The Determination of Molecular Quantities from Measurements on Macroscopic Systems. I

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For many molecules the determination of molecular quantities, as electric dipole moments or molar absorption coefficients, has to be based on measurements on solutions or other dense phases. The evaluation of such data is rather involved due to the interactions between neighboring molecules, and taking this into account, a general method is presented. Some quantities appropriate for the description of a macroscopic system (bulk quantities) are defined and their properties are discussed, especially partial molar quantities (PMQ's) ,which are well known from thermodynamics. To any PMQ some corresponding model molar quantities (MMQ's) can be introduced, each MMQ based on a particular molecular model. The MMQ's are related to the interesting molecular quantities and may allow their estimation. The values of PMQ's can be determined uniquely from experimental data, if the investigated system meets just a very few general requirements, whereas the values of the corresponding MMQ's are generally dependent on the chosen model and hence unique only, if a true model is available. As examples, approximate molecular models are introduced for MMQ's corresponding to the Gibbs energy and to quantities convenient for the evaluation of permittivity, optical absorption and electro-optical absorption measurements.

1. Introduction

The physical properties of macroscopic systems may be described by means of suitable measurable quantities; the definition of such quantities, called macroscopic quantities, are operational ones. Many of the macroscopic quantities are considered to be the result of the corresponding properties of the constituents of the system, that is ultimately of properties of the molecules contained in the system. The properties of molecules are described by molecular quantities defined on the basis of some theoretical model. Hence there are relations between molecular quantities and macroscopic quantities, and one often tries to determine the molecular quantities from macroscopic quantities which can be measured on the macroscopic system. A few methods suitable for this purpose are treated here, and a few applications shall be reported in the following papers. Some of the results reported in this paper (and also in the fourth paper of this series [1]) have been obtained previously by other authors, usually with other methods or in another connection. To keep the paper consistent, we repaet such results but do not claim any originality.

In any arbitrary system the relations between molecular quantities and macroscopic quantities can be extremely complex, and hence we will restrict our further consideration to systems and quantities meeting the following requirements at least in sufficient approximation.

If there are two or more systems where all observed macroscopic quantities have equal values, then these systems shall be called identical systems. The first requirement which should be met by all considered quantities is:

(1) Given are l identical systems with the values γ_{gi} $(i=1, \ldots, Y)$ of Y macroscopic quantities. If the l identical systems (partial systems) are lumped together to one system (total system), then the value $\gamma_{\mathrm{S}gi}$ of each macroscopic quantity of the total system is given by

$$\gamma_{\mathrm{S}gi} = l^g \gamma_{gi} \quad (i = 1, \ldots, Y), \tag{1}$$

where g is an integer ($g \in \mathbb{Z}$).

If requirement (1) is not met, either the partial systems are not identical systems or the quantity γ_{gi} is of a kind not admitted in the following considerations.

The further requirements which should be met by all macroscopic quantities of the considered systems are:

(2) The macroscopic quantities do not depend continuously on the location.

(3) The macroscopic quantities either do not depend on time or, if they depend on time, they

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can be represented by composite functions with some time-dependent parameters, which at any fixed time can be considered as macroscopic quantities of the regarded kind.

Because of requirement (2), the systems consist of one homogeneous phase or of some homogeneous phases separated from each other by singular surfaces where discontinuous changes of macroscopic quantities can occur. The considered properties of the system do not depend on the shape of the phase, and boundary effects are neglected.

If the macroscopic quantities are not time-dependent, then the system is in a stationary state. If, after isolating the system from its surroundings, the quantities are still stationary, then the system is in an equilibrium state. If the system is in a state different from the stationary state, each macroscopic quantity is assumed to depend on some parameters β_p, which are functions of time.

The macroscopic properties described by quantities meeting requirements (1) to (3) shall be called bulk properties, the corresponding quantities bulk quantities; for these quantities, the thermodynamic limit (infinite volume limit) is assumed to exist [2]. Each one of these quantities belongs to a definite class of bulk quantities characterized by the integer g. Of special interest are quantities of the class $g = 1$, called extensive quantities, and of the class $g = 0$, called intensive quantities*.

2. Primarily Measured Bulk Quantities, Primitive and Independent Variables

To gain information on molecular properties from measurements on macroscopic systems, some appropriate bulk quantities have to be determined. For some bulk quantities of a given system in a well specified state, the values can be determined by a single measurement with a suitable instrument. Examples are (1) the total mass m_0 of the system, (2) the masses m_{0k} of the constituents $k = 1, 2, \ldots, E$ used to generate the system, (3) the temperature T, and (4) the density ϱ of a phase, (5) the volume V of a phase, (6) the total volume, and (7) the pressure p of a closed system. For other bulk quantities, the values can be calculated from the values of a few other macroscopic quantities, which need not necessarily be bulk quantities. Examples are (1) the amount of substance n_{0J} of any pure substance A_J used as one of the constituents of the system, calculated from the mass m_{0J} of this substance and its molar mass M_J**, (2) the volume of a phase from its mass m_0 and its density, or reversely (3) the density from its mass and volume, (4) the absorption coefficient a of a phase from the radiant flux transmitted through some absorbing probe, the incident radiant flux and the length of the light path in the probe, (5) the increase of the enthalpy H of a system due to some electric work. There are furthermore bulk quantities which have to be determined from the functional dependence of some bulk quantity. Examples are (1) any partial molar quantity as the partial molar volume V_{0J} of some substance A_J, (2) the heat capacity of a phase or of a system, (3) the increase of the entropy of a phase with increasing temperature derived from its heat capacity, (4) the temperature of a phase from the dependence of the enthalpy of the phase on its entropy. Any bulk quantity either measured directly or calculated from independently measured quantities can be regarded as a primarily measured bulk quantity; a bulk quantity calculated from primarily measured bulk quantities shall be called a derived bulk quantity***.

In any experimental investigation of the kind considered here, the values of some macroscopic quantities are measured. All further evaluations are based on that set of data. The choice of the primarily measured quantities is determined by the investigated object, the purpose of the investigation and by the possibility, the accuracy and the convenience of appropriate measurements. Each primarily measured bulk quantity γ_{hk} may be considered as an element of an ordered set $\mathrm{Q_p} = (\gamma_{hk})$.

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* The expressions extensive and intensive quantities are used by several authors for differently defined sets of quantities. We will use them only in the above sense.

** The quantity n_J, that is the amount of a substance A_J actually present in a phase, can meet the requirements (1) to (3) of Sect. 1, but generally it is no macroscopic quantity, and therefore no bulk quantity. In a system, where a chemical reaction occurs, the quantity n_J cannot be defined without introducing a molecular model, especially one about the chemical reaction. Hence n_J is to be regarded as a molecular quantity.

*** The primarily measured bulk quantities are not a class of quantities because one and the same bulk quantity can be considered either as a primarily measured quantity or as a derived bulk quantity depending on the system, the kinds of measurements performed and the free choice of the investigator.

To each particular state s of the investigated system corresponds a set of values $(\gamma_{hk})_{\mathrm{s}}$ of these quantities. The totality of such values may be considered as a set $D_{\mathrm{p}} = \{(\gamma_{hk})_{\mathrm{s}}\}$, the set of available data. The values of any primarily measured quantity or of any other scalar bulk quantity γ_{gi} are restricted to some interval $\mathrm{d}_{gi} \subset \mathbb{R}$, where $\mathbb{R}$ is the set of real numbers.

If the set $\mathrm{Q_p}$ can be partitioned into two disjoint subsets $\mathrm{Q_v} = (\gamma_{\mathrm{v}hk})$ and $\mathrm{Q_f} = (\gamma_{\mathrm{f}hk})$ with the properties

(1) $\mathrm{Q_v} \cup \mathrm{Q_f} = \mathrm{Q_p}$,

(2) $\mathrm{Q_v} \cap \mathrm{Q_f} = \emptyset$,

(3) for fixed values of all $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$ the values of all $\gamma_{\mathrm{f}ei} \in \mathrm{Q_f}$ are uniquely determined,

(4) each $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$ can be varied arbitrarily without causing a variation of any other $\gamma_{\mathrm{v}qm} \in \mathrm{Q_v}$, $\gamma_{\mathrm{v}qm} \neq \gamma_{\mathrm{v}hk}$,

then the quantities $\gamma_{\mathrm{f}ei} \in \mathrm{Q_f}$ can be regarded as functions $\gamma_{\mathrm{f}ei} = \gamma_{\mathrm{f}ei}(\gamma_{\mathrm{v}hk})$ whose arguments are the quantities $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$. The quantities $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$ shall be called primitive variables. Usually there are several choices for the set $\mathrm{Q_v}$ of primitive variables. One commonly chooses that set embracing the quantities $\gamma_{\mathrm{v}hk}$ whose values are most easily and accurately determined, and which is most conveniently used for the further evaluation of data*.

Each arbitrary variation $\Delta\gamma_{\mathrm{v}hk}$ of a quantity $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$ may be considered as a process leading from a specified state of the system to another specified state. It may happen that the state of the system after any particular variation $\Delta\gamma_{\mathrm{v}hk}$ of $\gamma_{\mathrm{v}hk}$ is identical with the state after a sequence of variations $\Delta\gamma_{\mathrm{v}ql}$ of other quantities $\gamma_{\mathrm{v}ql} \in \mathrm{Q_v}$, in which case the former primitive variable $\gamma_{\mathrm{v}hk}$ may be considered as dependent on the latter ones, i.e. $\gamma_{\mathrm{v}hk} = \gamma_{\mathrm{v}hk}(\gamma_{\mathrm{v}ql})$. If the interval d_{hk} of the variable $\gamma_{\mathrm{v}hk}$ is a subset of the cartesian product $\prod_{ql} \mathrm{d}_{ql}$ of the intervals d_{ql} of all $\gamma_{\mathrm{v}ql}$, i.e. $\mathrm{d}_{hk} \subset \prod_{ql} \mathrm{d}_{ql}$, the quantity $\gamma_{\mathrm{v}hk}$ can be eliminated from the set $\mathrm{Q_v}$, reducing the number of primitive variables by one. There may be further dependences between other $\gamma_{\mathrm{v}rm} \in \mathrm{Q_v}$ leading to a further reduction of the number of primitive variables. For any given interval $\mathrm{d_w} \subset \mathrm{d_v} = \prod_{\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}} \mathrm{d}_{hk}$ there is a minimal set $\mathrm{Q}_{\mathrm{v_{min}}} \subset \mathrm{Q_v}$ of primitive variables, where all $\gamma_{\mathrm{v}hk} \in \mathrm{Q}_{\mathrm{v_{min}}}$ are mutually independent and $\mathrm{Q}_{\mathrm{v_{min}}}$ or $\gamma_{\mathrm{v}hk} \in \mathrm{Q}_{\mathrm{v_{min}}}$, respectively, satisfy the above conditions (1) to (4). The number of elements of $\mathrm{Q}_{\mathrm{v_{min}}}$, that is the number of independent variables $\gamma_{\mathrm{v}hk} \in \mathrm{Q}_{\mathrm{v_{min}}}$, shall be $\mathrm{v_{min}}$. The number $\mathrm{v_{min}}$ and the individual variables $\gamma_{\mathrm{v}hk}$ which have to be chosen, can depend on the considered interval $\mathrm{d_w}$. The interval $\mathrm{d_w}$ is $\mathrm{v_{min}}$-dimensional and therefore $\mathrm{d_w} \subset \mathbb{R}^{\mathrm{v_{min}}}$, where $\mathbb{R}^{\mathrm{v_{min}}}$ is the $\mathrm{v_{min}}$-dimensional point space. For the whole interval $\mathrm{d_v}$ there is similarly a minimal set $\mathrm{Q}_{\mathrm{v}_{\overline{\mathrm{min}}}}$ of primitive variables, their number is $\mathrm{v}_{\overline{\mathrm{min}}}$. For any arbitary $\mathrm{d_w} \subset \mathrm{d_v} \subset \mathbb{R}^{\mathrm{v}_{\overline{\mathrm{min}}}}$ it is $\mathrm{Q}_{\mathrm{v_{min}}} \subset \mathrm{Q}_{\mathrm{v}_{\overline{\mathrm{min}}}}$ and $\mathrm{v_{min}} \leqq \mathrm{v}_{\overline{\mathrm{min}}}$.

If the set $\mathrm{Q_p}$ of primarily measured bulk quantities includes all primarily measurable bulk quantities possible for the considered system, it shall be called $\mathrm{Q_t}$. A set of all independent primitive variables included in $\mathrm{Q_t}$ and satisfying the above conditions (1) to (4) shall be called $\mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$, and the number of those variables shall be $\mathrm{v}_{\overline{\overline{\mathrm{min}}}}$. The totality of the variables $\gamma_{\mathrm{v}hk} \in \mathrm{Q}_{\overline{\overline{\mathrm{min}}}}$ covers a $\mathrm{v}_{\overline{\overline{\mathrm{min}}}}$-dimensional subset $\mathrm{d_t} \subset \mathbb{R}^{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$ where $\mathrm{d_t} = \prod_{\gamma_{\mathrm{v}hk} \in \mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}} \mathrm{d}_{\mathrm{v}hk}$ is the cartesian product of the intervals $\mathrm{d}_{\mathrm{v}hk}$ of all $\gamma_{\mathrm{v}hk} \in \mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$. If each $\mathrm{d}_{\mathrm{v}hk}$ covers all possible values of $\gamma_{\mathrm{v}hk}$, then the set $\mathrm{d_t}$ shall be called a complete set of variables for the considered system. Any bulk quantity $\gamma_{gi} \notin \mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$ of this system can be represented as a function with arguments from the set $\mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$ in some set $\mathrm{d_t} \cap \mathscr{D}_{gi}$, where $\mathscr{D}_{gi}$ is the domain of the function γ_{gi}.

If the set $\mathrm{Q}_{\mathrm{v}_{\overline{\mathrm{min}}}} \subset \mathrm{Q_p}$ is a proper subset of $\mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$, i.e. $\mathrm{Q}_{\mathrm{v}_{\overline{\mathrm{min}}}} \subset \mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$ but $\mathrm{Q}_{\mathrm{v}_{\overline{\mathrm{min}}}} \neq \mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}}$, then $\mathrm{v}_{\overline{\mathrm{min}}} < \mathrm{v}_{\overline{\overline{\mathrm{min}}}}$. In this case the set of primitive variables $\mathrm{Q_v}$ generally is not sufficient for a complete representation of all bulk quantities $\gamma_{gi} \notin \mathrm{Q_v}$. One commonly assumes firstly, that the set $\mathrm{D_p}$ of available data could be extended to a set $\mathrm{D_t} = \mathrm{D_p} \cup \mathrm{D_e} = \{(\gamma_{gi})_{\mathrm{s}}\}$, where $\mathrm{D_e} = \{(\gamma_{\mathrm{v}lm})_{\mathrm{s}}\}$ is the set of values of all variables $\gamma_{\mathrm{v}lm} \in (\mathrm{Q}_{\mathrm{v}_{\overline{\overline{\mathrm{min}}}}} - \mathrm{Q}_{\mathrm{v}_{\overline{\mathrm{min}}}})$ for the system in the particular state s, and secondly, that each of those variables $\gamma_{\mathrm{v}lm}$ has one and the same fixed value $\gamma^{0}_{\mathrm{v}lm}$ in all considered sets $(\gamma_{gi})_{\mathrm{s}}$. If this requirement is met, each bulk quantity $\gamma_{gi} \notin \mathrm{Q_v}$ can be represented as a function $\gamma_{gi} = \gamma_{gi}(\gamma_{\mathrm{v}hk})$

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* For a phase consisting of the pure substances $\mathrm{A_1}$, $\mathrm{A_2}$ and $\mathrm{A_3}$, for example, it could be chosen $\mathrm{Q_p} = (n_{01}, n_{02}, n_{03}, T, p, H, \varrho, a, V)$, then a possible choice for the set of primitive variables is $\mathrm{Q_v} = (n_{01}, n_{02}, n_{03}, T, p)$ and hence the set of functions is $\mathrm{Q_f} = (H, \varrho, a, V)$. Derived bulk quantities of this system are V_{01}, V_{02}, V_{03}, for example.

with arguments $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$ in some set $\mathrm{d_w} \cap \mathscr{D}_{gi}$, where $\mathrm{d_w} = \prod_{hk} \mathrm{d}_{hk}$ is the cartesian product of the intervals d_{hk} of the primitive variables $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$, and where $\mathrm{d_w} \subset \mathbb{R}^{\overline{\mathrm{v}_{\min}}}$.

To discuss two different systems we designate any quantity by A' if it relates to the first system, by A'' if it relates to the second one. If the two sets of all regarded independent variables of the two systems can be chosen so that they are equal, i.e. $\mathrm{Q}'_{\overline{\mathrm{v}_{\min}}} = \mathrm{Q}''_{\overline{\mathrm{v}_{\min}}}$, we call the systems similar. One or more of the variables $\gamma_{1m} \in \mathrm{Q}_{\overline{\mathrm{v}_{\min}}}$ describe the mass of the system, the masses of the constituents used to generate the system, or related quantities describing the amount of the system. If $\gamma'_{1m} = \gamma''_{1m}$ for all quantities of this kind, the two systems shall be denoted as equal systems. If

$$\lambda^{\mathrm{h}} \gamma'_{hk} = \gamma''_{hk} \quad \text{for all} \quad \gamma'_{hk} \in \mathrm{Q}'_{\overline{\mathrm{v}_{\min}}} \quad \text{and} \quad \gamma''_{hk} \in \mathrm{Q}''_{\overline{\mathrm{v}_{\min}}},$$

where $\lambda \in \mathbb{R}_+$, it is said that the two systems are in an equal state. Two systems in an equal state are necessarily similar systems. If two equal systems are in an equal state, and if this state is a stationary state, they are called identical systems with respect to the sets Q'_{p} and $\mathrm{Q}''_{\mathrm{p}}$, where all quantities meeting the requirements (1) to (3) of section 1 have equal values.

To select the correct primitive variables $\gamma_{\mathrm{v}hk} \in \mathrm{Q_v}$ to form a set $\mathrm{Q}_{\mathrm{v}_{\min}}$ or the set $\mathrm{Q}_{\overline{\mathrm{v}_{\min}}}$, one has to have some knowledge about the composition of the constituents of the system and about the chemical reactions occurring in the system. But such information commonly is obtained only from an analysis based on the set $\mathrm{D_p}$ of data, and therefore the sets $\mathrm{Q}_{\mathrm{v}_{\min}}$ and $\mathrm{Q}_{\overline{\mathrm{v}_{\min}}}$ can be determined only after the results of the investigation of the system are known.

An aim of many experimental investigations is the determination of functions $\gamma_{gi} \in \mathrm{Q_f}$ corresponding to bulk quantities and of further derived functions leading to molecular quantities. For the necessary evaluation of the set $\mathrm{D_p}$ of data, any set of primitive variables $\mathrm{Q_v} \supset \mathrm{Q}_{\mathrm{v}_{\min}}$ determined in some interval $\mathrm{d_w}$ and satisfying the above conditions (1) to (4) may be used. Many functions $\gamma_{gi}(\gamma_{\mathrm{v}hk})$ are differentiable in any order at any point $(\gamma_{\mathrm{v}hk}) \in \mathrm{d_d} \subset (\mathrm{d_w} \cap \mathscr{D}_{gi})$. In such cases, which are met especially if the system consists of only one phase, the function γ_{gi} is completely determined in the space $\mathrm{d_d}$ if it is accurately known in any subspace $\mathrm{d_s} \subset \mathrm{d_d}$ whose measure in $\mathrm{d_d}$ is different from zero. Because all quantities of the set $\mathrm{D_p}$ of available data necessarily are associated with finite errors, an accurate determination of any function γ_{gi} is impossible. To keep the disturbances caused by those errors as low as possible, the investigated range of the functions γ_{gi} should be as large as possible; that is, one should choose the interval $\mathrm{d_w}$ of the set $\mathrm{Q_v}$ as large as possible. For the determination of many molecular quantities the limits of some appropriate bulk quantities are sufficient. In such a case the experimental investigation may be restricted to a smaller interval of the appropriate primitive variables.

For a complete description of a system all possible independent bulk functions γ_{gi} should be investigated in a range corresponding to the whole interval of a complete set $\mathrm{Q}_{\overline{\overline{\mathrm{v}_{\min}}}}$. Neither the number of independent bulk functions γ_{gi} nor the number of primitive variables in the complete set $\mathrm{Q}_{\overline{\overline{\mathrm{v}_{\min}}}}$ can easily be found even for simple systems. Therefore a macroscopic system cannot be described completely, and one has to confine oneself to the description of a selected set $\mathrm{Q_f}$ of functions γ_{gi} regarding only a selected set $\mathrm{Q_v}$ of primitive variables γ_{hk}.

3. Some General Relations for Macroscopic Quantities

For the description of macroscopic quantities of a system meeting the requirements (1) to (3), Sect. 1, v primitive variables γ_{hk} may be chosen; they constitute the set $\mathrm{Q_v}$. Each other bulk quantity γ_{gi} can be represented by a function

$$\gamma_{gi} = \gamma_{gi}(\gamma_{hk}), \tag{2}$$

which is assumed to be differentiable at $(\gamma_{hk}) \in \mathrm{d_d}$. A function $\gamma_{\lambda gi}$ may be defined by

$$\gamma_{\lambda gi} = \lambda^{g} \gamma_{gi}, \tag{3}$$

where λ is any real number $(\neq 0)$ or any quantity representing a bulk property. With the definition

$$\gamma_{\lambda hk} = \lambda^{h} \gamma_{hk} \tag{4}$$

it follows from eq. (1) that

$$\begin{aligned} \gamma_{\lambda gi} &= \gamma_{gi}(\gamma_{\lambda hk}) = \lambda^{g} \gamma_{gi}(\gamma_{hk}) \\ &= \gamma_{gi}(\lambda^{h} \gamma_{hk}). \end{aligned} \tag{5}$$

Under those conditions Euler's theorem for homogeneous functions holds *

$$g\,\gamma_{gi}(\gamma_{hk}) = \sum_{hk} \left(\frac{\partial \gamma_{gi}}{\partial \gamma_{hk}}\right)_{\gamma_{hk}'} h\,\gamma_{hk} \tag{6}$$

and furthermore it follows

$$(h-g)\left(\frac{\partial \gamma_{gi}}{\partial \gamma_{hk}}\right)_{\gamma_{hk}'} + \sum_{lm}\left(\frac{\partial^2 \gamma_{gi}}{\partial \gamma_{hk}\,\partial \gamma_{lm}}\right) \cdot l\,\gamma_{lm} = 0\,. \tag{7}$$

For the representation of a bulk quantity γ_{gi} of the class $g \neq 0$ according to (6) at least one variable γ_{hk} of a class $h \neq 0$ is necessary, for the representation of an intensive quantity γ_{0i} (class $g=0$) the primitive variables γ_{hk} may be of any class. The derivatives of the functions γ_{gi} are related according to (6) and (7).

Of special interest are macroscopic quantities of the class $g=0$ (intensive quantities), which are according to (5) independent of the amount of the system, and quantities of the class $g=1$ (extensive quantities), which are proportional to the amount of the system. If quantities of these classes are used as primitive variables, i.e. the intensive quantities $\eta_1, \ldots, \eta_w$ and the extensive quantities $\Gamma_1, \ldots, \Gamma_v$, then according to (6) it holds true for any function Φ representing another extensive quantity

$$\Phi = \sum_{l=1}^{v}\left(\frac{\partial \Phi}{\partial \Gamma_l}\right)_{\Gamma_l', \eta_\iota} \Gamma_l \tag{8}$$

and according to (7)

$$\sum_{l=1}^{v}\left(\frac{\partial}{\partial \Gamma_l}\left(\frac{\partial \Phi}{\partial \Gamma_k}\right)_{\Gamma_k', \eta_\iota}\right)_{\Gamma_l', \eta_\iota} \Gamma_l = 0\,, \quad k = 1, \ldots, v\,. \tag{9}$$

If the variable Γ_m corresponds to an extensive quantity which can vanish, whereas the other variables Γ_l need not necessarily vanish, then according to (8) and (9)

$$\lim_{\Gamma_m \to 0}\left(\frac{\partial \Phi}{\partial \Gamma_m}\right)_{\Gamma_m', \eta_\iota} \Gamma_m = 0\,, \tag{10}$$

$$\lim_{\Gamma_m \to 0}\left(\frac{\partial}{\partial \Gamma_m}\left(\frac{\partial \Phi}{\partial \Gamma_k}\right)_{\Gamma_k', \eta_\iota}\right)_{\Gamma_m', \eta_\iota} \Gamma_m = 0\,, \quad k \neq m\,. \tag{11}$$

4. The Phase and its Primarily Measured Bulk Properties

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} of the substances A_J. Commonly m_{0J} can easily and very accurately be determined and hence we shall consider these quantities as primary ones. In many cases the molar masses M_J of the substances are known, thus the values of the initial amounts of substance n_{0J} can be calculated according to

$$n_{0J} = m_{0J}/M_J\,. \tag{12}$$

In such cases the information given by the set of values $\{(n_{0J})\}$ is equivalent to that given by the set $\{(m_{0J})\}$. Both of these quantities are of class $g=1$, and therefore both can be used equally well as primitive variables if the dependence of other bulk properties on the composition and amount of the phase are investigated. For convenience we shall generally use the set (n_{0J}); if desired, one or all the n_{0J} can be substituted by the corresponding m_{0J} according to (12). Commonly a set $(\vartheta_\iota) = (T, p, \vartheta_3, \ldots, \vartheta_\varepsilon)$ of intensive bulk quantities (of class $g=0$), which are usually directly measurable with appropriate instruments, is used as further primitive variables. The set $\mathrm{Q}_\mathrm{v} = (n_{0J}, \vartheta_\iota)$ of primitive variables is usually sufficient for the description of other bulk properties in any stationary state. A set $(n_{0J}, \vartheta_\iota)_\mathrm{s}$ with fixed values for all variables specifies a particular phase in a particular stationary state. Each other bulk quantity $\gamma_{hk} \in \mathrm{Q}_\mathrm{f}$ can be regarded as a function.

$$\begin{aligned}\gamma_{hk} &= \gamma_{hk}(n_{01}, \ldots, n_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon)\\ &= \gamma_{hk}(n_{0J}, \vartheta_\iota)\,,\end{aligned} \tag{13}$$

as has been discussed in section 2.

If γ_{hk} represents a quantity of class $h \neq 0$ at most $E-1$ of the set of variables n_{0J}, which belong to class $g=1$, can be replaced by other ones of class $g=0$, as can be recognized from eq. (6). If γ_{0k} is a quantity of class $h=0$, any number of the E variables n_{0J} can be replaced by variables of class $g=0$. Such variables may be generated by any set of independent functions homogeneous of zeroth degree in $n_{01}, \ldots, n_{0E}$. Commonly they are defined

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* The subscripts of a partial derivative denote the variables to be kept constant when differentiating the function, γ_{hk}' abbreviates the set of all variables of the designed kind but exclusive of the variable γ_{hk}.

by the formula

$$\psi_{0J} = \frac{n_{0J}}{\chi_J \Psi}\,, \tag{14}$$

where Ψ is some function homogeneous of first degree in $n_{01}, \ldots, n_{0E}$ and the same for all substances A_J, and χ_J is some constant possibly different for different A_J. The quantities ψ_{0J} shall be called concentration variables. A few of the usual choices are listed in table 1; $m_0 = \sum_{J=1}^{E} m_{0J}$ is the total mass, $n_0 = \sum_{J=1}^{E} n_{0J}$ the total amount of substance, and V the volume of the phase. With the values of the E concentration variables ψ_{0J} the relative composition of the phase is completely specified. One of the concentration variables may be a constant, for example $b_{01} = M_1^{-1}$ and $r_{01} = 1$, or the sum

$$\sum_{J=1}^{E} \psi_{0J} = \frac{1}{\Psi} \sum_{J=1}^{E} \chi_J^{-1} n_{0J} \tag{15}$$

may be a constant, for example $\sum_I w_{0I} = \sum_I x_{0I} = 1$, hence at most $(E-1)$ of the set of E concentration variables w_{0J} and x_{0J} are independent of each other.

If $E - E'$ of the variables n_{0J} of γ_{hk}, Eq. (13), are replaced by ψ_{0J}, the function is represented as

$$\gamma_{hk} = \gamma_{hk}(n_{01}, \ldots, n_{0E'}, \psi_{0E'+1}, \ldots, \psi_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon) = \gamma_{hk}(n_{0L}, \psi_{0G}, \vartheta_\iota)\,. \tag{16}$$

We assume the function γ_{hk} differentiable at the point $(n_{0L}, \psi_{0G}, \vartheta_\iota)$ and in some neighborhood Δn_{0L}, $\Delta \psi_{0G}$, $\Delta \vartheta_\iota$ enclosing that point, i.e. $(n_{0L} + \Delta n_{0L}, \psi_{0G} + \Delta \psi_{0G}, \vartheta_\iota + \Delta \vartheta_\iota) \in \mathrm{d_d}$, then it is true in linear order for any arbitrary variation $\Delta n_{0L}, \Delta \psi_{0G}, \Delta \vartheta_\iota$:

$$\begin{aligned}
\gamma_{hk}(n_{0L} + \Delta n_{0L}, \psi_{0G} + \Delta \psi_{0G}, \vartheta_\iota + \Delta \vartheta_\iota) &= \gamma_{hk}(n_{0L}, \psi_{0G}, \vartheta_\iota) \\
&+ \sum_{L=1}^{E'} \left[\left(\frac{\partial \gamma_{hk}}{\partial n_{0L}} \right)_{n_{0L'}, \vartheta_\iota} + \left(1 - \sum_{H=E'+1}^{E} \chi_H \psi_{0H} \Psi_{0H} \right)^{-1} \Psi_{0L} \sum_{H=E'+1}^{E} \chi_H \psi_{0H} \left(\frac{\partial \gamma_{hk}}{\partial n_{0H}} \right)_{n_{0H'}, \vartheta_\iota} \right] \Delta n_{0L} \\
&+ \Psi \sum_{G=E'+1}^{E} \chi_G \left[\left(\frac{\partial \gamma_{hk}}{\partial n_{0G}} \right)_{n_{0G'}, \vartheta_\iota} + \left(1 - \sum_{H=E'+1}^{E} \chi_H \psi_{0H} \Psi_{0H} \right)^{-1} \Psi_{0G} \sum_{H=E'+1}^{E} \chi_H \psi_{0H} \left(\frac{\partial \gamma_{hk}}{\partial n_{0H}} \right)_{n_{0H'}, \vartheta_\iota} \right] \Delta \psi_{0G} \\
&+ \sum_{\iota=1}^{\varepsilon} \left[\left(\frac{\partial \gamma_{hk}}{\partial \vartheta_\iota} \right)_{n_{0J}, \vartheta_{\iota'}} + \left(1 - \sum_{H=E'+1}^{E} \chi_H \psi_{0H} \Psi_{0H} \right)^{-1} \left(\frac{\partial \Psi}{\partial \vartheta_\iota} \right)_{n_{0J}, \vartheta_{\iota'}} \sum_{H=E'+1}^{E} \chi_H \psi_{0H} \left(\frac{\partial \gamma_{hk}}{\partial n_{0H}} \right)_{n_{0H'}, \vartheta_\iota} \right] \Delta \vartheta_\iota\,.
\end{aligned} \tag{17}$$

Ψ_{0J} is a partial molar quantity of Ψ as defined by eq. (22) with $\Phi = \Psi$. From (17) follow formulas for the transformation of the partial derivatives of the bulk quantity γ_{hk} considering it either as function with the variables n_{0J}, as shown in (13), or n_{0L} and ψ_{0G}, as shown in (16), with any E' $(1 \leqq E' < E)$. Particularly for $E' = E - 1$ it is

$$\left(\frac{\partial \gamma_{hk}}{\partial \psi_{0G}} \right)_{n_{0G'}, \vartheta_\iota} = (1 - \chi_G \psi_{0G} \Psi_{0G})^{-1} \chi_G \Psi \left(\frac{\partial \gamma_{hk}}{\partial n_{0G}} \right)_{n_{0G'}, \vartheta_\iota} \tag{18}$$

and for $E' = 1$

$$\left(\frac{\partial \gamma_{hk}}{\partial \psi_{0G}} \right)_{n_{01}, \psi_{0G'}, \vartheta_\iota} = \chi_G \Psi \left[\left(\frac{\partial \gamma_{hk}}{\partial n_{0G}} \right)_{n_{0G'}, \vartheta_\iota} - \frac{\Psi_{0G}}{\Psi_{01}} \left(\frac{\partial \gamma_{hk}}{\partial n_{01}} \right)_{n_{01'}, \vartheta_\iota} + \frac{\Psi_{0G}}{n_{01} \Psi_{01}} h \gamma_{hk} \right], \tag{19}$$

where (6) was used. The derivatives of any function γ_{hk} with respect to two different concentration variables, let us say

$$\psi_{0G}^{(1)} = n_{0G} / \chi_G^{(1)} \Psi^{(1)} \quad \text{and} \quad \psi_{0G}^{(2)} = n_{0G} / \chi_G^{(2)} \Psi^{(2)}\,,$$

are related as

$$\left(\frac{\partial \gamma_{hk}}{\partial \psi_{0G}^{(2)}} \right)_{n_{0L}, \vartheta_\iota} = \frac{(1 - \chi_G^{(1)} \psi_{0G}^{(1)} \Psi_{0G}^{(1)})\, \chi_G^{(2)} \Psi^{(2)}}{(1 - \chi_G^{(2)} \psi_{0G}^{(2)} \Psi_{0G}^{(2)})\, \chi_G^{(1)} \Psi^{(1)}} \left(\frac{\partial \gamma_{hk}}{\partial \psi_{0G}^{(1)}} \right)_{n_{0L}, \vartheta_\iota}. \tag{20}$$

In most cases, to gain knowledge of a further bulk property of a phase, either the corresponding extensive quantity Φ or its adjoint density D_Φ, defined as

$$D_\Phi = \Phi V^{-1}, \tag{21}$$

together with the mass density ϱ of the phase are directly measured with optimal accuracy. Hence we shall consider the set (Φ) or equivalently the set (D_Φ, ϱ) of such quantities together with $(n_{0J}, \vartheta_\iota)$

Table 1. Concentration variables and related quantities.

Name of quantity	ψ_{0J}	χ_J	Ψ	ψ_{01}	$\Psi_{0J}(J \neq 1)$	Ψ_{01}	m_0/Ψ	$\sum_{J=1}^{E} \psi_{0J} = \sum_{J=1}^{E} \frac{n_{0J}}{\chi_J \Psi}$
molality	b_{0J}	1	m_{01}	$M_1{}^{-1}$	0	M_1	m_0/m_{01}	n_0/m_{01}
mole ratio	r_{0J}	1	n_{01}	1	0	1	m_0/n_{01}	n_0/n_{01}
mass fraction	w_{0J}	$M_J{}^{-1}$	m_0	m_{01}/m_0	M_J	M_1	1	1
mole fraction	x_{0J}	1	n_0	n_{01}/n_0	1	1	m_0/n_0	1
concentration (density of amount of substance)	c_{0J}	1	V	n_{01}/V	V_{0J}	V_{01}	ϱ	n_0/V

as the set $\mathrm{Q_p} = (n_{0J}, \vartheta_\iota, \Phi)$ or $\mathrm{Q_p} = (n_{0J}, \vartheta_\iota, D_\Phi, \varrho)$ of primarily measured bulk quantities. The set $(n_{0J}, \vartheta_\iota, D_{\Phi 1}, D_{\Phi 2}, \ldots, \varrho)_\mathrm{s}$ with all known densities $D_{\Phi 1}, D_{\Phi 2}, \ldots$ and particular values for all those quantities is a collection of the information known about the specified phase in its specified state. The set $\mathrm{D_p} = \{(n_{0J}, \vartheta_\iota, D_{\Phi 1}, D_{\Phi 2}, \ldots, \varrho)_\mathrm{s}\}$ is the set of available data; all further evaluations are based on that set.

The main goal treated in this paper, the determination of molecular quantities from macroscopic quantities, may be reached rather easily if suitable measurements can be made on gaseous phases at sufficiently low mass density. If measurements on dense phases as liquids, for example, have to be evaluated, the situation is much more complex. Generally the desired results can be obtained easier if the investigated phases are dilute solutions of the molecules of interest in some solvent, which may consist of one or a few substances. We assume that the solvent consists of the substances $\mathrm{A}_1, \ldots, \mathrm{A}_S$, and that the initial solutes are $A_{S+1}, \ldots, A_E$. If a chemical reaction occurs, some additional substances $A_{E+1}, \ldots, A_K$ can be present in the phase. These substances and the effects caused by them can be considered only on the basis of a molecular model, and therefore they don't have to be taken into account as long as bulk quantities alone are being considered.

5. Partial Molar Quantities and Some of Their Properties

A function $\Phi (= \gamma_{1k})$ representing an extensive bulk property is homogeneous of first degree in $n_{01}, \ldots, n_{0E}$ and depends on further variables $\vartheta_1, \ldots, \vartheta_\varepsilon$, for which intensive bulk quantities can be chosen. The function Φ can be represented as a hypersurface ω_f with dimension $\mathrm{v_{min}} \leqq E + \varepsilon$ in a space spanned by the $n_{01}, \ldots, n_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon, \Phi$, which may be bound for several reasons as, for example, restricted solubility. Φ is assumed differentiable in an interval $\mathrm{d_d}$. Then at any point $(n_{0I}, \vartheta_\iota) \in \mathrm{d_d}$ the partial derivatives $(\partial \Phi / \partial n_{0J})_{n_{0J'}, \vartheta_\iota}$ exist. If two of the intensive variables ϑ_ι are the temperature T and the pressure p, such a derivative is called partial molar quantity Φ_{0J} (hereafter abbreviated as PMQ),

$$\Phi_{0J} = \left(\frac{\partial \Phi}{\partial n_{0J}} \right)_{n_{0J'}, \vartheta_\iota}, \quad \vartheta_1 = T, \quad \vartheta_2 = p, \quad J = 1, \ldots, E. \tag{22}$$

The functions Φ_{0J} are homogeneous of zeroth degree in $n_{01}, \ldots, n_{0E}$ and depend on the further variables $\vartheta_1, \ldots, \vartheta_\varepsilon$. They can be represented as a $(\mathrm{v_{min}} - 1)$-dimensional hypersurface in a space spanned by the variables $\psi_{02}, \ldots, \psi_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon, \Phi_{0J}$, for example. The PMQ Φ_{0J} is assumed differentiable at any point $(\psi_{02}, \ldots, \psi_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon) \in \mathrm{d_d}$. For the limit $n_{0J} \to \infty$ it always holds true

$$\lim_{n_{0J} \to \infty} \Phi_{0J} = \Phi^\circ_{0J}(\vartheta_\iota), \quad \text{for fixed } \vartheta_\iota, n_{0I}, I \neq J, \tag{23}$$

where $\Phi^\circ_{0J}(\vartheta_\iota)$ is the corresponding molar quantity of the pure substance A_J at specified values of the ϑ_ι's.

Due to their behavior at $n_{0J} \to 0$ the PMQ's can be partitioned into two classes of quantities. For the one class, called A, the values of Φ_{0J} are finite everywhere,

$$\lim_{n_{0J} \to 0} \Phi_{0J} = \text{finite}, \tag{24}$$

and for the other class, called B,

$$\left| \lim_{n_{0J} \to 0} \Phi_{0J} \right| = \infty, \tag{25}$$

for fixed ϑ_ι, n_{0I}, $I \neq J$, $(n_{01} \neq 0)$. For the PMQ's of class A

$$\lim_{n_{0J} \to 0} \left(\frac{\partial \Phi_{0J}}{\partial n_{0J}} \right)_{n_{0J'},\, \vartheta_\iota} = \text{finite} \tag{26}$$

or the limit does not exist

$$\left| \lim_{n_{0J} \to 0} \left(\frac{\partial \Phi_{0J}}{\partial n_{0J}} \right)_{n_{0J'},\, \vartheta_\iota} \right| = \infty \tag{27}$$

depending on the kind of substance A_J considered. The first case shall be called Aa, the second one Ab. The PMQ's of class B always satisfy eq. (27).

For the PMQ's of both classes it holds true

$$\Phi_{0J}\, n_{0J} = \text{finite, everywhere}, \tag{28}$$

$$\lim_{n_{0J} \to 0} \Phi_{0J}\, n_{0J} = 0, \tag{29}$$

$$\left(\frac{\partial \Phi_{0I}}{\partial n_{0J}} \right)_{n_{0J'},\, \vartheta_\iota} = \text{finite for } I \neq J, \text{ everywhere}, \tag{30}$$

and

$$\lim_{n_{0J} \to 0} \left(\frac{\partial \Phi_{0I}}{\partial n_{0J}} \right)_{n_{0J'},\, \vartheta_\iota} n_{0J} = 0 \quad \text{for} \quad I \neq J. \tag{31}$$

Furthermore, for quantities of class Aa

$$\lim_{n_{0J} \to 0} \left(\frac{\partial \Phi_{0J}}{\partial n_{0J}} \right)_{n_{0J'},\, \vartheta_\iota} n_{0J} = 0 \tag{32}$$

and for quantities of classes Ab and B

$$\lim_{n_{0J} \to 0} \left(\frac{\partial \Phi_{0J}}{\partial n_{0J}} \right)_{n_{0J'},\, \vartheta_\iota} n_{0J} = \text{finite}. \tag{33}$$

These facts are trivial for the PMQ's of class Aa, while for those of classes Ab and B they follow from eqs. (8) to (11). From eqs. (32) and (9), for quantities of class Aa

$$\lim_{n_0 \to n_{0I}} \left(\frac{\partial \Phi_{0J}}{\partial n_{0I}} \right)_{n_{0I'},\, \vartheta_\iota} = 0, \tag{34}$$

but, for a phase containing three or more substances, this derivative does not necessarily vanish for $n_{0J} \to 0$.

In case of a solution of the substances $A_{S+1}, \ldots, A_E$ in a mixed solvent generated from the substances $A_1, \ldots, A_S$, the definition of an average PMQ $\Phi_{0\mathrm{m}}^{(S)}$ of the solvent can be advantageous,

$$\Phi_{0\mathrm{m}}^{(S)} = \frac{1}{n_0^*} \sum_{L=1}^{S} \Phi_{0L}\, n_{0L}, \tag{35}$$

where

$$n_0^* = \sum_{L=1}^{S} n_{0L}. \tag{36}$$

Any quantity with a star as a superscript is the limit of this quantity for the pure mixed solvent, i.e. for $n_{0H} \to 0$, $H = S+1, \ldots, E$, with fixed values of n_{0L}, $L = 1, \ldots, S$, and ϑ_ι, $\iota = 1, \ldots, \varepsilon$, whenever this limit exists, or with any quantity γ_{hk} owning this property

$$\begin{aligned} \gamma_{hk}^* &= \gamma_{hk}^*(n_{01}, \ldots, n_{0S}, \vartheta_1, \ldots, \vartheta_\varepsilon) \\ &= \lim_{n_0 \to n_0^*} \gamma_{hk}(n_{01}, \ldots, n_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon), \\ &\quad\; n_{0L},\ L = 1, \ldots, S, \ \text{and} \ \vartheta_\iota, \\ &\quad\; \iota = 1, \ldots, \varepsilon, \ \text{fixed}. \end{aligned} \tag{37}$$

For a solvent consisting of only a single substance, let us say A_1, such a limit is equivalent to the limit for the pure solvent, i.e. for $n_0 \to n_{01}$. Any substance A_J, for which the mole ratio n_{0J}/n_{01} has a fixed value in a set of data, may be considered as a component of the solvent in the above sense or as a solute and therefore, in such a particular case, J can be included in one of the sets $1, \ldots, S$ (solvent) or $S+1, \ldots, E$ (solute), whatever is more convenient.

Another limit is denoted with a cross as a superscript; it is defined as

$$\begin{aligned} \gamma_{hk(G)}^{+} &= \gamma_{hk(G)}^{+}(n_{01}, \ldots, n_{0E-1}, \vartheta_1, \ldots, \vartheta_\varepsilon) \\ &= \lim_{n_{0G} \to 0} \gamma_{hk}(n_{01}, \ldots, n_{0E-1}, n_{0G}, \vartheta_1, \ldots, \vartheta_\varepsilon) \\ &\quad\; n_{0L},\ L = 1, \ldots, E-1, \ \text{and} \ \vartheta_\iota, \\ &\quad\; \iota = 1, \ldots, \varepsilon, \ \text{fixed}, \end{aligned} \tag{38}$$

that is $\gamma_{hk(G)}^{+}$ is the limit of γ_{hk} for vanishing concentration of one of the substances, the subscript in brackets indicates the vanishing kind of substance, i.e. A_G in (38). If in (37) it is chosen $S = E-1$ and $E = G$, both limits are identical, i.e. $\gamma_{hk(G)}^{+} = \gamma_{hk}^*$ in that particular case.

For the average PMQ $\Phi_{0\mathrm{m}}^{(S)}$ there is according to (9) a relation similar to (34), namely

$$\begin{aligned} \left(\frac{\partial \Phi_{0\mathrm{m}}^{(S)}}{\partial n_{0G}} \right)^{*}_{n_{0G'},\, \vartheta_\iota} &= \frac{1}{n_0^*} \sum_{L=1}^{S} n_{0L} \left(\frac{\partial \Phi_{0L}}{\partial n_{0G}} \right)^{*}_{n_{0G'},\, \vartheta_\iota} = 0, \\ G &= S+1, \ldots, E. \end{aligned} \tag{39}$$

Any PMQ can be represented as

$$\Phi_{0J} = \Phi^*_{0J} + R_{\Phi J}\,, \tag{40}$$

where for PMQ's of class A of the solutes $A_{S+1}, \ldots, A_E$,

$$\Phi^*_{0G} = \lim_{n_0 \to n_0^*} \Phi_{0G}\,,$$
$$G = S+1, \ldots, E\,(\Phi_{0G} \text{ of class A})\,, \tag{41}$$

hence $\lim\limits_{n_0 \to n_0^*} R_{\Phi G} = 0$, and for PMQ's of class B

$$\Phi^*_{0G} = \lim_{n_0 \to n_0^*} (\Phi_{0G} - R_{\Phi G})\,,$$
$$G = S+1, \ldots, E\,(\Phi_{0G} \text{ of class B})\,, \tag{42}$$

with $\left|\lim\limits_{n_0 \to n_0^*} R_{\Phi J}\right| = \infty$, so that the values Φ^*_{0G} are finite for PMQ's of class A as well as of class B. If the solvent consists of only a single substance A_1 it is

$$\Phi^*_{01} = \Phi^{\circ}_{01} \quad (\Phi_{01} \text{ of class A or B})\,. \tag{43}$$

For a mixed solvent the limit $\Phi^{(S)*}_{0\mathrm{m}}$ of the average PMQ $\Phi^{(S)}_{0\mathrm{m}}$, as defined by (35), may be used instead of Φ°_{01}, i.e. $\Phi^{(S)}_{0\mathrm{m}} = \Phi^{(S)*}_{0\mathrm{m}} + R_{\Phi\mathrm{m}}$ instead of (40). The limits Φ^*_{0J} are naturally independent of the concentrations of the solutes ψ_{0G}, $G = S+1, \ldots, E$, but their value can be different for different solvents or solvents with different composition. The quantities $R_{\Phi J}$ can be considered as functions of the variables $\psi_{0S+1}, \ldots, \psi_{0E}, \vartheta_1, \ldots, \vartheta_\varepsilon$; their values are different for different solvents. They have to satisfy (24) to (34), respectively.

Assuming a PMQ Φ_{0J} of class Aa differentiable everywhere, the corresponding quantity $R_{\Phi J}$ can be expanded in a series in $\psi_{0S+1}, \ldots, \psi_{0E}$,

$$R_{\Phi J} = \sum_{\alpha_{S+1}=0}^{\infty} \cdots \sum_{\alpha_E=0}^{\infty} \Lambda_{\psi\Phi J\alpha_{S+1}\ldots\alpha_E}\, \psi_{0S+1}^{\alpha_{S+1}} \cdots \psi_{0E}^{\alpha_E}\,,$$
$$J = \mathrm{m}\,(\text{or } 1)\,, \quad S+1, \ldots, E$$
$$(\Phi_{0J} \text{ of class Aa})\,, \tag{44}$$

where the coefficients $\Lambda_{\psi\Phi J\alpha_{S+1}\ldots\alpha_E}$ are independent of the composition of the phase, but their values can be different for different solvents. Because of (41) it is $\Lambda_{\psi\Phi J00\ldots0} = 0$ and from (39) it follows

$$\Lambda_{\psi\Phi\mathrm{m}\alpha_{S+1}\ldots\alpha_E} = 0\,, \quad \text{if} \sum_{G=S+1}^{E} \alpha_G < 2\,. \tag{45}$$

Since (9), (31), (32) and (39) have to be satisfied, there exist relations between the coefficients $\Lambda_{\psi\Phi J\alpha_{S+1}\ldots\alpha_E} \ldots \alpha_E$, $J = \mathrm{m}\,(\text{or } 1)$, $S+1, \ldots, E$.

With fixed values of $E-1$ variables n_{0L} (or n_{0L}/n_{01}), $L = 1, \ldots, E-1$, and $E = G$, the quantities $R_{\Phi J}$ depend on just one variable ψ_{0G}, the concentration of the solute A_G. For quantites of class Aa the expansion, eq. (44), can be simplified to

$$R_{\Phi J} = R^+_{\Phi J(G)} + \sum_{\alpha_G=1}^{\infty} \Lambda^+_{\psi\Phi J(G)\alpha_G}\, \psi_{0G}^{\alpha_G}\,, \tag{46}$$
$$J = \mathrm{m}\,(\text{or } 1)\,, \quad S+1, \ldots, E-1\,, G$$
$$(\Phi_{0J} \text{ of class Aa})\,,$$

where $R^+_{\Phi I(G)}$, $I = S+1, \ldots, E-1$, G, and $R^+_{\Phi\mathrm{m}(G)}$ are defined by

$$\Phi^+_{0I(G)} = \Phi^*_{0I} + R^+_{\Phi I(G)}\,,$$
$$I = S+1, \ldots, E-1\,,\ G\,, \tag{47}$$

$$\Phi^{(S)*}_{0\mathrm{m}(G)} = \Phi^{(S)*}_{0\mathrm{m}} + R^+_{\Phi\mathrm{m}(G)}\,. \tag{48}$$

For similar expansions with the variable n_{0G} the coefficients in (46) have to be replaced by $\Lambda^+_{n\Phi J(G)\alpha_G}$. Since $(\partial^{\alpha_G}\Phi_{0\mathrm{m}}/\partial\psi_{0G}^{\alpha_G})^+_{\vartheta_\iota(G)} = \alpha_G!\,\Lambda^+_{\psi\Phi J(G)\alpha_G}$, repeated application of (18) leads to relations between the different sets of coefficients. The first few are:

$$\Lambda^+_{n\Phi J(G)1} = (\chi_G \Psi^+)^{-1} \Lambda^+_{\psi\Phi J(G)1}\,, \tag{49}$$

$$\Lambda^+_{n\Phi J(G)2} \tag{50}$$
$$= (\chi_G \Psi^+)^{-2} (\Lambda^+_{\psi\Phi J(G)2} - 2\chi_G \Psi^+_{0G} \Lambda^+_{\psi\Phi J(G)1})\,,$$

$$\Lambda^+_{n\Phi J(G)3} \tag{51}$$
$$\begin{aligned} = (\chi_G \Psi^+)^{-3} \{&\Lambda^+_{\psi\Phi J(G)3} - 6\chi_G \Psi^+_{0G} \Lambda^+_{\psi\Phi J(G)2} \\ &+ 3\,[2\,(\chi_G \Psi^+_{0G})^2 \\ &- \chi_G \Lambda^+_{\psi\Psi J(G)1}]\, \Lambda^+_{\psi\Phi J(G)1}\}\,, \end{aligned}$$

where particularly $\Lambda^+_{\psi\Phi\mathrm{m}(G)1} = 0$.

In dilute solutions, the first few terms of the expansions (44) or (46), respectively, are usually sufficient, at least if no chemical reactions occur. At larger concentrations or when chemical reactions happen, the expansion can become very long and possibly cannot be applied any more.

For PMQ's of class B the function $R_{\Phi J}$ can be represented by

$$R_{\Phi J} = B_{\Phi J} \ln (\psi_{0J}/\psi^{\ominus}) + C_{\Phi J}\,, \tag{52}$$
$$J = \mathrm{m}\,(\text{or } 1)\,, \quad S+1, \ldots, E\,,$$
$$(\Phi_{0J} \text{ of class B})\,,$$

where $B_{\Phi J}$ is a quantity independent of the composition of the phase, $\psi^{\ominus}$ is some standard quantity with an arbitrary value and a unit equal to that one of ψ_{0J}. The function $C_{\Phi J} = C_{\Phi J}(\psi_{0I}, \vartheta_\iota)$ is restricted by the requirements according to eqs. (28) to (31) and (33).

6. The Determination of Partial Molar Quantities

The fundamental equation for the determination of a PMQ Φ_{0G} is the definition, eq. (22), or, after substitution of a concentration variable ψ_{0G} for n_{0G} according to eq. (18),

$$\Phi_{0G} = \frac{1 - \chi_G \psi_{0G} \Psi_{0G}}{\chi_G \Psi} \left(\frac{\partial \Phi}{\partial \psi_{0G}} \right)_{n_{0L}, \vartheta_\iota}. \tag{53}$$

Equations (22) or (53) could be used for the estimation of Φ_{0G}, if the extensive quantity Φ can be determined. For the evaluation according to the former equation a set of data $\{(n_{0G}, \Phi)_s\}$ is necessary, to the latter one a set $\{(\psi_{0G}, \Phi)_s\}$, with fixed values of n_{0J}, $J \neq G$, $J = 1, \ldots, E$, and ϑ_ι, $\iota = 1, \ldots, \varepsilon$, and various values of n_{0G} or ψ_{0G}, respectively.

For many bulk properties there are no experimental devices in use to measure the corresponding extensive quantity Φ but rather others, measuring the density D_Φ adjoint to Φ, as defined by (21). For other bulk properties the quantities D_Φ are measurable more easily and with less error than the adjoint Φ. In all such cases it is preferable to obtain the PMQ's Φ_{0J} by evaluation of sets $\{(n_{0J}, D_\Phi)_s\}$ of values of D_Φ for varying composition of the phase. According to the definition of D_Φ, (21), the PMQ's Φ_{0J} are given by

$$\Phi_{0J} = V \left(\frac{\partial D_\Phi}{\partial n_{0J}} \right)_{n_{0J'}, \vartheta_\iota} + D_\Phi V_{0J}. \tag{54}$$

From (54) it can be recognized that for the determination of Φ_{0J} by this method not only some sets $\{(n_{0J}, D_\Phi)_s\}$ with varying n_{0J} and fixed n_{0I}, $I \neq J$, are necessary but also some sets of values $\{(n_{0J}, V)_s\}$ measured under similar conditions. Usually the measurement of the mass density ϱ is much easier and more accurate than that of V, especially if modern equipment is used. In this case one introduces $V = \varrho^{-1} m_0$ into eq. (54), so that after substitution of ψ_{0G} for n_{0G} it follows

$$\Phi_{0G} = \frac{(1 - \chi_G \psi_{0G} \Psi_{0G}) m_0}{\chi_G \Psi} \left(\frac{\partial D_\Phi \varrho^{-1}}{\partial \psi_{0G}} \right)_{n_{0L}, \vartheta_\iota} + D_\Phi \varrho^{-1} M_G. \tag{55}$$

Equations (22) and (53) to (55) allow the estimation of Φ_{0G} if an appropriate set of data D_p is available. For that purpose the number of data and their accuracy must be large enough, to that the derivatives with respect to n_{0G} or ψ_{0G} can be determined with an adequately small error. The quantity $(R_{\Phi G} - R^+_{\Phi G(G)})$ corresponding to a PMQ of class Aa as defined by (40), (41) and (47) is in sufficiently dilute solutions necessarily small compared to the limit $\Phi^+_{0G(G)}$ of the PMQ, whenever this quantity is different from zero. Therefore measurements in such solutions should allow a reliable estimation of $\Phi^+_{0G(G)}$, which can be used for the determination of molecular quantities, as will be discussed in the next section. The values of any extensive quantity Φ, density D_Φ or of ϱ^{-1} measured in sufficiently dilute solutions show a linear dependence as well on n_{0G} as on any commonly used ψ_{0G} for fixed values of n_{0L}, $L \neq G$, and ϑ_ι. Hence it seems easy to estimate the limits $(\partial D_\Phi / \partial \psi_{0G})^+_{\vartheta_\iota (G)}$, $(\partial \varrho^{-1} / \partial \psi_{0G})^+_{\vartheta_\iota (G)}$, $(\partial D_\Phi \varrho^{-1} / \partial \psi_{0G})^+_{\vartheta_\iota (G)}$ or similar ones and calculate the limits $\Phi^+_{0G(G)}$ with these values and the appropriate equations. If there is an exact linear relation between a quantity X ($X = \Phi$, D_Φ, ϱ^{-1}, $D_\Phi \varrho^{-1}$, for example) and a particular one of the concentration variables, let us say $\psi^{(1)}_{0G}$, then generally with another one $\psi^{(2)}_{0G}$ the relation cannot be strictly linear as can be recognized from (20). Due to the unavoidable errors of measurements the non-linear contributions cannot be recognized from data obtained with sufficiently dilute solutions. A linear regression leads to an estimator for the limit of the derivative, its deviation from the true value depends not only on the statistical errors of individual data but also on the non-linear contributions. Consequently, the evaluation of data can be based on any one of the Eqs. (22), (53), (54) or (55), each evaluation leads to a particular estimator of $\Phi^+_{0G(G)}$, whose deviation from the true value can be larger than its statistical error. Hence, for a reliable evaluation of data, especially for the estimation of the limit $\Phi^+_{0G(G)}$ these equations are not so well suited as the following ones.

Using the average PMQ $\Phi^{(S)}_{0\mathrm{m}}$ of the solvent as defined by (35), any extensive bulk quantity Φ can be represented according to (8) as

$$\Phi = \frac{D_\Phi m_0}{\varrho} = \Phi^{(S)}_{0\mathrm{m}} n^*_0 + \sum_{G=S+1}^{E} \Phi_{0G} n_{0G}. \tag{56}$$

We can define a generalized density $\mathsf{P}_{\psi\Phi}$ as

$$\mathsf{P}_{\psi\Phi} = \Phi / \Psi, \tag{57}$$

where Ψ is any extensive quantity wherefore we commonly choose the same one as used for the definition of the concentration variables ψ_{0G}, Equation (14)*. It is

$$\mathsf{P}_{\psi\Phi} = \frac{D_\Phi m_0}{\varrho \Psi} = \Phi_{0\mathrm{m}}^{(S)} \frac{n_0^*}{\Psi} + \sum_{G=S+1}^{E} \chi_G \Phi_{0G} \psi_{0G}, \quad (58)$$

or, after introducing an average $\chi_{\mathrm{m}}^{(S)}$ of the χ_L's of the solvent,

$$\chi_{\mathrm{m}}^{(S)} = n_0^* \Big/ \sum_{L=1}^{S} \frac{n_{0L}}{\chi_L}, \quad (59)$$

and (15)

$$\mathsf{P}_{\psi\Phi} = \chi_{\mathrm{m}}^{(S)} \Phi_{0\mathrm{m}}^{(S)} \sum_{J=1}^{E} \frac{n_{0J}}{\chi_J \Psi} + \sum_{G=S+1}^{E} (\chi_G \Phi_{0G} - \chi_{\mathrm{m}}^{(S)} \Phi_{0\mathrm{m}}^{(S)}) \psi_{0G}. \quad (60)$$

For the determination of the limit $\Phi_{0G(G)}^{+}$ of the PMQ we choose $S = E - 1$ and $E = G$ in (56) to (60). Introduction of (40) and (46) to (48) leads to

$$\Phi = \Phi_{0\mathrm{m}(G)}^{(E-1)^+} n_{0(G)}^{+} + \Phi_{0G(G)}^{+} n_{0G} + (\Lambda_{n\Phi G(G)1}^{+} + \Lambda_{n\Phi\mathrm{m}(G)2}^{+} n_{0(G)}^{+}) n_{0G}^{2}$$
$$+ (\Lambda_{n\Phi G(G)2}^{+} + \Lambda_{n\Phi\mathrm{m}(G)3}^{+} n_{0(G)}^{+}) n_{0G}^{3} + \cdots, \quad (61)$$

$$\mathsf{P}_{\psi\Phi} = \Phi_{0\mathrm{m}(G)}^{(E-1)^+} \frac{n_{0(G)}^{+}}{\Psi} + \chi_G \Phi_{0G(G)}^{+} \psi_{0G} + \left(\chi_G \Lambda_{\psi\Phi G(G)1}^{+} + \Lambda_{\psi\Phi\mathrm{m}(G)2}^{+} \frac{n_{0(G)}^{+}}{\Psi}\right) \psi_{0G}^{2}$$
$$+ \left(\chi_G \Lambda_{\psi\Phi G(G)2}^{+} + \Lambda_{\psi\Phi\mathrm{m}(G)3}^{+} \frac{n_{0(G)}^{+}}{\Psi}\right) \psi_{0G}^{3} + \cdots, \quad (62)$$

$$\mathsf{P}_{\psi\Phi} = \chi_{\mathrm{m}}^{(E-1)} \Phi_{0\mathrm{m}(G)}^{(E-1)^+} \sum_{J=1}^{E} \frac{n_{0J}}{\chi_J \Psi} + (\chi_G \Phi_{0G(G)}^{+} - \chi_{\mathrm{m}}^{(E-1)} \Phi_{0\mathrm{m}(G)}^{(E-1)^+}) \psi_{0G}$$
$$+ \left(\chi_G \Lambda_{\psi\Phi G(G)1}^{+} + \chi_{\mathrm{m}}^{(E-1)} \Lambda_{\psi\Phi\mathrm{m}(G)2}^{+} \sum_{J=1}^{E} \frac{n_{0J}}{\chi_J \Psi}\right) \psi_{0G}^{2}$$
$$+ \left[\chi_G \Lambda_{\psi\Phi G(G)2}^{+} + \chi_{\mathrm{m}}^{(E-1)} \left(\Lambda_{\psi\Phi\mathrm{m}(G)3}^{+} \sum_{J=1}^{E} \frac{n_{0J}}{\chi_J \Psi} - \Lambda_{\psi\Phi\mathrm{m}(G)2}^{+}\right)\right] \psi_{0G}^{3} + \cdots, \quad (63)$$

where

$$\Phi_{0\mathrm{m}(G)}^{(E-1)^+} n_{0(G)}^{+} = (D_{\Phi(G)}^{+} m_{0(G)}^{+} / \varrho_{(G)}^{+}) \quad (64)$$

and

$$\Phi_{0\mathrm{m}(G)}^{(E-1)^+} \frac{n_{0(G)}^{+}}{\Psi_{(G)}^{+}} = \chi_{\mathrm{m}}^{(E-1)} \Phi_{0\mathrm{m}(G)}^{(E-1)^+} \left(\sum_{J=1}^{E} \frac{n_{0J}}{\chi_J \Psi}\right)_{(G)}^{+} = \frac{D_{\Phi(G)}^{+} m_{0(G)}^{+}}{\varrho_{(G)}^{+} \Psi_{(G)}^{+}}. \quad (65)$$

If a set of data $\mathrm{D_p} = \{(n_{0G}, \Phi)_\mathrm{s}\}$ or $\mathrm{D_p} = \{(n_{0G}, m_0, \varrho, D_\Phi)_\mathrm{s}\}$ with fixed values of n_{0J}, $J = 1, \ldots, E$, $J \neq G$ and ϑ_ι, $\iota = 1, \ldots, \varepsilon$, is available, the further evaluation can be based on (61). With a multiple regression analysis the number of coefficients significantly different from zero can be determined (F- and t-test, for example). If only the linear term is significantly different from zero, linear regression leads to an estimator for $\Phi_{0G(G)}^{+}$ and the information that within the given errors of data all other coefficients are zero. With a set of data $\mathrm{D_p} = \{(\psi_{0G}, m_0, \varrho, D_\Phi)_\mathrm{s}\}$ a similar multiple regression analysis is possible, based on (62) or (63). A proper evaluation according to (62) is possible only with such concentration variables ψ_{0G}, where the corresponding Ψ, Eq. (14), is independent of ψ_{0G}, i.e. $\psi_{0G} = r_{0G}$ or $\psi_{0G} = b_{0G}$, for example. Analogously, for a proper evaluation according to (63) it is necessary that $\sum_{J=1}^{E} n_{0J}/\chi_J \Psi$ is independent of ψ_{0G}, as is the case if either the concentration variable $\psi_{0G} = w_{0G}$ or $\psi_{0G} = x_{0G}$ is chosen (compare Table 1).

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* For a few special choices of Ψ the generalized densities $\mathsf{P}_{\psi\Phi}$ are well-known quantities: For $\Psi = V$ follows $\psi_{0J} = c_{0J}$ and $\mathsf{P}_{c\Phi} = D_\Phi$ is the common density adjoint to Φ; for $\Psi = m_0$ follows $\psi_{0J} = w_{0J}$ and $\mathsf{P}_{w\Phi}$ is the specific quantity adjoint to Φ; for $\Psi = n_0$ follows $\psi_{0J} = x_{0J}$ and $\mathsf{P}_{x\Phi}$ is the average PMQ $\Phi_{0\mathrm{m}}^{(E)}$ adjoint to Φ (Eq. (35) with $S = E$).

If with the given set of data there is one term or are more terms beside the linear term significantly different from zero, the corresponding coefficients in eqs. (61) to (63), respectively, can be estimated, i.e. the limits

$$(\partial \Phi_{0G}/\partial \psi_{0G})^{+}_{\vartheta_\iota(G)}, \ldots, (\partial^n \Phi_{0G}/\partial \psi^n_{0G})^{+}_{\vartheta_\iota(G)}$$

of higher order derivatives of Φ. In solutions with more than one solute, these derivatives as well as the quantity $\Phi^{+}_{0G(G)}$ are functions of the concentrations ψ_{0H} of all other solutes. From the dependence of $\Phi^{+}_{0G(G)}$ and the derivatives on those variables some further knowledge can be gained, for example, about chemical reactions which may occur in this phase.

Estimators for the quantities

$$\Phi_{0G}, \ \Phi^{+}_{0G(G)}, \ldots, (\partial^n \Phi_{0G}/\partial \psi^n_{0G})^{+}_{\vartheta_\iota(G)}$$

of the solute molecules can be obtained from the experimental data of phases meeting a very few requirements listed in Sect. 1 without introducing any further model or any additional assumption. From such data the average PMQ's $\Phi^{(S)}_{0\mathrm{m}}$ of the solvent can be calculated according to

$$\Phi^{(S)}_{0\mathrm{m}} = \frac{D_\Phi m_0}{\varrho n_0^*} - \frac{1}{n_0^*} \sum_{G=S+1}^{E} \Phi_{0G} n_{0G}. \tag{66}$$

Analogous equations hold for the limits $\Phi^{(S)*}_{0\mathrm{m}}$ and $\Phi^{(S)+}_{0\mathrm{m}(G)}$. All further information which one wishes to gain from the measurements, especially such relating to some molecular behavior, have to be based on a model usually founded on theory. We will consider the problems for phases without a chemical reaction in the following sections and for phases with chemical reactions in paper IV of this series [1]).

7. The Model Molar Quantities

The validity of (8) and (56) is based on the requirement (1) of Section 1. According to this requirement, the value Φ of an extensive quantity of the total system, which is the considered phase, is equal to the sum of the values $\Phi^{(k)}$ of partial systems. To guarantee the validity of requirement (1) and hence of (8), the partial systems into which the total system may be decomposed, have to be sufficiently large, that the contributions to the quantity Φ due to interactions between molecules in different partial systems are negligible. According to (8) and (22), a PMQ Φ_{0J} may be interpreted as the average contribution of the molecules of the initial substance A_J (per unit of amount of substance) to the quantity Φ, but the Φ_{0J} are defined only for sufficiently large phases. The interactions between the molecules in the phase contribute also to Φ and this causes the dependence of Φ_{0J} on the composition on the phase. The contribution to Φ, due to the interactions between all molecules, is partitioned onto the PMQ's Φ_{0J}, assigned to the initial substances A_J, in a rather special way as specified by the definition of the Φ_{0J} by (22).

A theoretical calculation of any macroscopic quantity is usually founded on a molecular model. For extensive quantities one generally assumes that Φ may be represented as the sum of the contributions π_k, due to each molecule k contained in the phase, or as the sum of the contributions, due to all the species A_J contained in the phase. The contribution due to one species can be represented as the product of the number N_J of particles of the species A_J and of the average $\overline{\pi_J}$ of the contribution of one molecule A_J to the quantity Φ. Hence

$$\Phi = \sum_k \pi_k = \sum_{J=1}^{K} \overline{\pi_J} N_J. \tag{67}$$

Using the average molecular quantity $\overline{\pi_J}$, a molar quantity φ_J can be defined by

$$\varphi_J = N_\mathrm{A} \overline{\pi_J}, \tag{68}$$

where N_A is the Avogadro constant. The quantity φ_J shall be called model molar quantity (MMQ) of the substance A_J to distinguish it from the PMQ Φ_{0J} as introduced by (22). From (67) and (68) it follows

$$\Phi = \sum_{J=1}^{K} \varphi_J n_J, \tag{69}$$

where

$$n_J = N_J/N_\mathrm{A} \tag{70}$$

is the amount of substance of the species A_J present in the phase. Using the quantities n_J, concentrations

$$\psi_J = n_J/\chi_J \Psi \tag{71}$$

can be defined similar to those in (14)*. The

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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. Then $\sum_{J=1}^{K} x_J = \sum_{I=1}^{K} n_I \Big/ \sum_{I=1}^{E} n_{0I}$, which is not necessarily equal to one.

density D_Φ adjoint to Φ can be represented using the MMQ's φ_J by

$$D_\Phi = V^{-1}\Psi \sum_{J=1}^{K} \chi_J \varphi_J \psi_J = \sum_{J=1}^{K} \varphi_J c_J\,, \tag{72}$$

where $c_J = n_J/V$.

Whereas in the sum in eq. (8) only the initial substances A_J composing the phase ($J = 1, \ldots, E$) are included, the sums in eqs. (67), (69) and (72) have to be extended over all species A_J actually present in the considered phase ($J = 1, \ldots, K$). If no chemical reactions occur in the mixture of initial substances, then usually $K = E$; otherwise usually $K \geqq E$.

The quantities $\overline{\pi_J}$ are average values of the corresponding molecular quantities π_k contributing to the bulk quantity Φ. In a gaseous phase at sufficiently low density the quantities π_k are those of the individual isolated molecules; in a dense phase they usually have to be modified to take into account the effects due to the interactions with surrounding molecules. The influence of neighboring molecules on a molecular quantity can be treated on the basis of a suitable model usually employing a quantum mechanical perturbation method and/or a classical electrostatic model. The contributions caused by the intermolecular interactions to the macroscopic quantity Φ are partitioned onto the quantities $\overline{\pi_J}$, assigned to the individual species, in a peculiar way determined by the model used for the theoretical treatment. The partitioning of the contributions due to intermolecular interactions onto the average molecular quantities $\overline{\pi_J}$ and hence also onto the MMQ's φ_J is usually different from the partitioning onto the PMQ's Φ_{0J} even in phases without chemical reactions ($K = E$). Therefore generally $\varphi_J \neq \Phi_{0J}$.

The PMQ Φ_{0J} can be determined experimentally from the dependence of Φ or an equivalent quantity on the composition of the phase as has been discussed in Section 6. With the knowledge of all quantities of interest, Φ_{0J}, in dependence on all corresponding primitive variables, the system is in the space of those variables completely described. The aim of some research is usually not restricted to the knowledge of these quantities but one wants to obtain an understanding of the system, that is an interpretation of the properties based on a molecular model. To reach this aim one has to obtain a quantitative knowledge not only of the amounts of the initial substances used to generate the system, but of the amounts of all species existing in the different phases of the system. Hence, if chemical reactions occur in the system, they all have to be quantitatively analyzed. Furthermore the MMQ's φ_J (or equivalently the average molecular quantities $\overline{\pi_J}$) should be determined and, if possible, also the values of the molecular quantities π_k, assigned to individual molecules. The determination of the values φ_J will be treated in the next section for a phase without a chemical reaction; in the fourth paper of this series the method is extended for a phase where chemical reactions occur [1]. The values of the quantities φ_J, $\overline{\pi_J}$ and π_k are always dependent on the molecular model used for the evaluation of data, but the values of the PMQ's Φ_{0J} are independent of any molecular model. Hence, in papers on experimental research the values of Φ_{0J} (or equivalent quantities) should be reported also, so that a treatment of the data on the basis of some other molecular model is still possible at any later time.

8. The Relations Between Partial Molar Quantities (PMQ's) and Model Molar Quantities (MMQ's) for Phases Without Chemical Reactions

The molecular quantities π_k, $\overline{\pi_J}$ and the MMQ's φ_J have to be introduced on the basis of a theoretical model. According to such a model they usually will depend on some variables $\alpha_1, \ldots, \alpha_\varrho$, hence

$$\varphi_J = \varphi_J(\alpha_\varkappa)\,. \tag{73}$$

In a stationary state the variables $\alpha_\varkappa$ can usually be chosen as some quantities of class $g = 0$, examples are the permittivity, the refractive index or the average distance between two molecules. Such quantities can be represented by homogeneous functions of the zeroth degree of $n_{01}, \ldots, n_{0E}$ and of some intensive variables $\vartheta_1, \ldots, \vartheta_\varepsilon$, i.e.

$$\alpha_\varkappa = \alpha_\varkappa(n_{0I}, \vartheta_\iota)\,. \tag{74}$$

Consequently any MMQ φ_J may also be considered as a homogeneous function of zeroth degree of $n_{01}, \ldots, n_{0E}$ and of $\vartheta_1, \ldots, \vartheta_\varepsilon$, that is

$$\varphi_J = \varphi_J(n_{0I}, \vartheta_\iota)\,. \tag{75}$$

With those primitive variables it follows from (69)

$$\Phi(n_{0J} + \Delta n_{0J}, \vartheta_\iota + \Delta\vartheta_\iota) = \Phi(n_{0J}, \vartheta_\iota) + \sum_{I=1}^{E} \sum_{J=1}^{K} \left[\varphi_J \left(\frac{\partial n_J}{\partial n_{0I}} \right)_{n_{0I}', \vartheta_\iota} + n_J \left(\frac{\partial \varphi_J}{\partial n_{0I}} \right)_{n_{0I}', \vartheta_\iota} \right] \Delta n_{0I} + \sum_{\iota=1}^{\varepsilon} \sum_{J=1}^{K} \left[\varphi_J \left(\frac{\partial n_J}{\partial \vartheta_\iota} \right)_{n_{0I}, \vartheta_\iota'} + n_J \left(\frac{\partial \varphi_J}{\partial \vartheta_\iota} \right)_{n_{0I}, \vartheta_\iota'} \right] \Delta\vartheta_\iota , \tag{76}$$

which is correct in linear order for any arbitrary variation Δn_{0I} and $\Delta\vartheta_\iota$ so that

$$(n_{0I} + \Delta n_{0I}, \vartheta_\iota + \Delta\vartheta_\iota) \in \mathrm{d_d} .$$

If there is no chemical reaction and $K = E$, then $n_J = n_{0J}$, $J = 1, \ldots, E$, and from (76) follows that

$$\Phi_{0J} = \varphi_J + \sum_{I=1}^{E} n_{0I} \left(\frac{\partial \varphi_I}{\partial n_{0J}} \right)_{n_{0J}', \vartheta_\iota} . \tag{77}$$

The case where chemical reactions occur is more complicated and will be treated in the fourth paper of this series [1]. In the case without chemical reactions, the PMQ Φ_{0J} is, according to (77), a sum of two contributions. The first part is the MMQ φ_J, the quantity needed for the determination of the molecular quantities $\overline{\pi_J}$ and π_k. The second part, the sum on the right-hand side of (77), stems from the dependence of the φ_I of all substances A_I present in the phase on its composition*. This contribution vanishes if the theoretical model is so chosen that

$$(\partial\varphi_I / \partial n_{0J})_{n_{0J}', \vartheta_\iota} = (\partial\varphi_J / \partial n_{0I})_{n_{0I}', \vartheta_\iota}$$

for $I, J = 1, \ldots, E$. Only in this special case are the MMQ's φ_J, based on a true model, identical with the PMQ's Φ_{0J}.

Using the variables ψ_{0I}, as defined by (14), and (18) it follows from (77) that

$$\Phi_{0J} = \varphi_J + \frac{1 - \chi_J \psi_{0J} \Psi_{0J}}{\chi_J} \cdot \sum_{I=1}^{E} \chi_I \psi_{0I} \left(\frac{\partial \varphi_I}{\partial \psi_{0J}} \right)_{n_{0J}', \vartheta_\iota} . \tag{78}$$

The derivatives $(\partial\varphi_I / \partial\psi_{0J})_{n_{0J}', \vartheta_\iota}$ can also be represented by

$$\left(\frac{\partial \varphi_I}{\partial \psi_{0J}} \right)_{n_{0J}', \vartheta_\iota} = \sum_{\varkappa=1}^{\varrho} \left(\frac{\partial \varphi_I}{\partial \alpha_\varkappa} \right)_{\alpha_\varkappa', \vartheta_\iota} \left(\frac{\partial \alpha_\varkappa}{\partial \psi_{0J}} \right)_{n_{0J}', \vartheta_\iota} , \tag{79}$$

which is advantageously applied when the derivatives $(\partial\alpha_\varkappa / \partial\psi_{0J})_{n_{0J}', \vartheta_\iota}$ can be determined from experimental data, as is often the case.

For solutions in a mixed solvent consisting of the substances $\mathrm{A}_1, \ldots, \mathrm{A}_S$ one can introduce an average MMQ $\varphi_{\mathrm{m}}^{(S)}$ of the solvent, defined in a manner analogous to the average PMQ $\Phi_{0\mathrm{m}}^{(S)}$, Eq. (35), that is

$$\varphi_{\mathrm{m}}^{(S)} = \frac{1}{n_0^*} \sum_{L=1}^{S} \varphi_L n_{0L} . \tag{80}$$

A relation of this average MMQ to the corresponding average PMQ of the solvent follows from (77) as

$$\Phi_{\mathrm{m}}^{(S)} = \varphi_{\mathrm{m}}^{(S)} + \frac{1}{n_0^*} \sum_{L=1}^{S} \sum_{G=S+1}^{E} n_{0L} n_{0G} \cdot \left[\left(\frac{\partial \varphi_G}{\partial n_{0L}} \right)_{n_{0L}', \vartheta_\iota} - \left(\frac{\partial \varphi_L}{\partial n_{0G}} \right)_{n_{0G}', \vartheta_\iota} \right] . \tag{81}$$

According to (81) it is $\Phi_{0\mathrm{m}}^{(S)*} = \varphi_{\mathrm{m}}^{(S)*}$, where the starred quantities are defined by eq. (37). For a solvent consisting of only a single substance A_1 it follows $\Phi_{01}^* = \Phi_{01}^{\circ} = \varphi_1^*$, i.e. the limit of any MMQ of the pure solvent is equal to its corresponding molar quantity.

For solutions of a single substance A_G in a mixed solvent, the limit Φ_{0G}^* of a PMQ Φ_{0G} of class A becomes according to (78) and (80)

$$\Phi_{0G}^* = \varphi_G^* + \frac{n_0^*}{\chi_G \Psi^*} \left(\frac{\partial \varphi_{\mathrm{m}}^{(S)}}{\partial \psi_{0G}} \right)_{n_{0L}, \vartheta_\iota}^* . \tag{82}$$

The MMQ's φ_J of quantities of class Aa can be expanded in a series in $\psi_{0S+1}, \ldots, \psi_{0E}$ similar to the PMQ's Φ_{0J}, as described by (40) and (44), i.e.

$$\varphi_J = \varphi_J^* + \sum_{\alpha_{S+1}=0}^{\infty} \cdots \sum_{\alpha_E=0}^{\infty} \lambda_{\psi\varphi J \alpha_{S+1} \ldots \alpha_E} \cdot \psi_{0S+1}^{\alpha_{S+1}} \cdots \psi_{0E}^{\alpha_E} , \tag{83}$$

$$J = \mathrm{m}\,(\text{or } 1), \quad S+1, \ldots, E, \quad (\Phi_{0J} \text{ of class Aa}) .$$

Also series expansions analogous to (46) are possible with coefficients $\lambda_{\psi\varphi J(G)\alpha_G}^{+}$. In dilute solutions the

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* A particular case where the Φ_{0J}'s are related to data from permittivity measurements has been treated by Smith [3].

first few terms of such expansions are usually sufficient.

From (77), (78), (82) and (79) it can be recognized that a further evaluation of data is possible only on the basis of a suitable model which allows the representation of the MMQ's φ_I in dependence of the variables $\alpha_\varkappa$ and the calculation of the limits, e.g. $(\partial\varphi_I/\partial\alpha_\varkappa)^*_{\alpha_\varkappa', \vartheta_\iota}$. The derivatives $(\partial\alpha_\varkappa/\partial\psi_{0J})_{n_{0J}', \vartheta_\iota}$ and their limits $(\partial\alpha_\varkappa/\partial\psi_{0J})^*_{n_{0L}, \vartheta_\iota}$, for example, usually can be obtained from experimental data. Then knowing the experimental value of Φ^*_{0G}, eq. (82) together with the limit of an equation analogous to eq. (79) but $\varphi^{(S)}_{\mathrm{m}}$ substituted for φ_I can be used to determine the value of φ^*_G and also of $\bar{\pi}^*_G = \lim\limits_{n_0 \to n_0^*} \bar{\pi}_G$. Using the theoretical model again, the molecular quantity π_k may be obtained from $\bar{\pi}^*_G$.

9. Introduction of Molecular Models

9.1. The Complete Molecular Model (CMM), the Separated Molecular Model (SMM) and the Lumped Molecular Model (LMM)

We consider a phase, where the substances $A_1, \ldots, A_S$ constitute a mixed solvent and the substances $A_{S+1}, \ldots, A_G, \ldots, A_K$ are solutes. Usually the molecular model is chosen so that any MMQ $\varphi_J = \varphi_J(\psi_{02}, \ldots, \psi_{0E}, \vartheta_\iota)$ can be separated into a sum of three terms

$$\varphi_J = \varphi_{\mathrm{f}J} + \varphi_{\mathrm{s}J} + \varphi_{gJ}, \quad J = 1, \ldots, K. \qquad (84)$$

$\varphi_{\mathrm{f}J}$ is the MMQ of isolated free molecules A_J, $\varphi_{\mathrm{s}J}$ is the contribution due to the interactions between the molecules A_J and their surrounding solvent molecules $A_1, \ldots, A_S$ to the MMQ φ_J, and φ_{gJ} is the contribution due to the interactions between the molecules A_J and the solute molecules $A_{S+1}, \ldots, A_K$. Hence

$$\varphi_{\mathrm{s}J} = \varphi_{\mathrm{s}J}(\psi_{02}, \ldots, \psi_{0S}, \vartheta_\iota), \qquad (85)$$

$$\varphi_{gJ} = \varphi_{gJ}(\psi_{02}, \ldots, \psi_{0S}, \psi_{0S+1}, \ldots, \psi_{0E}, \vartheta_\iota) \qquad (86)$$

$$\text{and} \quad \lim_{n_0 \to n_0^*} \varphi_{gJ} = \varphi^*_{gJ} = 0.$$

For a gaseous phase at sufficiently low density $\varphi_{\mathrm{s}J} = \varphi_{gJ} = 0$ and consequently the MMQ's φ_J of quantities of type A, where the limits $\Phi^+_{0J(J)}$ exist, are independent of the composition of the phase, so that according to eq. (78)

$$\Phi_{0J} = \Phi^+_{0J(I)} = \varphi_{\mathrm{f}J} = \varphi_J = \varphi^+_{J(I)}, \quad I, J = 1, \ldots, E. \qquad (87)$$

Under such conditions the value of the MMQ φ_J is equal to the value of the PMQ Φ_{0J} and the determination of φ_J is reduced to the determination of Φ_{0J}.

In a dense phase, the MMQ's φ_J are influenced by the interactions between different constituents of the phase. In spite of the general interactions the molecules usually keep their individuality as is well known. Otherwise, if there are specific interactions between some molecules, new identities will be formed as electron donor-acceptor complexes, for example, and the phase has to be treated as one where chemical reactions occur (fourth paper of this series). Due to the individuality of the molecules the vibronic states of a molecule are maintained in the dense phase but more or less perturbed by interactions with the surrounding molecules. The intermolecular interactions inhibit the translational and rotational motions peculiar to free molecules and cause vibrational and torsional motions, called librations, of a molecule relative to its neighbors, i.e. displacements of the molecule as a whole from its momentary equilibrium position. The momentary equilibrium position drifts in physical space causing translational diffusion and rotational diffusion of the molecule and related phenomena.

For a solution of molecules A_G $(G = S+1, \ldots, K)$ in a solvent the molecular model used for a further treatment usually belongs to one of three types. In the first type, which shall be called complete molecular model (CMM), the extensive quantity Φ_{mod} corresponding to φ_J is calculated using an appropriate molecular model for the complete phase. From that quantity the MMQ's φ_J can be obtained by $\varphi_J = (\partial\Phi_{\mathrm{mod}}/\partial n_{0J})_{n_{0J}', \vartheta_\iota}$. Then necessarily

$$(\partial\varphi_J/\partial n_{0I})_{n_{0I}', \vartheta_\iota} = (\partial\varphi_I/\partial n_{0J})_{n_{0J}', \vartheta_\iota}$$

and therefore $\Phi_{0J} = \varphi_J$. The MMQ's φ_J obtained with such a molecular model can be compared directly with the experimental PMQ's Φ_{0J}.

In the second type, which shall be called separated molecular model (SMM), the effects of the solute molecules A_G on the MMQ's are separated into contributions of individual molecules $A_1, \ldots, A_S$, $A_{S+1}, \ldots, A_K$, that is, the quantities

$$\varphi_{gJ} \neq 0 \quad \text{for} \quad J = 1, \ldots, K, \qquad (88)$$

are calculated using an appropriate molecular model, where usually $(\partial\varphi_J/\partial n_I)_{n_I', \vartheta_\iota} \neq (\partial\varphi_I/\partial n_J)_{n_J, \vartheta_\iota'}$ and $(\partial\varphi_J/\partial\psi_{0G})^*_{n_{0G}', \vartheta_\iota} \neq 0$ for $I, J = 1, \ldots, K$. Therefore even φ_G^* can only be obtained from Φ_{0G}^*, using (82) for example, after introducing a specified model allowing the evaluation of $(\partial\varphi_{\mathrm{m}}^{(S)}/\partial\psi_{0G})_{n_{0L},\vartheta_\iota}$.

In the third type of a molecular model, which shall be called lumped molecular model (LMM), all effects due to the solvent molecules and due to the interactions between them are lumped together and all effects due to interactions under participation of a solute molecule are assigned to this solute molecule, that is one sets

$$\varphi_{gJ} = 0 \quad \text{for} \quad J = 1, \ldots, S \tag{89}$$

in eq. (84), or equivalently

$$\varphi_J = \Phi_{0J}^* \quad \text{for} \quad J = 1, \ldots, S\,. \tag{90}$$

According to eqs. (78) and (90) it becomes

$$\begin{aligned} \Phi_{0G} = \varphi_G + {} & \frac{(1 - \chi_G\,\psi_{0G}\,\Psi_{0G})}{\chi_G} \\ & \cdot \sum_{H=S+1}^{E} \chi_H\,\psi_{0H}\left(\frac{\partial\varphi_H}{\partial\psi_{0G}}\right)_{n_{0G'},\vartheta_\iota}, \\ G = S + 1, \ldots, E\,, & \end{aligned} \tag{91}$$

and therefore, when the limit of Φ_{0G} for the pure (mixed) solvent exists, it is

$$\varphi_G^* = \Phi_{0G}^*; \tag{92}$$

hence the limit φ_G^* of the MMQ determined on the basis of an LMM can be compared with the limit Φ_{0G}^* of the PMQ, which usually can rather easily be estimated from experimental data.

In the following subsections we will consider a few examples. The usage of PMQ's is well known from thermodynamics, a corresponding MMQ will be formulated and discussed for the Gibbs energy, as an example. Appropraite PMQ's, convenient for the evaluation of data obtained from permittivity, optical absorption and electro-optical absorption measurements will be defined and the connections to MMQ's will be shown. Suitable PMQ's and MMQ's corresponding to other bulk quantities can be introduced in a similar manner, as for refractometric measurements and dispersion, for the Kerr effect and Faraday effect, for measurements of NMR, ESR, circular dichroism and rotation dispersion. Some applications of these methods to concrete systems will be presented in papers II [4], III [5] and V [6] of this series, where also particular molecular models are discussed.

9.2. Model Molar Quantities for the Gibbs Energy

For the description of the Gibbs energy G, which is a quantity of class B, the chemical potential is quite commonly used. The chemical potential μ_J of a substance A_J in some phase is in many cases defined as

$$\mu_J = \left(\frac{\partial G}{\partial n_{0J}}\right)_{n_{0J'},\vartheta_\iota} = G_{0J}\,, \tag{93}$$

but in other cases also as

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{n_{J'},\vartheta_\iota}. \tag{94}$$

According to the first definition the chemical potential is identical to the PMQ G_{0J}. In systems where no chemical reactions occur, both definitions are equivalent, in systems with chemical reactions the quantity μ_J defined by (94) should rather be an MMQ. The reason is that the amounts of substance n_J actually present in the phase are not primitive variables, because they can be determined only, if all occurring chemical reactions are completely and quantitatively known. In a chemical equilibrium, necessarily [1]

$$\left(\frac{\partial G}{\partial n_J}\right)_{n_{J'},\vartheta_\iota} = \left(\frac{\partial G}{\partial n_{0J}}\right)_{n_{0J'},\vartheta_\iota}, \tag{95}$$

and therefore, under that particular condition, both definitions, (93) and (94) are equivalent and the chemical potential μ_J is identical with the PMQ G_{0J}. Naturally (95) makes sense only for such substances A_J, which can be used as pure substances to generate the considered phase. The chemical potential of other species, as of ions for example, could be defined only as by (94). Then μ_J is a particular MMQ, $\mu_J = g_J$, with the special property $(\partial g_J/\partial n_I)_{n_{I'},\vartheta_\iota} = (\partial g_I/\partial n_J)_{n_{J'},\vartheta_\iota}$ for all I, $J = 1, \ldots, K$. To avoid any misapprehension, we won't use the expression chemical potential, but rather specify a PMQ by G_{0J} and any MMQ by g_J.

The definition of the MMQ's g_J has to be based on some theoretical molecular model, allowing a representation of the Gibbs energy G of a phase as

$$G = \sum_{J=1}^{K} g_J\, n_J\,. \tag{96}$$

If it is possible to represent the Gibbs energy $G = G_{\mathrm{mod}}$ of the phase by application of a model, where all the constituents of the phase are taken into account as molecules (that is by application of a CMM), then the MMQ's $g_J = (\partial G_{\mathrm{mod}}/\partial n_{0J})_{n_{0J'},\vartheta,\iota}$ correspond to the PMQ's G_{0J}, which can be determined from experimental data. Such a CMM is applicable for a gaseous phase at sufficiently low mass density, where any MMQ g_J can be separated into three contributions,

$$g_J = g_{\mathrm{t}J} + g_{\mathrm{r}J} + g_{\mathrm{v}J}\,, \tag{97}$$

where $g_{\mathrm{t}J}$, $g_{\mathrm{r}J}$ and $g_{\mathrm{v}J}$ are due to the translational, rotational and vibronic (vibrational and electronic) degrees of freedom, respectively. According to statistical theory, for sufficiently large values of T and V

$$g_{\mathrm{t}J} = RT \ln (\theta_J n_J / V)\,, \tag{98}$$

where

$$\theta_J = \left(\frac{h^2 N_{\mathrm{A}}^2}{2\pi M_J RT}\right)^{3/2} N_{\mathrm{A}}\,, \tag{99}$$

h is the Planck constant and R the gas constant. Using (97), (98) and (77), the relation between the PMQ G_{0J} and the MMQ g_J becomes

$$G_{0J} = g_J + RT\left(1 - \frac{\sum\limits_{I=1}^{E} n_{0I} V_{0J}}{V}\right), \tag{100}$$

and hence, at sufficiently low mass density, where $V = \sum\limits_{I=1}^{E} n_{0I} V_{0J}$, the value of the PMQ is equal to the value of the MMQ.

In a dense phase a CMM is usually rather complex and therefore cannot be developed in detail. A molecular description of a homogeneous phase can be based on an SMM. If the phase is considered as a solution, the substances $\mathrm{A}_1, \ldots, \mathrm{A}_S$ constitute the solvent and the substances $\mathrm{A}_{S+1}, \ldots, \mathrm{A}_K$ are solutes. If the phase is considered as a mixture, its components are the substances $\mathrm{A}_1, \mathrm{A}_2, \ldots, \mathrm{A}_K$. n_I is the amount of the substance A_I, $N_I = n_I N_{\mathrm{A}}$ is the number of molecules, $n = \sum\limits_{I=1}^{K} n_I$ is the total amount of substance and $N = \sum\limits_{I=1}^{K} N_I$ the total number of molecules in the system.

If some molecules A_I are brought into the mixture, the interactions of each molecule A_I with its surrounding molecules will cause a change of the local structure and hence of the energy states of the system. The change of the local structure is a time dependent process, which may be separated into a few processes because their characteristic relaxation times are quite different. The introduction of a molecule A_I causes a change of the electronic distributions with a relaxation time $\tau_{\mathrm{Re}} \approx 10^{-15}$ s, it causes a change of the distribution of the nuclei of the molecules with fixed orientation and location in physical space with a relaxation time $\tau_{\mathrm{Rv}} \approx 10^{-13}$ s, it causes a change of the distribution of the molecules relative to their momentary equilibrium positions with a relaxation time $\tau_{\mathrm{Rl}} \approx 10^{-12}$ s. If the orientational distribution of the ensemble of molecules A_I brought into the mixture is anisotropic at the initial time, then there is also a time-dependent process, namely the rotational diffusion leading to an isotropic orientational distribution of the molecules A_I with a relaxation time $\tau_{\mathrm{R}\varrho}$ which is in a mixture with low viscosity at room temperature of the order 10^{-11} s and which may become arbitrarily long at sufficiently high viscosity and low temperature. If the spatial distribution of the ensemble of molecules A_I is not homogeneous at the initial time, translational diffusion is leading to a homogeneous distribution. The relaxation time $\tau_{\mathrm{R}\tau} \approx l/v_\tau$ of this process depends on the diffusion velocity v_τ and on the size of the phase (length l). For macroscopic systems usually $\tau_{\mathrm{R}\tau}$ is much larger than $\tau_{\mathrm{R}\varrho}$. In a system in contact with a temperature reservoir (heat bath) and with a sufficiently large heat conductivity, a local thermal equilibrium state is obtained at a time $t \gg \tau_{\mathrm{Rl}}$ after introducing an ensemble of molecules A_I and after a time $t \gg \tau_{\mathrm{R}\tau}$ the state of a phase without any chemical reaction is a complete thermal equilibrium state. Corresponding to the relaxation processes with different relaxation times, the internal energy U of the phase can approximately be separated into several parts

$$U = \sum_{I=1}^{K} N_I(\varepsilon_{\mathrm{ev}I} + \varepsilon_{\varrho I} + \varepsilon_{\tau I}) + U_{\mathrm{i}} + U_{\mathrm{l}}\,, \tag{101}$$

where $\varepsilon_{\mathrm{ev}I}$ is the average vibronic energy of the molecule A_I, $\varepsilon_{\varrho I}$ the average rotational energy, and $\varepsilon_{\tau I}$ the average translational energy corresponding to the drift of the momentary equilibrium position of A_I in physical space (rotational and translational diffusion, respectively). U_{i} is the interaction energy of the ensemble of molecules averaged over all fixed configurations (momentary equilibrium positions), and U_{l} is the contribution to the internal energy caused by the librations of all molecules, i.e. by the translational and torsional vibrations of the molecules as wholes. The interaction energy can be represented as

$$U_{\mathrm{i}} = \sum_{j=1}^{N} \Bigg(\tfrac{1}{2} \sum_{\substack{k=1 \\ k \neq j}}^{N} e_{jk} + \mathrm{h.o.} \Bigg), \tag{102}$$

where e_{jk} is the pair interaction energy of the molecules j and k and by h.o. are abbreviated contributions due to triple and higher interactions. Since the interaction energy between noncharged molecules decreases faster than r_{jk}^{-3}, where r_{jk} is the distance between the molecules j and k, only those molecules in a rather small neighborhood of any molecule contribute to the interaction energy. Hence

$$U_{\mathrm{i}} = \sum_{j=1}^{N} \Bigg(\tfrac{1}{2} \sum_{\substack{k=a_j \\ k \neq j}}^{a_j+N_j} e_{jk} + \mathrm{h.o.} \Bigg) = \sum_{I=1}^{K} N_I \bar{e}_I , \tag{103}$$

where N_j is the number of molecules in the neighborhood of the molecule j contributing to the interaction energy and $\bar{e}_I$ is the average interaction energy of a molecule of substance A_I averaged over all fixed configurations,

$$\bar{e}_I = \frac{1}{N_I} \sum_{j=b_j}^{b_j+N_I} \Bigg(\tfrac{1}{2} \sum_{\substack{k=a_j \\ k \neq j}}^{a_j+N_j} e_{jk} + \mathrm{h.o.} \Bigg). \tag{104}$$

The first sum in (104) has to be extended over all molecules of the substance A_I.

The librations are translational and rotational vibrations of one or more molecules in the potential energy field caused by the surrounding molecules. Hence one may assume that librations can be represented by contributions due to pair, triple and higher interactions, and therefore similarly to (102)—(104) the quantity U_{l} is represented by

$$U_{\mathrm{l}} = \sum_{j=1}^{N} \Bigg(\tfrac{1}{2} \sum_{\substack{k=1 \\ k \neq j}}^{N} l_{jk} + \mathrm{h.o.} \Bigg) = \sum_{I=1}^{K} N_I \bar{l}_I , \tag{105}$$

where $\bar{l}_I$ is the average libration energy of a molecule of substance A_I. Using (101)—(105) the MMQ $u_I^{(\mathrm{s})}$ of the internal energy becomes

$$\begin{aligned} u_I^{(\mathrm{s})} &= N_{\mathrm{A}} (\varepsilon_{\mathrm{ev}I} + \varepsilon_{\varrho I} + \varepsilon_{\tau I} + \bar{e}_I + \bar{l}_I) \\ &= u_{\mathrm{ev}I} + u_{\varrho I} + u_{\tau I} + u_{\mathrm{i}I} + u_{\mathrm{l}I} . \end{aligned} \tag{106}$$

For the MMQ $h_I^{(\mathrm{s})}$ corresponding to the enthalpy follows

$$h_I^{(\mathrm{s})} = u_I^{(\mathrm{s})} + p v_I^{(\mathrm{s})} , \tag{107}$$

where $v_I^{(\mathrm{s})}$ is the MMQ of the volume, and for the MMQ $s_I^{(\mathrm{s})}$ of the entropy

$$\begin{aligned} s_I^{(\mathrm{s})} &= s_{\mathrm{ev}I} + s_{\varrho I} + s_{\tau I} + s_{\mathrm{i}I} \\ &\quad + s_{\mathrm{l}I} + s_{\mathrm{a}I} + s_{\mathrm{o}I} , \end{aligned} \tag{108}$$

where

$$\begin{aligned} s_{\xi I}(T, p) &= s_{\xi I}(0, p) \\ &\quad + \int_0^T \frac{1}{T'} \left(\frac{\partial h_{\xi I}(T', p)}{\partial T'} \right)_{p,\, n_{\mathrm{B}}} \mathrm{d}T' , \\ \xi &= \mathrm{ev},\ \varrho,\ \tau,\ \mathrm{i},\ \mathrm{l},\ \mathrm{a}, \end{aligned} \tag{109}$$

and $h_{\mathrm{ev}I} = N_{\mathrm{A}} \varepsilon_{\mathrm{ev}I}$, $h_{\varrho I} = N_{\mathrm{A}} \varepsilon_{\varrho I}$, $h_{\tau I} = N_{\mathrm{A}} \varepsilon_{\tau I}$, $h_{\mathrm{i}I} = N_{\mathrm{A}} \bar{e}_I$, $h_{\mathrm{l}I} = N_{\mathrm{A}} \bar{l}_I$ and $h_{\mathrm{a}I} = p v_I^{(\mathrm{s})}$. The quantity $s_{\mathrm{o}I} = s_{\mathrm{o}I}\,(0, p)$ contains contributions to the entropy by any other causes at $T = 0$ K and is chosen to be independent of the composition of the phase.

The MMQ $g_I^{(\mathrm{s})}$ corresponding to the Gibbs energy can be partitioned similarly,

$$\begin{aligned} g_I^{(\mathrm{s})} = h_I^{(\mathrm{s})} - T s_I^{(\mathrm{s})} &= g_{\mathrm{ev}I} + g_{\varrho I} + g_{\tau I} \\ &\quad + g_{\mathrm{i}I} + g_{\mathrm{l}I} + g_{\mathrm{a}I} - T s_{\mathrm{o}I} \end{aligned} \tag{110}$$

where

$$\begin{aligned} g_{\xi I} &= h_{\xi I} - T s_{\xi I} , \\ \xi &= \mathrm{ev},\ \varrho,\ \tau,\ \mathrm{i},\ \mathrm{l},\ \mathrm{a} . \end{aligned} \tag{111}$$

The quantities $g_{\xi I}$ are dependent on the composition of the phase, $g_{\xi I} = g_{\xi I}(\psi_J)$. In the limit $n_0 = \sum_{J=1}^{E} n_{0J} \rightarrow n_{0I}$, the MMQ $g_I^{(\mathrm{s})}$ becomes the molar Gibbs energy g_I^{o} of the pure substance A_I,

$$\begin{aligned} \lim_{n_0 \to n_{0I}} g_I^{(\mathrm{s})} = g_I^{\mathrm{o}} &= g_{\mathrm{ev}I}^{\mathrm{o}} + g_{\varrho I}^{\mathrm{o}} + g_{\tau I}^{\mathrm{o}} \\ &\quad + g_{\mathrm{i}I}^{\mathrm{o}} + g_{\mathrm{l}I}^{\mathrm{o}} + g_{\mathrm{a}I}^{\mathrm{o}} - T s_{\mathrm{o}I} , \end{aligned} \tag{112}$$

where

$$g_{\xi I}^{\mathrm{o}} = \lim_{n_0 \to n_{0I}} g_{\xi I} . \tag{113}$$

The limit of $g_I^{(\mathrm{s})}$ for $n_I \to 0$ with fixed values for n_{0J}, $J \neq I$, or for $n_0 \to n_0^* = \sum_{L=1}^{S} n_{0L}$ (pure mixed solvent) does not exist,

$$\lim_{n_0 \to n_0^*} g_I^{(\mathrm{s})} = -\infty , \quad I = S+1, \ldots, K , \tag{114}$$

and hence the Gibbs energy G is a quantity of class B. This fact is caused by the term $g_{\tau I}$ in (110); the limit of all other terms for $n_0 \to n_0^*$ does exist,

$$\lim_{n_0 \to n_0^*} g_{\xi I} = g_{\xi I}^*, \quad \xi = \mathrm{ev}, \ \varrho, \ \mathrm{i}, \ \mathrm{l}, \ \mathrm{a}. \tag{115}$$

The quantity $g_{\tau I}$ contains the contribution to the Gibbs energy due to the different realizations of the molecular arrangements in space, which may be created from any one of the possible configurations by possible translations of all molecules of the system. It is represented as usual by

$$g_{\tau I} = g_{\mathrm{t}I} + g_{\psi I}^{(\mathrm{t})} + g_{\psi I}^{(\mathrm{r})} + RT \ln \frac{\psi_I}{\psi^\ominus}, \tag{116}$$

where $\psi^\ominus$ is a standard quantity with an arbitrary value and a unit equal to the one of ψ_I. The quantity $g_{\mathrm{t}I}$ is chosen independent of the choice of the concentration variable ψ_I and with the properties

$$\lim_{n_0 \to n_{0I}} g_{\mathrm{t}I} = g_{\tau I}^{\mathrm{o}}, \quad \lim_{n_0 \to n_0^*} g_{\mathrm{t}I} = g_{\mathrm{t}I}^*. \tag{117}$$

The quantities $g_{\psi I}^{(\mathrm{t})}$ and $g_{\psi I}^{(\mathrm{r})}$ can depend on the choice of ψ_I. If $g_{\psi I}^{(\mathrm{r})}$ is chosen so that

$$\lim_{n_0 \to n_{0I}} g_{\psi I}^{(\mathrm{r})} = 0, \tag{118}$$

then choosing $g_{\psi I}^{(\mathrm{t})}$ as a constant it follows from (116) to (118)

$$g_{\psi I}^{(\mathrm{t})} = -RT \ln \left(\frac{\psi_I^{\mathrm{o}}}{\psi^\ominus} \right), \tag{119}$$

where $\psi_I^{\mathrm{o}} = \lim\limits_{n_0 \to n_{0I}} \psi_I$, i.e. the concentration in the pure substance A_I. Introducing the quantity

$$\begin{aligned} g_{\mathrm{m}I} = g_{\mathrm{ev}I} + g_{\varrho I} + g_{\mathrm{i}I} + g_{\mathrm{l}I} \\ + g_{\mathrm{a}I} + g_{\mathrm{t}I} - T s_{\mathrm{o}I} \end{aligned} \tag{120}$$

with the limits

$$\lim_{n_0 \to n_{0I}} g_{\mathrm{m}I} = g_{\mathrm{m}I}^{\mathrm{o}} \tag{121}$$

and

$$\lim_{n_0 \to n_0^*} g_{\mathrm{m}I} = g_{\mathrm{m}I}^*, \tag{122}$$

the MMQ $g_I^{(\mathrm{s})}$ can be written

$$\begin{aligned} g_I^{(\mathrm{s})} = g_{\mathrm{m}I} - RT \ln \left(\frac{\psi_I^{\mathrm{o}}}{\psi^\ominus} \right) + g_{\psi I}^{(\mathrm{r})} \\ + RT \ln \left(\frac{\psi_I}{\psi^\ominus} \right), \end{aligned} \tag{123}$$

where all terms but the second one on the right-hand side may depend on the composition of the phase. According to (123) all choices for the concentration variable ψ_I are equivalent, each choice leads to a particular value of $g_{\psi I}^{(\mathrm{r})}$. If it is possible to distinguish one or a few of the choices as the most appropriate ones, the selection has to be based on an additional requirement. The quantity $g_{\mathrm{m}I}$ defined by (120) describes the contributions to $g_I^{(\mathrm{s})}$ caused by the molecules A_I and by all interactions between any A_I and any other molecule of the system. If a change of the solvent or of the composition of the mixture causes a change of these interactions, the value of $g_{\mathrm{m}I}$ will vary. Let us consider two solutions (phase′ and phase″) consisting of the solvent A_1 or A_2, respectively, and the solute A_I. The size of the solvent molecules shall be different, i.e. $V_1' \neq V_2''$. Let us assume that the solvents A_1 and A_2 have very similar average interactions between the solvent molecules and the solute molecule A_I and nearly equal volume densities of all properties, i.e. $\Phi'/V' = \Phi''/V''$ or equivalently $c_{01}' \Phi_{01}' = c_{02}'' \Phi_{02}''$ for all bulk quantities*. According to the model considered above one has to expect for one and the same solute A_I in the two solutions equal values of $g_I^{(\mathrm{s})}$ and of $g_{\mathrm{m}I}$ if the number density or equivalently if the density of the amount of substance c_I is equal in both phases. Hence for $c_I' = c_I'' = c_I$ it is

$$\begin{aligned} g_I^{(\mathrm{s})\prime}(c_I) = g_I^{(\mathrm{s})\prime\prime}(c_I) \quad \text{and} \\ g_{\mathrm{m}I}'(c_I) = g_{\mathrm{m}I}''(c_I). \end{aligned} \tag{124}$$

Introducing eqs. (124) into eq. (123) and choosing $\psi_I = c_I$ leads to

$$g_{cI}^{(\mathrm{r})\prime}(c_I) = g_{cI}^{(\mathrm{r})\prime\prime}(c_I). \tag{125}$$

According to the considered model all concentration dependent interaction effects are included in the quantity $g_{\mathrm{m}I}(c_I)$. Hence with the choice $\psi_I = c_I$ and in agreement with (125) the quantity $g_{cI}^{(\mathrm{r})}$ is a constant and because of (118) it follows $g_{cI}^{(\mathrm{r})} = 0$. For other choices of the concentration variable ψ_I it may be $g_{\psi I}^{(\mathrm{r})} \neq 0$.

With the considered MMQ's $g_I^{(\mathrm{s})}$ generally $(\partial g_I^{(\mathrm{s})}/\partial n_J)_{n_J', \vartheta_\iota} \neq (\partial g_J^{(\mathrm{s})}/\partial n_I)_{n_I', \vartheta_\iota}$ and hence a quantity $g_I^{(\mathrm{s})}$ cannot be compared with the corresponding

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* An example of two solvents satisfying the conditions at least approximately is ethylcyclohexane C_8H_{16} and 1,4-dicyclohexylbutane $C_{16}H_{30}$.

PMQ G_{0I}, even if there is no chemical reaction occurring in the phase. Therefore we define further MMQ's g_I by

$$g_I = g_I^{(\mathrm{s})} + \sum_{J=1}^{K} n_J \left(\frac{\partial g_J^{(\mathrm{s})}}{\partial n_I} \right)_{n_{I'}, \vartheta_\iota}, \qquad (126)$$

$$I = 1, \ldots, K .$$

Necessarily

$$(\partial g_I / \partial n_J)_{n_{J'}, \vartheta_\iota} = (\partial g_J / \partial n_I)_{n_{I'}, \vartheta_\iota}, \qquad (127)$$

whenever g_I and g_J are differentiable. If $g_I^{(\mathrm{s})}$ is based on a true model of the mixture and if there is no chemical reaction occurring in the phase, then $g_I = G_{0I}$. Hence the values of the MMQ's g_I based on any suitable model can be compared with the values of the PMQ's G_{0I}.

It is customary to describe the concentration dependence of g_I by suitable defined activities or activity coefficients. An activity coefficient $f_{\psi I}$ related to the pure substance A_I as standard state is defined by

$$g_I = g_I^{\mathrm{o}} + RT \ln \left(\frac{\psi_I f_{\psi I}}{\psi_I^{\mathrm{o}}} \right). \qquad (128)$$

Since $\lim\limits_{n_0 \to n_{0I}} g_I = g_I^{\mathrm{o}} = g_{\mathrm{m}I}^{\mathrm{o}}$ it follows from (128), if the same units are used for ψ_I and ψ_I^{o},

$$\lim_{n_0 \to n_{0I}} f_{\psi I} = 1 \qquad (129)$$

and from (123), (126) and (128)

$$RT \ln f_{\psi I} = g_{\mathrm{m}I} - g_{\mathrm{m}I}^{\mathrm{o}} + RT \ln \frac{\Psi}{V} \left(\frac{V}{\Psi} \right)^{\mathrm{o}} + \sum_{J=1}^{K} n_J \left(\frac{\partial g_{\mathrm{m}J}}{\partial n_I} \right)_{n_{I'}, \vartheta_\iota} + RT \left(1 - \frac{v_I}{v_{\mathrm{m}}} \right), \qquad (130)$$

where $v_I = (\partial V / \partial n_I)_{n_{I'}, \vartheta_\iota}$ is the model molar volume of the substance A_I and $v_{\mathrm{m}} = V \big/ \sum\limits_{J=1}^{K} n_J$ is the average model molar volume of the phase. The activity coefficients defined by (128) for different concentration variables $\psi_I^{(1)}$ and $\psi_I^{(2)}$ are related by

$$f_{\psi^{(2)} I} = \frac{\Psi^{(2)}}{\Psi^{(1)}} \left(\frac{\Psi^{(1)}}{\Psi^{(2)}} \right)^{\mathrm{o}} f_{\psi^{(1)} I} . \qquad (131)$$

An activity coefficient $\check{f}_{\psi I}$ related to the pure mixed solvent consisting of the constituents A_1, $\mathrm{A}_2, \ldots, \mathrm{A}_S$ with amounts $n_{0L} = n_{0L}^*$ and $n_0^* = \sum\limits_{L=1}^{S} n_{0L}^*$ as standard state is defined by

$$g_I = g_{\psi I}^* + RT \ln (\psi_I \check{f}_{\psi I} / \psi^\ominus) \qquad (132)$$

and

$$g_{\psi I}^* = \lim_{n_0 \to n_0^*} (g_I - RT \ln (\psi_I / \psi^\ominus)) . \qquad (133)$$

From the definitions (132) and (133) it follows

$$\lim_{n_0 \to n_0^*} \check{f}_{\psi I} = 1 \qquad (134)$$

and from (132), (133), (123) and (126)

$$g_{\psi I}^* = g_{\mathrm{m}I}^* - RT \ln \frac{\psi_I^{\mathrm{o}}}{\psi^\ominus} + RT \ln \frac{\chi_I \psi^\ominus}{c^\ominus} \left(\frac{\Psi}{V} \right)^* + \sum_{L=1}^{S} \left[n_L \left(\frac{\partial g_{\mathrm{m}L}}{\partial n_I} \right)_{n_{I'}, \vartheta_\iota} \right]^* + RT \left(1 - \frac{v_I^*}{v_{\mathrm{m}}^*} \right) \qquad (135)$$

and

$$RT \ln \check{f}_{\psi I} = g_{\mathrm{m}I} - g_{\mathrm{m}I}^* + RT \ln \frac{\chi_I \psi^\ominus \Psi}{c^\ominus V} \left(\frac{V}{\Psi} \right)^* + \sum_{J=1}^{K} n_J \left(\frac{\partial g_{\mathrm{m}J}}{\partial n_I} \right)_{n_{I'}, \vartheta_\iota} - \sum_{L=1}^{S} \left[n_L \left(\frac{\partial g_{\mathrm{m}L}}{\partial n_I} \right)_{n_{I'}, \vartheta_\iota} \right]^* + RT \left(\frac{v_I^*}{v_{\mathrm{m}}^*} - \frac{v_I}{v_{\mathrm{m}}} \right), \qquad (136)$$

where the starred quantities are as usual the limits for the pure mixed solvent ($n_0 \to n_0^*$ or equivalently $\psi_{0I} \to 0$ for fixed values of $n_{01}, \ldots, n_{0S}$) and χ_I, $\psi^\ominus$ and Ψ are those quantities as are used defining ψ_I by (71). The quantities $g_{\psi I}^*$, defined by (133), and the activity coefficients $\check{f}_{\psi I}$, defined by (132), for differently chosen concentration variables $\psi_I^{(1)}$ and $\psi_I^{(2)}$ and standard quantities $\psi^{\ominus(1)}$ and $\psi^{\ominus(2)}$ are related by

$$g_{\psi^{(2)} I}^* = g_{\psi^{(1)} I}^* + RT \ln \frac{\chi_I^{(2)} \psi^{\ominus(2)}}{\chi_I^{(1)} \psi^{\ominus(1)}} \left(\frac{\Psi^{(2)}}{\Psi^{(1)}} \right)^* \qquad (137)$$

and $$\check{f}_{\psi^{(2)} I} = \frac{\Psi^{(2)}}{\Psi^{(1)}} \left(\frac{\Psi^{(1)}}{\Psi^{(2)}} \right)^* \check{f}_{\psi^{(1)} I} . \qquad (138)$$

A relation between $f_{\psi I}$ and $\check{f}_{\psi I}$ may be obtained from (130) and (136). Equation (135) allows the calculation of the quantity $g^*_{\psi I}$ and (130) and (136) of the activity coefficients $f_{\psi I}$ and $\check{f}_{\psi I}$, respectively, of any molecule A_I in a solution or a mixture, if a suitable model is chosen for the representation of the quantities included in g_{mI} according to eq. (120). Choosing $\psi_I = c_I$ as concentration variable simplifies (130), (135) and (136) since the third term of the right-hand side of each of these equations becomes zero under this condition. A molecular model for the calculation of activity coefficients will be treated in detail and applied for some binary mixtures in paper VI of this series [9].

The above discussed model leads to MMQ's of the entropy s_I, the enthalpy h_I, the internal energy u_I and the volume v_I, where equations analogous to (127) hold true. Therefore each one of the MMQ's is equal to the corresponding PMQ, if the molecular model is a true model. The relations for the MMQ's based on (132) are

$$s_I = -\left(\frac{\partial g_I}{\partial T}\right)_{n_J,\,\vartheta_\iota'} = s^*_{\psi I} - R\ln\frac{\psi_I \check{f}_{\psi I}}{\psi^{\ominus}} + \frac{RT}{\Psi}\left(\frac{\partial \Psi}{\partial T}\right)_{n_J,\,\vartheta_\iota'} - RT\left(\frac{\partial \ln \check{f}_{\psi I}}{\partial T}\right)_{n_J,\,\vartheta_\iota'}, \tag{139}$$

$$h_I = g_I + T s_I = \left(\frac{\partial g_I/T}{\partial 1/T}\right)_{n_J,\,\vartheta_\iota'} = h^*_{\psi I} + \frac{RT^2}{\Psi}\left(\frac{\partial \Psi}{\partial T}\right)_{n_J,\,\vartheta_\iota'} - RT^2\left(\frac{\partial \ln \check{f}_{\psi I}}{\partial T}\right)_{n_J,\,\vartheta_\iota'}, \tag{140}$$

$$v_I = \left(\frac{\partial g_I}{\partial p}\right)_{n_J,\,\vartheta_\iota'} = v^*_{\psi I} - \frac{RT}{\Psi}\left(\frac{\partial \Psi}{\partial p}\right)_{n_J,\,\vartheta_\iota'} + RT\left(\frac{\partial \ln \check{f}_{\psi I}}{\partial p}\right)_{n_J,\,\vartheta_\iota'} \tag{141}$$

where

$$s^*_{\psi I} = -\left(\frac{\partial g^*_{\psi I}}{\partial T}\right)_{n_I,\,\vartheta_\iota'}, \tag{142}$$

$$h^*_{\psi I} = g^*_{\psi I} + T s^*_{\psi I} = \left(\frac{\partial g^*_{\psi I}/T}{\partial 1/T}\right)_{n_J,\,\vartheta_\iota'} \tag{143}$$

and

$$v^*_{\psi I} = \left(\frac{\partial g^*_{\psi I}}{\partial p}\right)_{n_J,\,\vartheta_\iota'}. \tag{144}$$

Similar relations may be obtained based on (128).

The values of the quantities $s^*_{\psi I}$, $h^*_{\psi I}$ and $v^*_{\psi I}$, commonly called standard MMQ's, defined with differently chosen concentration variables $\psi^{(1)}_I$ and $\psi^{(2)}_I$ and standard quantities $\psi^{\ominus(1)}$ and $\psi^{\ominus(2)}$, respectively, are related as

$$s^*_{\psi^{(2)} I} = s^*_{\psi^{(1)} I} + R\ln\frac{\Psi^{*(1)}\,\psi^{\ominus(1)}\,\chi^{(1)}_I}{\Psi^{*(2)}\,\psi^{\ominus(2)}\,\chi^{(2)}_I} + RT\left(\frac{\partial \ln(\Psi^{*(1)}/\Psi^{*(2)})}{\partial T}\right)_{n_{0J},\,\vartheta_\iota'}, \tag{145}$$

$$h^*_{\psi^{(2)} I} = h^*_{\psi^{(1)} I} + RT^2\left(\frac{\partial \ln(\Psi^{*(1)}/\Psi^{*(2)})}{\partial T}\right)_{n_{0J},\,\vartheta_\iota'}, \tag{146}$$

$$v^*_{\psi^{(2)} I} = v^*_{\psi^{(1)} I} - RT\left(\frac{\partial \ln(\Psi^{*(1)}/\Psi^{*(2)})}{\partial p}\right)_{n_{0J},\,\vartheta_\iota'}. \tag{147}$$

From (137) and (145), respectively, it may be recognized that the standard MMQ's of the Gibbs energy $g^*_{\psi I}$ and of the entropy $s^*_{\psi I}$ can obtain any value ($g^*_{\psi I} \in \mathbb{R}$, $s^*_{\psi I} \in \mathbb{R}$), 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 MMQ's are reported, the chosen quantity for the concentration variables ψ_{0I} and the chosen value for the standard quantity $\psi^{\ominus}$ should also be reported, otherwise those data would be worthless. To simplify the comparison of different data, one should agree on one particular quantity for the concentration and one particular value for the standard state. We recommend $\psi_{0I} = c_{0I}$ (with the unit mol · m^{-3}) and $\psi^{\ominus} = 1$ mol · m^{-3}. This choice is adapted to SI units. It has two further advantages: (1) The standard state, which is a solution with a concentration $c_{0I} = 1$ mol · m^{-3}, lies within the interval of concentration variables usually encountered in practice. (2) In the standard state the contribution to g_I and s_I caused by the term $RT \ln f_{cI}$ is negligibly small, if the solution does not contain ions, or can be approximately calculated using Debye-Hückel theory, for example.

According to (134), $\check{f}^*_{\psi I} = 1$ for any choice of the concentration variable ψ_I in the limit $n_0 \to n^*_0$ or equivalently $\psi_{0G} \to 0$, $G = S+1, \ldots, E$. One usually assumes that $\check{f}_{\psi I} = 1$ holds true not only in the limit for the pure solvent but also for values of $\psi_{0G} \neq 0$, $G = S+1, \ldots, E$, in a rather wide interval, at least if there are no ions in the solution. From (138) it can be recognized, that if this is correct for a particular choice of the concentration variable, let us say $\psi_I^{(\mathrm{t})}$, then it will be true for another one, let us say $\psi_I^{(\mathrm{s})}$, if and only if $\Psi^{(\mathrm{s})}/\Psi^{(\mathrm{t})}$ is independent of the ψ_{0G}, $G = S+1, \ldots, E$, at least in sufficient approximation. If we assume, for example, $\check{f}_{cI} = 1$ (choosing $\psi_I = c_I$) in some concentration interval, then $\check{f}_{xI}$ and $\check{f}_{rI}$ (choosing $\psi_I = x_I$ or $\psi_I = r_I$) usually are not constant in that interval, because the quantities $V \Big/ \sum\limits_{J=1}^{K} n_J$ and V/n_{01} commonly depend on ψ_{0G} [10]. Assuming Henry's law strictly satisfied for some solution of a substance A_2 in a one-component solvent (A_1), i.e. $\check{f}_{x1} = 1$ for all x_1, it becomes according to (138) $\check{f}_{r1} = x_1$, for example [11].

9.3. Partial Molar Quantities and Model Quantities Pertinent to Permittivity Measurements

The dielectric property of a phase without an electric dipole moment in absence of an applied field is characterized by its relative permittivity ε_{Er}, a quantity which can be measured directly with suitable instruments. The quantity ε_{Er} is related to the dielectric polarization $\boldsymbol{P}$ of the phase, created in an applied uniform electric field $\boldsymbol{E}_{\mathrm{a}}$, by

$$\boldsymbol{P} = \varepsilon_0 (\varepsilon_{Er} - 1)\, \boldsymbol{E}_{\mathrm{a}}, \tag{148}$$

where ε_0 is the permittivity of vacuum. The quantity $\boldsymbol{P}$ can be identified with a vectorial density analogously defined as (21). The adjoint extensive quantity is $\boldsymbol{P}V$, the electric dipole moment of the phase, induced by the applied electric field. For phases, isotropic in absence of an applied field, ε_{Er} is a scalar. Then a scalar density equivalent to $\boldsymbol{P}$ can be defined, that is the electric susceptibility, χ_{e},

$$D_{\mathbf{Z}} = \chi_{\mathrm{e}} = (\varepsilon_{\mathrm{r}} - 1) = \frac{1}{\varepsilon_0} \lim_{E_{\mathrm{a}}^2 \to 0} \left(\frac{\partial \tilde{\boldsymbol{E}}_{\mathrm{a}} \boldsymbol{P}}{\partial E_{\mathrm{a}}^2} \right)_{n_{0J},\, \vartheta_\iota'}, \tag{149}$$

where $\varepsilon_{\mathrm{r}} = \lim\limits_{E_{\mathrm{a}}^2 \to 0} \varepsilon_{Er}$. The adjoint extensive quantity is $\chi_{\mathrm{e}} V$, the magnitude of the dipole moment of the phase at unit field strength. The corresponding PMQ's Z_{0J} are according to (22) defined by

$$\mathsf{Z}_{0J} = \left(\frac{\partial (\varepsilon_{\mathrm{r}} - 1)\, V}{\partial n_{0J}} \right)_{n_{0J}',\, \vartheta_\iota}, \tag{150}$$

thus the susceptibility can according to (8) and (21) be represented by

$$\varepsilon_{\mathrm{r}} - 1 = \sum_{J=1}^{E} \mathsf{Z}_{0J}\, c_{0J}, \tag{151}$$

where the sum has to be extended over all substances $A_1, \ldots, A_E$ used to generate the phase. The relative permittivity ε_{r} and usually also the PMQ's Z_{0J} depend on the composition of the phase. Knowledge of the values of ε_{r} and of the mass density ϱ for varying compositions allows the determination of the PMQ's Z_{0J} by applying (55). Its limit $\overset{+}{\mathsf{Z}}_{0G(G)}$ for $\psi_{0G} \to 0$ and fixed values of n_{0I}/n_{01}, $I \neq G$, can be obtained from (63), choosing the concentration variable $\psi_{0G} = w_{0G}$, for example*,

$$\mathsf{P}_{w\mathbf{Z}} = \frac{\varepsilon_{\mathrm{r}} - 1}{\varrho} = \frac{\overset{+}{\varepsilon}_{\mathrm{r}(G)} - 1}{\overset{+}{\varrho}_{(G)}} + \left[\frac{\overset{+}{\mathsf{Z}}_{0G(G)}}{M_G} - \frac{\overset{+}{\varepsilon}_{\mathrm{r}(G)} - 1}{\overset{+}{\varrho}_{(G)}} \right] w_{0G} + \left[M_G^{-1} \overset{+}{\Lambda}_{w\mathbf{Z}G(G)1} + \chi_{\mathrm{m}}^{(E-1)} \overset{+}{\Lambda}_{w\mathbf{Z}\mathrm{m}(G)2} \right] w_{0G}^2 + \cdots. \tag{152}$$

The relative permittivity ε_{r} and the PMQ's Z_{0J} describe bulk properties of the phase and therefore are independent of any molecular model. To relate the PMQ to molecular quantities necessitates the introduction of an appropriate molecular model allowing the definition of corresponding MMQ's. In an SMM it is assumed that the dielectric polarization $\boldsymbol{P}$ of the phase can be represented by

$$\boldsymbol{P} = N_{\mathrm{A}} \sum_{J=1}^{K} \bar{\boldsymbol{p}}_{EJ}\, c_{EJ}, \tag{153}$$

where $\bar{\boldsymbol{p}}_{EJ}$ is the average electric dipole moment of a molecule and c_{EJ} the concentration of substance A_J in the presence of the applied field and where the sum has to be extended over all substances $A_1, \ldots, A_K$ present in the phase. This assumption allows one to introduce an MMQ ζ_J, defined by

$$\zeta_J = \frac{N_{\mathrm{A}}}{\varepsilon_0} \lim_{E_{\mathrm{a}}^2 \to 0} \left(\frac{\partial \tilde{\boldsymbol{E}}_{\mathrm{a}} \bar{\boldsymbol{p}}_{EJ}}{\partial E^2} \right)_{n_{0I},\, \vartheta_\iota'}. \tag{154}$$

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* The generalized density $\mathsf{P}_{w\mathbf{Z}}$ is related to the well-known "specific polarization" p [3, 12] as $\mathsf{P}_{w\mathbf{Z}} = p(\varepsilon_{\mathrm{r}} + 2)$. We do not use this quantity because firstly, if the quantity $\boldsymbol{P}$ as defined by (148) is called polarization, p is not the corresponding specific quantity, and secondly, the factor $(\varepsilon_{\mathrm{r}} + 2)$ introduces an additional dependence on the composition of the phase, which actually is introduced only due to a particular model [4]. The quantities p_J used in $p = \sum\limits_{J=1}^{K} p_J w_J$ are related to the MMQ's ζ_J, Eq. (154), as $\zeta_J = p_J M_J (2\varepsilon_{\mathrm{r}} + 1)$. Similarly the generalized density $\mathsf{P}_{x\mathbf{Z}}$, which is equal to the average PMQ $\mathsf{Z}_{0\mathrm{m}}^{(E)}$, is related to the "molecular polarization" $P = \sum\limits_{J=1}^{K} P_J x_J$ as

$$\mathsf{P}_{x\mathbf{Z}} = P(\varepsilon_{\mathrm{r}} + 2) \quad \text{and} \quad \zeta_J = (\varepsilon_{\mathrm{r}} + 2)\, P_J.$$

Based on such a model the electric susceptibility will be represented by

$$\varepsilon_{\mathrm{r}} - 1 = \sum_{J=1}^{K} \zeta_J c_J . \tag{155}$$

For a phase where no chemical reaction occurs, the MMQ's ζ_J are related to the PMQ's Z_{0J} by (78), for example. For a gaseous phase at sufficiently low density, ζ_J is independent of the composition of the phase and according to (89)

$$\zeta_J = \mathsf{Z}_{0J} . \tag{156}$$

In a dense phase the MMQ's ζ_J depend on the composition of the phase and (156) does not hold true any more. The further treatment has to be based on some molecular model. If it is assumed that the ζ_J's depend on the parameters $\alpha_1, \ldots, \alpha_\varrho$, Eqs. (78) and (79), choosing the concentration variable $\psi_{0G} = w_{0G}$ for example, leads to the following relation for the limit $\zeta^{+}_{G(G)}$ of the MMQ

$$\zeta^{+}_{G(G)} = \mathsf{Z}^{+}_{0G(G)} - M_G \sum_{\varkappa=1}^{\varrho} \left(\frac{\partial \alpha_\varkappa}{\partial w_{0G}} \right)^{+}_{n_{0G}',\, \vartheta_\iota(G)} \cdot \sum_{I=1}^{E} \frac{w^{+}_{0I(G)}}{M_I} \left(\frac{\partial \zeta_I}{\partial \alpha_\varkappa} \right)^{+}_{\alpha_\varkappa',\, \vartheta_\iota(G)} . \tag{157}$$

In most of the commonly used models it is assumed that the ζ_J's depend only on ε_{r}, at least for fixed values of T and p, but not on any other bulk quantity of the phase. Then the first sum of the second term on the right-hand side of (157) is reduced to one term, $(\partial \varepsilon_{\mathrm{r}} / \partial w_{0G})^{+}_{n_{0G}',\, \vartheta_\iota(G)}$. Using (21), (18) and (63) (with $\psi_{0G} = w_{0G}$ and $\Phi = V$), (157) becomes

$$\zeta^{+}_{G(G)} = \mathsf{Z}^{+}_{0G(G)} - \varrho^{+}_{(G)} [\mathsf{Z}^{+}_{0G(G)} - (\varepsilon^{+}_{\mathrm{r}(G)} - 1)\, V^{+}_{0G(G)}] \cdot \sum_{I=1}^{E} \frac{w^{+}_{0I(G)}}{M_I} \left(\frac{\partial \zeta_I}{\partial \varepsilon_{\mathrm{r}}} \right)^{+}_{\vartheta_\iota(G)} . \tag{158}$$

The limit $V^{+}_{0G(G)}$ of the partial molar volume of A_G can be estimated from (63) with $\psi_{0G} = w_{0G}$ and $\Phi = V$, i.e.

$$\mathsf{P}_{wV} = \frac{1}{\varrho} = \frac{1}{\varrho^{+}_{(G)}} + \left(\frac{V^{+}_{0G(G)}}{M_G} - \frac{1}{\varrho^{+}_{(G)}} \right) w_{0G} + (M_G^{-1} \Lambda^{+}_{wVG(G)1} + \chi_{\mathrm{m}}^{(E-1)} \Lambda^{+}_{wV\mathrm{m}(G)2})\, w^{+}_{0G} + \cdots . \tag{159}$$

All the quantities in (158) except the derivatives $(\partial \zeta_I / \partial \varepsilon_{\mathrm{r}})^{+}_{\vartheta_\iota(G)}$ can be determined from experimental data. For solutions of a single substance A_G in a mixed solvent $\mathrm{A}_1, \ldots, \mathrm{A}_S$ it is $\zeta^{+}_{G(G)} = \zeta^{*}_{G}$ and also all crossed quantities on the right-hand side of (158) are equal to the corresponding starred quantities, i.e. to their limits for $n_0 \to n_0^{*}$. In this case the one factor in the second term of (158) is reduced to $\varrho^{*} \sum_{L=1}^{S} (w^{*}_{0L} / M_L)(\partial \zeta_L / \partial \varepsilon_{\mathrm{r}})^{*}_{\vartheta_\iota}$ and hence depends only on properties of the solvent, but not on any property of the solute A_G. Therefore, if this quantity is determined once, it can be used for the evaluation of the MMQ's ζ^{*}_{G} of different solutes A_G in the same mixed solvent. This statement is based on the assumed molecular model and for this reason it is only necessarily true, if the model is a true one. An essential presupposition introduced was the assumption that $\zeta_I = \zeta_I(\varepsilon_{\mathrm{r}})$, i.e. the MMQ's depend on just one parameter ε_{r}. Particularly for mixed solvents this does not have to be true. Any interaction between a solute molecule and the surrounding solvent molecules causing some effects on their distribution makes the introduction of further parameters $\alpha_\varkappa$ necessary, which lead according to (157) to additional terms, each one being a product, where the first factor is dependent on properties of the solute and the second factor only on properties of the solvent. If the solvent consists of only a single substance A_1, one usually assumes that (158) is a sufficient approximation. In this case the sum is reduced to a single term and the solvent-dependent factor becomes $(\partial \zeta_1 / \partial \varepsilon_{\mathrm{r}})^{*}_{\vartheta_\iota} / V^{\circ}_{01}$. Comparison of experimental data indicates, that this is almost but not quite true; we will discuss this in a later paper.

The derivatives $(\partial \zeta_I / \partial \varepsilon_{\mathrm{r}})^{+}_{\vartheta_\iota(G)}$ or $(\partial \zeta_1 / \partial \varepsilon_{\mathrm{r}})^{*}_{\vartheta_\iota}$ have to be determined on the basis of a particular model, their values being dependent on the chosen model. A particular model is also needed for the further evaluation of the MMQ $\zeta^{+}_{G(G)}$ or ζ^{*}_{G} to obtain molecular quantities intrinsic to the isolated molecule A_G such as the permanent electric dipole moment and the electric polarizability. Some models will be discussed and a few applications will be reported in the second and fifth paper of this series [4, 6].

Analogous equations to the above ones can be derived for the evaluation of refractometric measurements by substituting the square of the refractive index n^2 for ε_{r}, Z'_{0G} for Z_{0G} and ζ'_G for ζ_G [4].

9.4. Partial Molar Quantities and Model Molar Quantities Pertinent to Optical Absorption Measurements

With devices used to measure the optical absorption of some phase usually the ratio τ (transmittance) of the radiant flux transmitted through the absorbing system to the incident radiant flux is primarily determined or the ratio τ' of the former flux to the flux transmitted through a similar system, where the phase does not contain the species whose optical behavior is investigated (reference system). Correcting for boundary and container influences and for contributions caused by scattering of light or neglecting those effects, which usually is allowed when τ' is determined, leads to the absorbance $A = -\log(\tau)_{\text{corrected}}$ or $A' = -\log(\tau')_{\text{corrected}}$ of the considered phase. Knowing the length l of the light path in the phase, one can calculate the absorption coefficient $a = A/l$ or $a' = A'/l$. If the absorbance of the reference system is A_{ref}, then $a' = a - A_{\text{ref}}/l$. The quantity a can be identified with a density as defined by (21). The adjoint extensive quantity is aV and the corresponding PMQ's, K_{0J}, are according to (22) defined by

$$\mathsf{K}_{0J} = \left(\frac{\partial(aV)}{\partial n_{0J}}\right)_{n_{0J'},\,\vartheta_\iota}. \tag{160}$$

With the PMQ's K_{0J} the absorption coefficient a of a phase can be represented by

$$a = \sum_{J=1}^{E} \mathsf{K}_{0J}\, c_{0J}, \tag{161}$$

where the sum has to be extended over all substances $A_1, \ldots, A_E$ used to generate the phase. The absorption coefficient a and usually the PMQ's K_{0J} depend on the composition of the phase. Knowledge of the values of a and of the mass density ϱ for varying compositions allows the determination of the PMQ's K_{0J} by applying (55). Its limit $\mathsf{K}^{+}_{0G(G)}$ for $\psi_{0G} \to 0$ and fixed values of n_{0I}/n_{01} ($I = 2, \ldots, E$; $I \neq G$) can be obtained from (63), choosing the concentration variable $\psi_{0G} = w_{0G}$ for example,

$$\begin{aligned}\mathsf{P}_{w\mathsf{K}} = \frac{a}{\varrho} = \frac{a^{+}_{(G)}}{\varrho^{+}_{(G)}} + \left[\frac{\mathsf{K}^{+}_{0G(G)}}{M_G} - \frac{a^{+}_{(G)}}{\varrho^{+}_{(G)}}\right] w_{0G} \\ + [M_G^{-1} \Lambda^{+}_{w\mathsf{K}G(G)1} \\ + \chi_{\text{m}}^{(E-1)} \Lambda^{+}_{w\mathsf{K}\text{m}(G)2}]\, w_{0G}^{2} + \cdots.\end{aligned} \tag{162}$$

$a^{+}_{(G)}$ is the absorption coefficient of the phase without substance A_G ($w_{0G} = 0$).

The absorption coefficient a and the PMQ's K_{0J} describe bulk properties of the phase and therefore are independent of any molecular model. To relate the PMQ's to molecular quantities necessitates the introduction of an appropriate molecular model allowing the definition of corresponding MMQ's. In an SMM it is assumed that the absorption coefficient a of a phase can be represented by

$$a = \sum_{J=1}^{K} \varkappa_J\, c_J, \tag{163}$$

where $\varkappa_J$ is the molar absorption coefficient of the substance A_J, which can be identified with an MMQ, and where the sum has to be extended over all substances $A_1, \ldots, A_K$ present in the phase.

For a phase where no chemical reaction occurs, the MMQ's $\varkappa_J$ are related to the PMQ's K_{0J} by (78), for example. For a gaseous phase at sufficiently low density, $\varkappa_J$ is independent of the composition of the phase and according to (89)

$$\varkappa_J = \mathsf{K}_{0J}. \tag{164}$$

In a dense phase the MMQ's $\varkappa_J$ generally depend on the composition of the phase and therefore (164) does not hold true any more. A further treatment has to be based on some molecular model. In some models it is assumed that $\varkappa_J$ does depend on the relative permittivity ε_{r} and on the square of the index of refraction n^2 of the phase only (at least for fixed values of T and p), but not on other bulk properties of the phase, that is $\varkappa_J = \varkappa_J(\varepsilon_{\text{r}}, n^2)$. In the range of such models it follows similarly to (158) for the limit $\varkappa^{+}_{G(G)}$ of the absorption coefficient for $w_{0G} \to 0$

$$\begin{aligned}\varkappa^{+}_{G(G)} = \mathsf{K}^{+}_{0G(G)} - \varrho^{+}_{(G)}[\mathsf{Z}^{+}_{0G(G)} - (\varepsilon^{+}_{\text{r}(G)} - 1)\, V^{+}_{0G(G)}] \sum_{I=1}^{E} \frac{w^{+}_{0I(G)}}{M_I} \left(\frac{\partial \varkappa_I}{\partial \varepsilon_r}\right)^{+}_{n,\,\vartheta_\iota(G)} \\ - \varrho^{+}_{(G)}[\mathsf{Z}'^{+}_{0G(G)} - (n^{2+}_{(G)} - 1)\, V^{+}_{0G(G)}] \sum_{I=1}^{E} \frac{w^{+}_{0I(G)}}{M_I} \left(\frac{\partial \varkappa_I}{\partial n^2}\right)^{+}_{\varepsilon_{\text{r}},\,\vartheta_\iota(G)}.\end{aligned} \tag{165}$$

The PMQ's Z_{0G} and Z'_{0G} are explained in Sect. 9.3 and in the second paper [4]. All the quantities on the right-hand side of (165) can be determined from experimental data except the derivatives

$(\partial\varkappa_I/\partial\varepsilon_{\mathrm{r}})^+_{n,\vartheta_\iota(G)}$ and $(\partial\varkappa_I/\partial n^2)_{\varepsilon_{\mathrm{r}},\vartheta_\iota(G)}$. For solutions of a single substance A_G in a mixed solvent or a one-component solvent, (165) is simplified analogous to (158) and the terms depending on $(\partial\varkappa_I/\partial\varepsilon_{\mathrm{r}})^+_{n,\vartheta_\iota(G)}$ and $(\partial\varkappa_I/\partial n^2)^+_{\varepsilon_{\mathrm{r}},\vartheta_\iota(G)}$ can be discussed similar to the terms depending on $(\partial\zeta_I/\partial\varepsilon_{\mathrm{r}})^+_{\vartheta_\iota(G)}$ in (158), as has been done there. The determination of the derivatives of $\varkappa_I$ is rather intricate. Models which could be used for such a purpose have been discussed previously [7, 8, 13]. For many systems the values of the second and third terms of (165) are rather small compared to the value of $\mathsf{K}^+_{0G(G)}$ and therefore they are disregarded altogether in most spectroscopic investigations. But one should realize that this neglect can introduce errors which may cause misinterpretation of physical facts.

To avoid the outlined difficulties in the evaluation of molar absorption coefficients, one usually tries to choose the solvents and wavenumber intervals so that the absorbance of the phase without substance A_G vanishes, i.e. $a^+_{(G)}=0$. Under this circumstance, necessarily $\varkappa_I=0$ $(I=1,\ldots,E,$ $I\neq G)$, so that with a very large probability all derivatives $(\partial\varkappa_I/\partial\varepsilon_{\mathrm{r}})_{n,\vartheta_\iota(G)}$ and $(\partial\varkappa_I/\partial n^2)_{\varepsilon_{\mathrm{r}},\vartheta_\iota(G)}$ vanish too, so that $\varkappa^+_{G(G)}=\mathsf{K}^+_{0G(G)}$. In such solutions with sufficiently small concentrations of the solute A_G, the generalized density $\mathsf{P}_{w\mathrm{K}}=a/\varrho$ is usually proportional to w_{0G} to a very good approximation, and then Beer's law holds and $\varkappa^+_{G(G)}$ can be determined as is commonly done by $\varkappa^+_{G(G)}=a/c_{0G}$ or $\varkappa^+_{G(G)}=a'/c_{0G}$. From solutions of a single substance A_G in a mixed solvent or a one-component solvent the limit $\varkappa^*_G$ can analogously be obtained.

The quantity $\varkappa^*_G$ is the limit of the molar absorption coefficient of the solute A_G in the considered solvent. Its value usually differs from the value of the intrinsic molar absorption coefficient of an isolated molecule, the differences are caused by the interactions of the molecule A_G with the solvent molecules in its environment. Relations between $\varkappa^*_G$ and the intrinsic molar absorption coefficient can be developed using the same molecular models as are used for the evaluation of the derivatives $(\partial\varkappa_I/\partial\varepsilon_{\mathrm{r}})_{n,\vartheta_\iota}$ and $(\partial\varkappa_I/\partial n^2)_{\varepsilon_{\mathrm{r}},\vartheta_\iota}$. A dependence of $\varkappa_G$ on c_{0G} (departure from Beer's law) can be caused by chemical reactions or by the change of ε_{r} and n^2 with varying c_{0G}. In the former case the dependence is only fictitious, it does not occur, when the chemical reaction is taken into account and the molar absorption coefficients are well defined as by (163). In the latter case the effect can be treated again on the basis of a suitable molecular model.

9.5. Partial Molar Quantities and Model Molar Quantities Pertinent to Electro-optical Absorption Measurements

With devices used to measure the electro-optical absorption [14, 15] the change of the absorption coefficient $\Delta a=(a_E-a)$ can primarily be determined, where a and a_E are the absorption coefficient in the absence and presence of an applied electric field. For phases isotropic in the absence of an applied field, Δa has for symmetry reasons to be an even function of the field strength. If the strength of the applied electric field is not too large, the quantity Δa is proportional to the square of the field strength; for solutions of not too large molecules this holds true up to the largest possible static field strength ($E_{\mathrm{a}}\approx 2\cdot 10^7\ \mathrm{Vm}^{-1}$). Therefore it is advantageous to consider the quantity M, defined by

$$M=\lim_{E_{\mathrm{a}}{}^2\to 0}\left(\frac{\partial a_E}{\partial E^2_{\mathrm{a}}}\right)_{n_{0I},\vartheta_\iota'}, \tag{166}$$

as the original experimental quantity characterizing the electro-optical absorption of phases isotropic in absence of an applied field. E_{a} is the magnitude of the applied uniform electric field. The quantity M can be identified with a density as defined by (21). The adjoint extensive quantity is MV and the corresponding PMQ's Y_{0J} are according to (22) defined by

$$\mathsf{Y}_{0J}=\left(\frac{\partial(MV)}{\partial n_{0J}}\right)_{n_{0J'},\vartheta_\iota}. \tag{167}$$

With the PMQ's Y_{0J} the quantity M of a phase can be represented by

$$M=\sum_{J=1}^{E}\mathsf{Y}_{0J}\,c_{0J}, \tag{168}$$

where the sum has to be extended over all substances $\mathrm{A}_1,\ldots,\mathrm{A}_E$ used to generate the phase. The quantity M and usually the PMQ's Y_{0J} depend on the composition of the phase. Knowledge of M and of the mass density for varying compositions allows the determination of the PMQ's Y_{0J} by applying (55). Its limit $\mathsf{Y}^+_{0G(G)}$ for $\psi_{0G}\to 0$ and fixed values of n_{0I}/n_{01} $(I=2,\ldots,E;\ I\neq G)$ can be obtained from an equation similar to (162) with a replaced by M.

The quantities M and Y_{0J} describe bulk properties of the phase and therefore are independent of any molecular model. To relate the PMQ's to molecular quantities necessitates the introduction of an appropriate molecular model allowing the definition of corresponding MMQ's. In an SMM it is assumed that M can be represented by

$$M = \sum_{J=1}^{K} v_J c_J . \tag{169}$$

The sum has to be extended over all substances present in the phase. The MMQ v_J can be represented by intrinsic molecular properties of the molecule A_J. According to the definition of M by (166) it is sufficient to develop the molecular model up to square terms in E_a leading to [8, 14]

$$v_J = \varkappa_J (L_J + q_J + s_E) , \tag{170}$$

where

$$L_J = \lim_{E_\mathrm{a}{}^2 \to 0} \frac{1}{\varkappa_{EJ}} \left(\frac{\partial \varkappa_{EJ}}{\partial E_\mathrm{a}^2} \right)_{n_{0I},\, \vartheta_\iota{}'} , \tag{171}$$

$$q_J = \lim_{E_\mathrm{a}{}^2 \to 0} \frac{1}{r_{EJ}} \left(\frac{\partial r_{EJ}}{\partial E_\mathrm{a}^2} \right)_{n_{0I}',\, \vartheta_\iota} , \tag{172}$$

and

$$s_E = \lim_{E_\mathrm{a}{}^2 \to 0} \left[\frac{1}{\varrho_E} \left(\frac{\partial \varrho_E}{\partial E_\mathrm{a}^2} \right)_{n_{0I},\, \vartheta_\iota{}'} + \left(\frac{m_{E0}}{m_{E01}} \right)^{(\mathrm{M})} \left(\frac{\partial (m_{E01}/m_{E0})^{(M)}}{\partial E_\mathrm{a}^2} \right)_{n_{0I}',\, \vartheta_\iota} \right] . \tag{173}$$

The equations apply for the commonly used experimental device [14, 15]. $\varkappa_J$, $\varkappa_{EJ}$, r_J, r_{EJ}, c_J, c_{EJ}, ϱ, ϱ_E, are the molar absorption coefficients, the mole ratios and the concentrations of the substance A_J and the mass densities in absence and presence of the applied uniform electric field $\boldsymbol{E}_\mathrm{a}$, respectively. The quantity L_J is the relative change of the molar absorption coefficient of substance A_J in unit field strength. It is in the considered molecular model [8, 14] dependent on some bulk properties of the phase as T, ε_r and n^2 and on intrinsic properties of the isolated molecule A_J such as the permanent electric dipole moments and polarizabilities in the ground state and the excited vibronic state corresponding to the wavenumber of the applied radiation field, the direction of the transition dipole moment relative to the direction of the dipole moments and axes of the polarizability tensor, and the transition polarizability. Hence knowledge of the MMQ v_J can allow the determination of these quantities in favorable cases. The quantity q_J is the relative change of the mole ratio of substance A_J in unit field strength. In a phase where a chemical reaction occurs, this change can be caused by the electric field dependence of the corresponding equilibrium constant [6]. Some contribution to q_J can also be caused by a change of the relative number densities of the different molecules in the phase inside and outside of the electric field, but this usually can be neglected. The first term of the quantity s_E describes the effects caused by the electrostriction of the solution and usually is assumed negligibly small. $(m_{E01}/m_{E0})^{(\mathrm{M})}$ is the ratio of the mass of the solvent A_1 and the total mass inside of the electric field, its derivative is negligibly small at least in sufficiently dilute solutions.

For a phase where no chemical reaction occurs, the MMQ's v_J are related to the PMQ Y_{0J} by (78), for example. For a gaseous phase at sufficiently low density v_J is independent of the composition of the phase and according to (89)

$$v_J = \mathsf{Y}_{0J} . \tag{174}$$

In a dense phase v_J is generally dependent on the composition of the phase and therefore (174) does not hold true any more. A further treatment has to be based on some molecular model. In the common models it is assumed that v_J depends on ε_r and n^2 in a manner similar to the molar absorption coefficient $\varkappa_J$. Then the limit $v^+_{G(G)}$ of v_G for $\psi_{0G} \to 0$ can be obtained by an equation similar to (165) with K_{0G} replaced by Y_{0G} and $\varkappa_I$ by v_I. If one or more of the derivatives $(\partial v_I / \partial \varepsilon_\mathrm{r})_{n,\, \vartheta_\iota}$ or $(\partial v_I / \partial n^2)_{\varepsilon_\mathrm{r},\, \vartheta_\iota}$ are appreciably different from zero, the accurate evaluation of $v^+_{G(G)}$ from the experimental data is as tedious as the evaluation of $\varkappa^+_{G(G)}$ under similar circumstances and for similar reasons. To avoid this difficulty one usually chooses the solvents and investigated wavenumber intervals so that the phase without substance A_G does not show an electrochromic effect, i.e. $M^+_{(G)} = 0$ (and usually also $a^+_{(G)} = 0$). Under this circumstance it is necessarily $v_I = 0$ $(I = 1, \ldots, E,\, I \neq G)$, so that with a very large probability all derivatives $(\partial v_I / \partial \varepsilon_\mathrm{r})^+_{n,\, \vartheta_\iota (G)}$ and $(\partial v_I / \partial n^2)_{\varepsilon_\mathrm{r},\, \vartheta_\iota (G)}$ vanish too, so that $v^+_{G(G)} = \mathsf{Y}^+_{G(G)}$. If such solutions are furthermore sufficiently dilute, the generalized density $\mathsf{P}_{w\mathrm{r}} = M/\varrho$ is usually proportional to w_{0G} to a very good approximation and then $v^+_{G(G)}$ can be determined according to

$$v^+_{G(G)} = M / c_{0G} . \tag{175}$$

Similar to eq. (57) we can define a particular generalized density

$$\mathsf{P}_{M/a}(\tilde{\nu}) = M(\tilde{\nu})/a(\tilde{\nu})\,. \tag{176}$$

With the relative contribution σ_J of the molecules A_J to the optical absorption coefficient a,

$$\sigma_J = \varkappa_J c_J \Big/ \sum_{I=1}^{K} \varkappa_I c_I \tag{177}$$

one obtains from (169), (170)—(173) and (176)

$$M/a = \sum_{J=1}^{K} \sigma_J (L_J + q_J) + s_E\,. \tag{178}$$

Under the above conditions, where $\nu_J = 0$ and $\varkappa_J = 0$ for $J \neq G$, it is $\sigma_G = 1$ and $\sigma_J = 0$, $J \neq G$. Neglecting the terms q_G and s_E, as can usually be done for a solution where no chemical reaction occurs, leads to

$$M/a = L_G\,. \tag{179}$$

According to (179) the quantity L_G can be determined even if the concentration c_{0G} of the solute A_G in the investigated solution is unknown.

The limit L_G^* of L_G differs from the value of the corresponding intrinsic molecular quantity of an isolated molecule, the differences being caused by the interactions of the molecules A_G with the solvent molecules in its environment. Relations between L_G^* and the intrinsic molar quantities have been published previously [8, 14]. Examples of a few applications will be reported in the third paper of this series [5], a more complicated case concerning the investigation of two coupled chemical reactions will be presented in the fifth paper [6].

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