_G / \psi^{\ominus})) \tag{28}$$

and

$$g_L^* = \lim_{n_0 \to n_0^*} g_L \,. \tag{29}$$

R is the gas constant and T the temperature. $\psi^{\ominus}$ is a standard quantity with an arbitrary value and a unit equal to that one chosen for the concentration variable ψ_G. g_L^* is equal to the PMQ G_{0L}^* of the substance A_L in the pure mixed solvent (i.e. for $n_0 \to n_0^*$), $\psi_L^* = \lim\limits_{n_0 \to n_0^*} \psi_L$. For a solvent consisting of one substance only, (27) becomes identical with (I.128). The activity coefficients $\check{f}_{\psi G}$ and $f_{\psi L}$ own according to (26) to (29) the properties

$$\lim_{n_0 \to n_0^*} \check{f}_{\psi G} = \lim_{n_0 \to n_0^*} f_{\psi L} = 1 \tag{30}$$

and can be estimated by (I.130) and (I.136).

Using this set of MMQ's, the condition for the chemical equilibrium state, Eq. (23), becomes

$$\begin{aligned} \sum_{G=S+1}^{K} \nu_{RG} g_{\psi G}^* + \sum_{L=1}^{S} \nu_{RL} g_L^* & \\ + RT \sum_{G=S+1}^{K} \nu_{RG} \ln \frac{\psi_G \check{f}_{\psi G}}{\psi^{\ominus}} & \\ + RT \sum_{L=1}^{S} \nu_{RL} \ln \frac{\psi_L f_{\psi L}}{\psi_L^*} & = 0 \,. \end{aligned} \tag{31}$$

With the abbreviations

$$K_{\psi R} = \prod_{G=S+1}^{K} \left(\frac{\psi_G}{\psi^{\ominus}} \right)^{\nu_{RG}} \prod_{L=1}^{S} \left(\frac{\psi_L}{\psi_L^*} \right)^{\nu_{RL}}, \tag{32}$$

$$\varDelta_R g_\psi^* = \sum_{G=S+1}^{K} \nu_{RG} g_{\psi G}^* + \sum_{L=1}^{S} \nu_{RL} g_L^*, \tag{33}$$

and

$$F_{\psi R} = \prod_{G=S+1}^{K} \check{f}_{\psi G}^{\nu_{RG}} \prod_{L=1}^{S} f_{\psi L}^{\nu_{RL}} - 1 \tag{34}$$

the equilibrium constant $K_{\psi R}^*$ for the reaction R, defined as

$$RT \ln K_{\psi R}^* = - \varDelta_R g_\psi^*, \tag{35}$$

becomes

$$K_{\psi R}^* = K_{\psi R} (1 + F_{\psi R})^{-1}, \quad R = 1, \ldots, U \,. \tag{36}$$

$K_{\psi R}^*$ is naturally independent of $n_{0S+1}, \ldots, n_{0E}$, but its value is different for different solvents. The quantity $F_{\psi R}$, which includes all activity effects, owns the property

$$\lim_{n_0 \to n_0^*} F_{\psi R} = 0 \,. \tag{37}$$

For reactions under participation of only uncharged molecules, $F_{\psi R}$ can be expanded in a series in $\psi_{0S+1}, \ldots, \psi_{0E}$,

$$F_{\psi R} = \sum_{\substack{\alpha_{S+1}=0 \\ \left(\sum\limits_{I=S+1}^{E} \alpha_I \neq 0 \right)}}^{\infty} \cdots \sum_{\alpha_E = 0}^{\infty} \eta_{\psi R \alpha_{S+1} \ldots \alpha_E} \psi_{0S+1}^{\alpha_{S+1}} \cdots \psi_{0E}^{\alpha_E} \,. \tag{38}$$

For reactions under participation of ions A_I there are further terms depending on $\psi_{0I}^{1/2}$. In dilute solutions the very first terms of the expansion (38) lead to a sufficient approximation.

Knowledge of the quantities ψ_J in the equilibrium state would allow the determination of the quantity $K_{\psi R}$ according to (32) and extrapolation of those values for $\psi_{0H} \to 0$, $H = S+1, \ldots, E$, would lead to $K_{\psi R}^*$. But actually, whenever a chemical reaction occurs, only the initial concentrations ψ_{0G}, $G = S+1, \ldots, E$, are primitive variables, and known as such, and not the equilibrium concentration ψ_G, $G = S+1, \ldots, K$, needed for (32). Hence, $K_{\psi R}$ cannot be calculated directly, but its functional dependence according to (32) and (36) is important for any determination of $K_{\psi R}^*$. The knowledge of $K_{\psi R}^*$ is according to (35) equivalent to that of the standard Gibbs reaction energy $\varDelta_R g_\psi^*$, defined by (33). The temperature dependence of the equilibrium constant $K_{\psi R}^*$ can be used for the determination of the standard reaction enthalpy $\varDelta_R h_\psi^*$ according to

$$\begin{aligned} R \left(\frac{\partial \ln K_{\psi R}^*}{\partial T^{-1}} \right)_{\vartheta_i'} & = \varDelta_R h_\psi^* \\ & = \sum_{G=S+1}^{K} \nu_{RG} h_{\psi G}^* + \sum_{L=1}^{S} \nu_{RL} h_L^* \,. \end{aligned} \tag{39}$$

h_L^* is equal to the partial molar enthalpy H_{0L}^* of the component A_L, $L = 1, \ldots, S$, in the pure mixed solvent ($\psi_{0H} \to 0$, $H = S+1, \ldots, E$). The standard MMQ's $h_{\psi G}^*$ are defined by eq. (I.143). With that quantity the standard reaction entropy $\Delta_R s^*_\psi$, defined by

$$\Delta_R s^*_\psi = -\left(\frac{\partial \Delta_R g^*_\psi}{\partial T}\right)_{\vartheta_i'} = \sum_{G=S+1}^{K} \nu_{RG}\, s^*_{\psi G} + \sum_{L=1}^{S} \nu_{RL}\, s^*_L\,, \tag{40}$$

can be obtained according to

$$\Delta_R s^*_\psi = T^{-1}(\Delta_R h^*_\psi - \Delta_R g^*_\psi)\,. \tag{41}$$

s^*_L is equal to the partial molar entropy S^*_{0L} of the component A_L in the pure mixed solvent. The standard MMQ's $s^*_{\psi G}$ are defined by (I.142).

Similarly, the pressure dependence of the equilibrium constant $K^*_{\psi R}$ can be used for the determination of the standard reaction volume $\Delta_R v^*_\psi$ according to

$$-RT\left(\frac{\partial \ln K^*_{\psi R}}{\partial p}\right)_{\vartheta_i'} = \Delta_R v^*_\psi = \sum_{G=S+1}^{K} \nu_{RG}\, v^*_{\psi G} + \sum_{L=1}^{S} \nu_{RL}\, v^*_L\,. \tag{42}$$

v^*_L is equal to the partial molar volume V^*_{0L} of the component A_L in the pure mixed solvent. The standard MMQ's $v^*_{\psi G}$ are defined by (I.144).

The values $K^*_{\psi^{(1)}R}$ and $K^*_{\psi^{(2)}R}$ defined with differently chosen concentration variables $\psi^{(1)}_G$ and $\psi^{(2)}_G$ and standard quantities $\psi^{\ominus(1)}$ and $\psi^{\ominus(2)}$, respectively, are related according to (35) and (I.137) as

$$K^*_{\psi^{(2)}R} = K^*_{\psi^{(1)}R} \prod_{G=S+1}^{K} \left[\frac{\Psi^{*(1)}\psi^{\ominus(1)}\chi^{(1)}_G}{\Psi^{*(2)}\psi^{\ominus(2)}\chi^{(2)}_G}\right]^{\nu_{RG}}. \tag{43}$$

The similar relation between the quantities $F_{\psi^{(1)}R}$ and $F_{\psi^{(2)}R}$ is

$$(1 + F_{\psi^{(2)}R}) = (1 + F_{\psi^{(1)}R}) \cdot \left[\frac{\Psi^{(1)}\Psi^{*(2)}}{\Psi^{*(1)}\Psi^{(2)}}\right]^{\sum_{G=S+1}^{K}\nu_{RG}}. \tag{44}$$

Whenever there is one particular choice for the concentration variable, let us say $\psi^{(t)}_G$ for example, so that $F_{\psi^{(t)}R} = 0$ for the chemical reaction in the considered concentration interval, then, as was recognized by Scott [6], with some other choice $\psi^{(s)}_G$ for example, it will usually be $F_{\psi^{(s)}R} \neq 0$, if $\sum_{G=S+1}^{K} \nu_{RG} \neq 0$. Relations similar to (43) between the thermodynamic standard reaction quantities are

$$\Delta_R g^*_{\psi^{(2)}} = \Delta_R g^*_{\psi^{(1)}} - RT \sum_{G=S+1}^{K} \nu_{RG} \ln\left[\frac{\Psi^{*(1)}\psi^{\ominus(1)}\chi^{(1)}_G}{\Psi^{*(2)}\psi^{\ominus(2)}\chi^{(2)}_G}\right], \tag{45}$$

$$\Delta_R h^*_{\psi^{(2)}} = \Delta_R h^*_{\psi^{(1)}} + RT^2\left(\frac{\partial \ln(\Psi^{*(1)}/\Psi^{*(2)})}{\partial T}\right)_{\vartheta_i'} \sum_{G=S+1}^{K}\nu_{RG}\,, \tag{46}$$

$$\Delta_R s^*_{\psi^{(2)}} = \Delta_R s^*_{\psi^{(1)}} + R \sum_{G=S+1}^{K} \nu_{RG} \ln\left[\frac{\Psi^{*(1)}\psi^{\ominus(1)}\chi^{(1)}_G}{\Psi^{*(2)}\psi^{\ominus(2)}\chi^{(2)}_G}\right] + RT\left(\frac{\partial \ln(\Psi^{*(1)}/\Psi^{*(2)})}{\partial T}\right)_{\vartheta_i'} \sum_{G=S+1}^{K}\nu_{RG}\,, \tag{47}$$

and

$$\Delta_R v^*_{\psi^{(2)}} = \Delta_R v^*_{\psi^{(1)}} - RT\left(\frac{\partial \ln(\Psi^{*(1)}/\Psi^{*(2)})}{\partial p}\right)_{\vartheta_i'} \sum_{G=S+1}^{K}\nu_{RG}\,. \tag{48}$$

According to (31) to (36) all choices for the concentration variable ψ_G are equivalent in the limit for the pure mixed solvent ($\psi_{0H} \to 0$, for all $H = S+1, \ldots, E$), each choice leads to particular values for the equilibrium constant $K^*_{\psi R}$ and the thermodynamic standard reaction quantities $\Delta_R g^*_\psi$, $\Delta_R h^*_\psi$, $\Delta_R s^*_\psi$ and $\Delta_R v^*_\psi$. From (43), (45) and (47), respectively, it may be recognized that the equilibrium constant $K^*_{\psi R}$, which is a dimensionless quantity, the standard Gibbs reaction energy $\Delta_R g^*_\psi$ and the standard reaction entropy $\Delta_R s^*_\psi$ can obtain any value ($K^*_{\psi R} \in \mathbb{R}_+$, $\Delta_R g^*_\psi \in \mathbb{R}$, $\Delta_R s^*_\psi \in \mathbb{R}$); their values are unique only if some particular standard state is defined by a fixed value of the standard quantity $\psi^\ominus$. Hence, if values of such quantities are reported, the chosen quantity for the concentration variables ψ_G and the chosen value for the standard quantity $\psi^\ominus$ should also be reported, otherwise those data would be worthless. As stated previously [1], one should agree on one particular quantity for the concentration variable and one particular value for the standard state to simplify the comparison of different data. We recommend $\psi_G = c_G$ (with the unit $\mathrm{mol \cdot m^{-3}}$) and $\psi^\ominus = 1\ \mathrm{mol \cdot m^{-3}}$. This choice is adapted to SI units.

6. The Evaluation of Measurements on Phases with Chemical Reactions

For the investigation of any chemical equilibrium reaction some extensive bulk quantities Φ or their adjoint densities D_Φ have to be determined for several solutions with varying concentrations. We assume that the values of N different bulk quantities are determined for M different solutions, i.e. a set of data

$$\mathrm{D_p} = \{(n_{01}, \dots, n_{0E}, \vartheta_1, \dots, \vartheta_\varepsilon, \\ \varrho, D_{\Phi 2}, \dots, D_{\Phi N})_s\}, \quad s = 1, \dots, M,$$

is available for further evaluation. From the values of these quantities those of the adjoint generalized densities $\mathsf{P}_{\psi\Phi}$ can be calculated according to (7), such that the available data are equivalently represented as

$$\mathrm{D_p} = \{(\psi_{0J}(k), \vartheta_\iota(k), \mathsf{P}_{\psi\Phi}(i,k))\},$$

$i = 1, \dots, N$; $k = 1, \dots, M$. The set of values $\{(\mathsf{P}_{\psi\Phi}(i,k))\}$ can be considered as a matrix with N rows and M columns, $\mathsf{P}_{\psi\Phi}(i,k)$ is the element in the i-th row and k-th column. The i-th row of the matrix relates to the i-th investigated property (i.e. the i-th density), the k-th column relates to the k-th solution. Hence the columns can be considered as values of a N-dimensional function of the set of variables $\psi_{02}, \dots, \psi_{0E}, \vartheta_1, \dots, \vartheta_\varepsilon$. The matrix $\{(\mathsf{P}_{\psi\Phi}(i,k))\}$ contains all information available, which can be used for the determination of the occurring chemical reactions, their equilibrium constants, their thermodynamic reaction quantities and the MMQ's of the products generated by those reactions.

If there are columns relating to varying values of just one concentration variable, let us say ψ_{0G}, but with fixed values of ϑ_ι, $\iota = 1, \dots, \varepsilon$, and n_{0I}/n_{01}, $I = 2, \dots, E$, $I \neq G$, the values of the PMQ's Φ_{0G} and their limits $\Phi^+_{0G(G)}$ can be estimated, as was described at (I.62) and (I.63). The set of values $\{(\Phi^+_{0G(G)}(i,l))\}$ can also be considered as a matrix, its columns are values of an $(N-1)$-dimensional function of a set of variables $\psi_{02}, \dots, \psi_{0G-1}, \psi_{0G+1}, \dots, \psi_{0E}$, that is they are independent of ψ_{0G} and therefore the further evaluation usually is simplified.

The further evaluation is based on (11) or (14), i.e. on the dependences of $\mathsf{P}_{\psi\Phi}$, Φ_{0J} or $\Phi^+_{0J(J)}$ on the composition of the solutions. The MMQ's φ_J and their dependence on the concentration variables ψ_{0I} have to be described by some molecular model. According to (I.83) a power-series expansion is possible for MMQ's φ_J corresponding to quantities of class Aa:

$$\varphi_J = \varphi_J^* + \sum_{\substack{\alpha_{S+1}=0 \\ \left(\sum\limits_{I=S+1}^{E} \alpha_I \neq 0\right)}}^{\infty} \cdots \sum_{\alpha_E=0}^{\infty} \lambda_{\psi\varphi J\alpha_{S+1}\dots\alpha_E} \psi_{0S+1}^{\alpha_{S+1}} \cdots \psi_{0E}^{\alpha_E}, \tag{49}$$

where φ_J^* is the limit of the MMQ for the pure mixed solvent $(n_0 \to n_0^*)$. Similarly it follows that,

$$\Delta_R \varphi = \Delta_R \varphi^* + \sum_{\substack{\alpha_{S+1}=0 \\ \left(\sum\limits_{I=S+1}^{E} \alpha_I \neq 0\right)}}^{\infty} \cdots \sum_{\alpha_E=0}^{\infty} \Delta_R \lambda_{\psi\varphi\alpha_{S+1}\dots\alpha_E} \psi_{0S+1}^{\alpha_S \neq 0} \cdots \psi_{0E}^{\alpha_E}. \tag{50}$$

In sufficiently dilute solutions only the first few terms of the expansions (49) and (50) are significantly different from zero. A representation of the dependences of the quantities $\xi_{\psi R}$ and their derivatives $(\partial \xi_{\psi R}/\partial \psi_{0J})_{n_{0J'}, \vartheta_\iota}$ on the concentration variables ψ_{0I} as needed in (11) and (14) is not possible in a general manner, but only for some particular models assumed for the occurring chemical reactions. This fact introduces a hypothesis into the evaluation which can be falsified by experiment but not proved. The choice of the chemical reactions taken into the hypothetical models cannot be formalized, but it is up to the imagination of the investigator to select all those from the enormous number of thinkable reactions which are relevant to the problem. If the set of hypothetical reaction models was chosen large enough and all but one of them could be refuted, then the remaining one has a good chance to be true.

Any hypothetical model for the chemical reactions has to be based on a set of reaction equations of the type of (1). For each reaction a quantity $K_{\psi R}$ is defined by (32), which is related to the equilibrium constant $K^*_{\psi R}$ by (36). According to this equation the dependence of $K_{\psi R}$ on the concentration variables ψ_{0I} can be represented by a power-series expansion, Eq. (38), which is similar to (49) and (50). The quantity $K_{\psi R}$, Eq. (32), together with (6) allows a representation of the $\xi_{\psi R}$'s and their derivatives $(\partial \xi_{\psi R}/\partial \psi_{0J})_{n_{0J'}, \vartheta_\iota}$ in dependence of the concentration variables ψ_{0I}. After introducing those equations and (49) and (50) into (11) or (14), respectively, a multiple regression analysis can either lead to estimators for the equilibrium constants, the quantities $\Delta_R \varphi^*$ and possibly for some coefficients $\Delta_R \lambda_{\psi\varphi\alpha_{S+1}\dots\alpha_E}$ and $\eta_{\psi R\alpha_{S+1}\dots\alpha_E}$ or to the rejection of the assumed model for chemical reactions.

The formulation of appropriate hypothetical reaction models would be facilitated if the number of independent reactions occurring in the solutions were known. An upper bound of the number of independent reactions, that can be recognized on a given set of data, follows from the rank of the matrix $\{(\mathsf{P}_{\psi\Phi}(i,k))\}$ (with fixed values ϑ_ι). Assuming the φ_I and $\Delta_R\varphi$ independent of the composition of the phase, then according to (11) the rank r of the matrix is smaller or equal to $E+U-G-H$, where G is the number of initial substances, for which $\varphi_I=0$ for all $i=1,\dots,N$, and H is the number of reactions, for which $\Delta_R\varphi=0$ for all $i=1,\dots,N$. Choosing the number N of investigated different properties (for example different wavenumbers $\tilde{\nu}$ in optical absorption measurements) and the number M of phases with different composition large enough, one may expect that in fact $r=E+U-G-H$ and $U-H$ is determined because E and G are usually known. But the requirement φ_I and $\Delta_R\varphi$ independent of $\psi_{02},\dots,\psi_{0E}$ need not be satisfied and therefore r can be larger than $E+U-G-H$. In spite of this, the knowledge of r is very valuable, because $r-E+G$ is the upper bound of the number of terms $\xi_{\psi R}\Delta_R\varphi$ that should be introduced in the second sum on the right-hand side of (11) in any hypothetical model about the chemical reactions. That number is actually not the upper bound of the number of independent reactions that can occur in the phase because there can be reactions for which $\Delta_R\varphi=0$ for all investigated properties. Such reactions have also to be included in the sum on the right-hand side of (6) for the calculation of ψ_J from ψ_{0J} and the $\xi_{\psi R}$. For the determination of the upper bound of $U-H$ it can be advantageous to form the quantities

$$\Xi_{\psi\Phi}(i,k)=\mathsf{P}_{\psi\Phi}(i,k)-\sum_{I=1}^{E}\chi_I\,\psi_{0I}(k)\,\varphi_I^*(i,k)\,, \tag{51}$$

whenever the φ_I^* can be determined from the corresponding one-solute phases. The rank of the matrix $\{(\Xi_{\psi\Phi}(i,k))\}$ formed from the elements $\Xi_{\psi\Phi}(i,k)$ shall be called t. According to the equation

$$\Xi_{\psi\Phi}=\sum_{I=1}^{E}\chi_I\,\psi_{0I}(\varphi_I-\varphi_I^*)+\sum_{R=1}^{U}\xi_{\psi R}\,\Delta_R\varphi \tag{52}$$

and assuming φ_I and $\Delta_R\varphi$ independent of $\psi_{02},\dots,\psi_{0E}$, it is $t=r-E+G=U-H$, and usually t is easier to be determined than r.

A similar analysis can be done with the rank f of the matrix $\{(\Phi_{0J}(i,k))\}$ (with fixed values ϑ_ι) formed from the elements $\Phi_{0J}(i,k)$. Assuming φ_I and $\Delta_R\varphi$ independent of $\psi_{02},\dots,\psi_{0E}$, it will be $f=U-H-I$, where I is the number of reactions for which $\Delta_R\varphi\neq 0$ but $(\partial\xi_{\psi R}/\partial\psi_{0J})_{n_{0J'},\vartheta_\iota}=0$. Hence from f follows an upper bound of the number of reactions contributing to the sum over R in (13).

The determination of chemical equilibria in solutions is based on the dependence of some density D_Φ on the composition of the solution. As a consequence, only such reactions can be investigated in this manner, where there is actually some dependence of D_Φ. The first prerequisite is, that $\Delta_R\varphi\neq 0$, as was recognized from (11), (13) and (14); we will assume that this is always satisfied. The second prerequisite is, also according to (13), that the derivative $(\partial\xi_R/\partial n_{0J})_{n_{0J'},\vartheta_\iota}$ is large enough, which can usually be obtained by choosing an appropriate interval of the concentration variables ψ_{0I}. But there are some types of chemical reactions where bulk quantities are not sensitive to the variation of the concentration of solutions. Three such cases will be considered in the next subsections. An application of the above methods will be treated in paper V of this series [4].

6.1. Equilibrium Constants for Systems with Association with the Solvent

Assume there is an association of some molecule A_B with λ solvent molecules A_1 according to

$$\lambda\,\mathrm{A}_1+\mathrm{A}_B\rightleftharpoons\mathrm{A}_{B\lambda};\quad \lambda=1,\dots,v_B;\quad B=1,\dots,K\,. \tag{53}$$

From (32) and (36) it follows for the equilibrium constant corresponding to (53)

$$K_{\psi B\lambda}^*=\frac{\psi_{B\lambda}}{\psi_B}\left(\frac{\psi_1^*}{\psi_1}\right)^{\lambda}(1+F_{\psi B\lambda})^{-1}\,. \tag{54}$$

We can define the total concentration $\psi_{\mathrm{t}B}$ of all the molecules $\mathrm{A}_B,\mathrm{A}_{B1},\dots,\mathrm{A}_{Bv_B}$ by

$$\psi_{\mathrm{t}B}=\sum_{\lambda=0}^{v_B}\psi_{B\lambda}\,, \tag{55}$$

where $\psi_{B0}=\psi_B$, and introduce a modified (relative) equilibrium constant $K_{\psi\mathrm{t}B\lambda}^*$ by

$$K_{\psi\mathrm{t}B\lambda}^*=\left(\sum_{\mu=0}^{v_B}K_{\psi B\lambda}^*\right)^{-1}K_{\psi B\lambda}^*\,, \tag{56}$$

where $K^*_{\psi B0} = 1$, then it follows

$$\psi_{B\lambda} = K^*_{\psi tB\lambda}(1 + F_{\psi tB\lambda})\,\psi_{tB}\left(\frac{\psi_1}{\psi_1^*}\right)^{\lambda}. \qquad (57)$$

From any observable quantity corresponding to a density D_Φ a generalized density $\mathsf{P}_{\psi\Phi}$ can be obtained according to (7), which can be represented as a function of the ψ_J's, Equation (10). Introducing the abbreviation

$$\varphi_{tB} = \sum_{\lambda=0}^{v_B} \varphi_{B\lambda}\,\chi_{B\lambda}\,K^*_{\psi tB\lambda}(1 + F_{\psi tB\lambda})\left(\frac{\psi_1}{\psi_1^*}\right)^{\lambda} \qquad (58)$$

into (10) leads to

$$\mathsf{P}_{\psi\Phi} = \sum_{\substack{J=1\\ J\neq B\lambda,\,B}}^{K} \varphi_J\,\chi_J\,\psi_J + \varphi_{tB}\,\psi_{tB}\,. \qquad (59)$$

From (59) it can be recognized that the contribution due to the molecules A_B and $A_{B\lambda}$ ($\lambda = 1, \ldots, v_B$) to the generalized density $\mathsf{P}_{\psi\Phi}$ is essentially dependent only on the total concentration ψ_{tB}. Some minor dependences could result through the $F_{\psi tB\lambda}$ and $(\psi_1/\psi_1^*)^\lambda$, but they are vanishing for sufficiently dilute solutions ($n_0 \to n_{01}$) and commonly cannot be used for the investigation of the reactions (53). The quantities φ_{tB}, obtainable from experimental data, are averages of the MMQ's $\varphi_{B\lambda}$ of all A_B, $A_{B1}, \ldots, A_{Bv_B}$, weighted by their relative equilibrium constant, defined by (56), multiplied by $\chi_{B\lambda}$. The values of φ_{tB} can hint at some association according to (53) especially, if the values of φ_{tB} in different solvents are compared or if changes of the φ_{tB} with varying variables ϑ_ι (T, p, for example) are observed.

Any chemical reaction under participation of molecules A_J, $A_{J1}, \ldots, A_{Jv_J}$, which are associated with solvent molecules A_1 according to (53), can be formulated as

$$\sum_{J=2}^{K} \nu_{RJ}\,A_{J\lambda_J} = 0; \quad \lambda_J = 0, 1, \ldots, v_J;$$

$$R = 1, 2, \ldots, U\,. \qquad (60)$$

The individual equilibrium constants for the reaction of molecules with a specified association state are

$$K^*_{\psi R\lambda_2\ldots\lambda_K} = \prod_{J=2}^{K} (\psi_{J\lambda_J}/\,\psi^{\ominus})^{\nu_{RJ}} \cdot (1 + F_{\psi R\lambda_2\ldots\lambda_K})^{-1}\,. \qquad (61)$$

Introducing (57) into (61) leads to the average equilibrium constant $K^*_{\psi Rt}$ of the reaction R

$$K^*_{\psi Rt} = \frac{K^*_{\psi R\lambda_2\ldots\lambda_K}(1 + F_{\psi R\lambda_2\ldots\lambda_K})}{\prod\limits_{J=2}^{K}[K^*_{\psi tJ\lambda_J}(1 + F_{\psi tJ\lambda_J})(\psi_1/\psi_1^*)^{\lambda}]^{\nu_{RJ}}(1 + F_{\psi Rt})}$$

$$= \prod_{J=2}^{K}\left(\frac{\psi_{tJ}}{\psi^{\ominus}}\right)^{\nu_{RJ}}(1 + F_{\psi Rt})^{-1}, \qquad (62)$$

where ψ_{tJ} is according to (55) the total concentration of the molecules A_J, $A_{J1}, \ldots, A_{J\lambda_J}$. The generalized density, Eq. (10), becomes

$$\mathsf{P}_{\psi\Phi} = \sum_{J=1}^{K} \varphi_{tJ}\,\psi_{tJ}\,, \qquad (63)$$

where

$$\varphi_{tJ} = \sum_{\lambda_J=0}^{v_J} \varphi_{J\lambda_J}\,\chi_{J\lambda_J}\,K^*_{\psi tJ\lambda_J}(1 + F_{\psi tJ\lambda_J})\,. \qquad (64)$$

From (62) it can be recognized that for any reaction R occurring in such a system, only the average equilibrium constant $K^*_{\psi Rt}$ can be determined from the dependence of $\mathsf{P}_{\psi\Phi}$ on the variables $\psi_{02}, \ldots, \psi_{0E}$, for example. The quantities φ_{tJ} also obtainable from such measurements are averages of the MMQ's $\varphi_{J\lambda_J}$ of all A_J, $A_{J1}, \ldots, A_{Jv_J}$ weighted by their relative equilibrium constants as represented in (64).

6.2. Equilibrium Constants for Systems with Different But Stoichiometrically Identical Molecules

Assume there exist some substances with identical stoichiometric composition but with, for example, different configuration. Such substances shall be called $A_{J\varkappa_J}$, where the first subscript $J = 1, \ldots, K$ denotes the stoichiometric composition and the second one $\varkappa_J = 1, \ldots, s_J$ differentiates those with any different property. To the chemical reaction (we drop the second subscript J for simplification)

$$A_{J\varkappa} \rightleftharpoons A_{J\varkappa'}\,, \qquad (65)$$

corresponds the equilibrium constant

$$K^*_{\psi UJ\varkappa\varkappa'} = (\psi_{J\varkappa'}/\psi_{J\varkappa})\,(1 + F_{\psi UJ\varkappa\varkappa'})^{-1}\,. \qquad (66)$$

With the total concentration ψ_{tJ} of all substances with identical stoichiometric composition

$$\psi_{tJ} = \sum_{\varkappa=1}^{s_J} \psi_{J\varkappa} \qquad (67)$$

and the abbreviation

$$K^*_{\psi UtJ\varkappa} = \left[\sum_{\varkappa'=1}^{s_J} K_{\psi UJ\varkappa\varkappa'}\right]^{-1} \qquad (68)$$

follows

$$\psi_{J\varkappa} = K^*_{\psi U\mathrm{t}J\varkappa}(1 + F_{\psi U\mathrm{t}J\varkappa})\,\psi_{\mathrm{t}J}\,. \tag{69}$$

From any observable quantity corresponding to a density D_Φ a generalized density $\mathsf{P}_{\psi\Phi}$ can be obtained according to (7) which can be represented as a function of the $\psi_{J\varkappa}$'s, Eq. (10). Introducing the abbreviation

$$\varphi_{\mathrm{t}J} = \sum_{\varkappa=1}^{s_J} \varphi_{J\varkappa}\,\chi_{J\varkappa}\,K^*_{\psi U\mathrm{t}J\varkappa}(1 + F_{\psi U\mathrm{t}J\varkappa}) \tag{70}$$

into (10) leads to

$$\mathsf{P}_{\psi\Phi} = \sum_{J=1}^{K} \varphi_{\mathrm{t}J}\,\psi_{\mathrm{t}J}\,. \tag{71}$$

Hence any dependence of $\mathsf{P}_{\psi\Phi}$ on the composition of the phase can only lead to the values $\varphi_{\mathrm{t}J}$, that is to average values of the MMQ's $\varphi_{J\varkappa}$ of all substances with identical stoichiometric composition weighted by factors as shown in (70), as was recognized by Orgel and Mulliken for a somewhat specialized case [7]. The values of $\varphi_{\mathrm{t}J}$ can hint at some different species $A_{J\varkappa}$ distinguished from each other by some different $\varphi_{J\varkappa}$, especially if the values $\varphi_{\mathrm{t}J}$ show some changes with varying ϑ_ι or with changes of the composition or kind of solvent (what can effect $K^*_{\psi U\mathrm{t}J\varkappa}$, especially, and therefore $\varphi_{\mathrm{t}J}$).

For any reaction of individual molecules $A_{J\varkappa_J}$ with other $A_{I\mu_I}$ according to

$$\sum_{J=1}^{K} \nu_{RJ}\,A_{J\varkappa_J} = 0\,, \quad \varkappa_J = 1, \ldots, s_J\,, \tag{72}$$

individual equilibrium constants $K^*_{\psi R\varkappa_1\ldots\varkappa_K}$ can be introduced by

$$K^*_{\psi R\varkappa_1\ldots\varkappa_K} = \prod_{J=2}^{K} \left(\frac{\psi_{J\varkappa}}{\psi^\ominus}\right)^{\nu_{RJ}} (1 + F_{\psi R\varkappa_1\ldots\varkappa_K})^{-1}\,. \tag{73}$$

Using (69) and the abbreviation

$$K^*_{\psi R\mathrm{t}} = \left[\prod_{J=2}^{K} (K_{\psi U\mathrm{t}J\varkappa})^{\nu_{RJ}}\right]^{-1} K^*_{\psi R\varkappa_1\ldots\varkappa_K} \tag{74}$$

it follows from (73)

$$K^*_{\psi R\mathrm{t}} = \prod_{J=2}^{K} \left(\frac{\psi_\mathrm{t}}{\psi^\ominus}\right)^{\nu_{RJ}} (1 + F_{\psi R\mathrm{t}})^{-1}\,. \tag{75}$$

Hence, in any phase where some reactions of the type (72) under participation of different molecules but with identical stoichiometric composition occur, only an average equilibrium constant $K^*_{\psi R\mathrm{t}}$ related to the total concentration $\psi_{\mathrm{t}J}$ can be determined from experimental data [7].

Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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