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The Notions of the Initial Components and Phases, Detailed Components and Chemical Forms in the Interpretations of Colligative Properties of Solutions

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Abstract—In the paper the relation of modern concepts on solutions with colligative solution properties is fully formalized. The necessity of obvious taking into account not only the well-known Vant-Hoff's principle about universal behavior of matter in the dissipated state, but the specificity of detailed components in comparison with initial (brutto-) components. The aggregate of consequences from Gibbs fundamental equation is supplemented by means of these grounds.

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Physicochemical decompositions of substances are multifaceted and multilevel in character. Two most common approaches to decomposition of a substance took shape as early as over 150 years ago (Periodic Law) and were constructively formalized by Gibbs in the *component* and *phase* terms [1]. The accumulated knowledge about phases-solutions (Mendeleev, Arrhenius, van't Hoff, Bjerrum, and many others) has provided the prerequisite that gives grounds for adding the concepts of homogeneous processes [reactants are only chemical forms (species) identified inside a phase of a variable composition] to the original concepts of one of the types of heterogeneous processes (phase reactions; reactants are only phases, including phases-solutions). This opens a scope for obtaining reproducible quantitative data on two other types of heterogeneous reactions (reactants are either chemical forms only, though in different phases, or phases and chemical forms). The concepts of reactants could not be developed without deeper elaboration of the concept of components: element (conservation in the general chemical sense), formal element (conservation within a limited, though objectively controlled set of the initial and boundary conditions), initial component (gross-component), and detailed component [2–4].

Here, we derived relations to supplement the consequences of the fundamental Gibbs equation, formalizing the relationship between the state of a substance in solutions with their colligative properties.

By now, much quantitative information has been accumulated about phase reactions (in terms normalized to mole of thermodynamic characteristics of individual substances [5, 6]) and about reactions involving chemical forms (mainly in terms of equilibrium constants [5, 7]). At the same time, approaches to deriving quantitative knowledge about chemical forms as reactants [8–12] are developed to a lesser extent compared to individual substances. In accordance with the fundamental reference data from [6], an individual substance [2, 4] is a specific phase of a constant composition, formed by one (with microimpurities disregarded) stoichiometrically defined component, which cannot always be described as a macroensemble of molecules of the same stoichiometry. World scientific literature assigns the term "pure substance" to an individual substance. It is not uncommon, however, that this term is also attributed to a gross-component having a definite (integer) stoichiometry, that has constituted the individual substance of interest. This dualism is undesirable, since any of the components is pure (does not contain microimpurities) by definition and can form, along with the substance considered, other individual substances of the same stoichiometry.

Meant by *chemical form* is a macroensemble of solvated particles formed in solution by stoichiometrically defined, charged or electrically neutral, microfragments of a substance (detailed component particles). However, the very fact of solvation is taken into account without being incorporated in the stoichiometric description of particles of the chemical form [3]. Therefore, chemical forms produced by the same detailed component in different solvents are different, though the same stoichiometry is assigned to them.

In the following, we will designate the stoichiometric formulas of individual substances, chemical forms, and their corresponding initial and detailed components by letters A, B, or B provided with superscripts/superscripts whose meaning will be disclosed in the context.

To achieve the above-stated goal, we will first consider the internal equilibrium liquid solutions whose formation is contributed by two initial stoichiometrically defined substances: liquid A (solvent) and solute B (individual solid, gas, or liquid). Naturally, any such solution can be abstractly characterized as a state of an open homogeneous system whose composition is described by vector $n^* = (n^*_A,\ n^*_B)$ with dimensionality $k^* = 2$. In these terms, the Gibbs–Duhem equation (as derived in either of the two ways [4]), which is the starting equation for further analysis, takes the form:

$$SdT - VdP + n^*_A d\mu^*_A + n^*_B d\mu^*_B = 0, \qquad (1)$$

where n^*_A, n^*_B and μ^*_A, μ^*_B are the molar amounts and chemical potentials of the two initial (independent according to Gibbs[1])[1] components, respectively.

Next, based on the three conjugate forms of the fundamental equation [3, 4] relating the characteristics of gross-components to those of detailed components, two other equalities can be easily obtained

$$\mu^*_A = \mu_A \text{ and } \mu^*_B = \mu_B, \qquad (2)$$

where μ_A and μ_B are the chemical potentials of the detailed components, stoichiometrically equivalent to the initial components.

However, the complete list of detailed components (with the dimensionality $l \geq k^*$ [3]) not always contains the component with stoichiometry B. In such cases, the right-hand side of the latter of the two equalities (2) is to be replaced by one of the acceptable combinations μ_{Bi} [$i = 1$ to $(l - 1)$]. In particular, for an aqueous solution of sodium chloride we will obtain:

$$\mu^*_{NaCl} = \mu_{Na^+} + \mu_{Cl^-}. \qquad (3)$$

In this simple example we have two initial components, H_2O [$\mu^*(H_2O)$] and NaCl (μ^*_{NaCl}), and three detailed components, H_2O [$\mu(H_2O)$], Na^+ (μ_{Na^+}), and Cl^- (μ_{Cl^-}). It should be noted that the chemical potential metrology for detailed components whose particles have integer charge (in terms of deficit or excess of electrons) is underlain, along with the laws of conservation of mass and elements, by the principle of macroscopic electrical neutrality of phases. Moreover, there is a need in introducing additional reference zeros, similar to “hydrogen zero” which has gained widespread acceptance as applied to aqueous solutions [5, 8].

To derive the desired relationships, let us fix T, P and consider the consequences of addition to the initially pure solvent ($C^{*\,0}_A$) of component B at the concentration ranging from $C^*_B = 0$ to $C^*_B \ll C^{*\,0}_A \cong \langle C^*_A\rangle$, where C^*_A and C^*_B are the molar concentrations of the initial components. Using Eq. (1) we will obtain a strict equality:

$$\langle C^*_A\rangle\, \Delta\mu^*_A + \int_{C^*_B = 0}^{C^*_B} C^*_B\, d\mu^*_B = 0. \qquad (4)$$

For more informative analysis, the first term in Eq. (4) will be replaced by the equivalent term $\langle C^*_A\rangle\, \Delta\mu_A$, and the second term, by the sum of integrals:

$$\int_{C^*_B = 0}^{C^*_B} C^*_B\, d\mu^*_B = \sum_i \int_{C_{Bi} = 0}^{C_{Bi}} C_{Bi}\, d\mu_{Bi}. \qquad (5)$$

Equation (5) is the result of conjugation of the starting Gibbs–Duhem equation with equations derived for any of acceptable detailed elaborations of the internal equilibrium system considered (with possible partiality and locality of equilibrium taken into account) [3, 4].

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[1] As indicated in collected works of Gibbs [1, pp. 68–69], *substances S_1, S_2, ... S_n that are supposed to constitute the mass* [a homogeneous n-component system (our comment*)*] *must naturally provide for independent differentials dm_1, dm_2, ... dm_n..*

Obviously, $C_{\mathrm{B}i}$ in Eq. (5) designates the molar concentrations of those detailed components that are specifically associated with the presence of gross-component B in the solution considered. The set of chemical transformations that occur in solution can lead to formation of macroensembles of particles that are only stoichiometrically defined fragments of gross-component A, whose presence in the form of independently existing particles of any of the detailed components in pure solvent is insignificant. They will also be included in the complete list of components B_i. For example, through solving the direct problem of chemical equilibrium [4] in an aqueous ammonia solution we will come to a conclusion that the mass balance of the system of interest (a subsystem of the initial system) consists exclusively of the detailed component A = H_2O and three components B_i: $\mathrm{B}_1 = \mathrm{NH}_3$, $\mathrm{B}_2 = \mathrm{NH}_4^+$, $\mathrm{B}_3 = \mathrm{OH}^-$. The last-named component is a macroensemble of the OH^- anions, whose significant number was the result of a proton transfer from a part of the water molecules to ammonia molecules, whereby NH_4^+ cations were produced.

To make further progress toward achieving the goal formulated we will use the well-known approximation [2, 3, 13]:

$$\mu_{\mathrm{B}i}\,(T, P, \mathrm{solv}, C_{\mathrm{B}i}) \cong \mu^0_{\mathrm{B}i,\mathrm{C}}\,(T, P, \mathrm{solv}) + RT \ln C_{\mathrm{B}i}. \qquad (6)$$

Naturally, the quantity under logarithm in this equation is only the numerical value of the molar concentration, since we referred $\mu^0_{\mathrm{B}i,\mathrm{C}}$ to its unit value in terms of this particular scale[2], as indicated by symbol C in the subscript [3]. In the general case, the superscript 0 integrates two aspects in standardizations of $\mu_{\mathrm{B}i}$ quantities. One aspect consists in that the concentration of the component considered is strictly equal to unity in terms of the scale accepted. The other aspect is that the accounting of the change in the medium is related to the states B_i in a conditionally pure solvent, i.e., in an extremely diluted (relative to the entire set of detailed components B_i) solution. It is appropriate to note in this connection that the "pure solvent" concept is not limited to an individual substance. Rather, this may be a pure simple solvent (single-component solvent, with microimpurities disregarded) and a pure complex solvent (two- or more-component solvent, with microimpurities disregarded) [2, 3, 8, 13]. The influence exerted by the nature of solvent on $\mu_{\mathrm{B}i}$, called by us the primary medium effect, appears as a constant term included in $\mu^0_{\mathrm{B}i}$ (pure simple solvent) or $\mu^{\otimes}_{\mathrm{B}i}$ (pure complex solvent). However, it should be reminded that, in example (1)–(6) and henceforth, we restrict ourselves to solutions based on liquid individual substances, i.e., pure simple solvents.[3] Obviously, to correctly estimate $\mu^0_{\mathrm{B}i}$ based on Eq. (6) and its consequences, we need precision data about the range of dilutions of the solution to provide grounds for neglecting the deviations from ideality, i.e., the secondary medium effects [2–4]. For this reason, and not only for justifying the replacement of $<C^*_{\mathrm{A}}>$ by $C^{*\,0}_{\mathrm{A}}$, commonly used in interpretations of colligative properties of dilute solutions, we limited the acceptable C^*_{B} values from above by the inequality $C^*_{\mathrm{B}} << C^{*\,0}_{\mathrm{A}} \cong <C^*_{\mathrm{A}}>$.

Taking approximation (6), we will obtain using Eqs. (1)–(5)

$$-<C^*_{\mathrm{A}}>\Delta\mu^*_{\mathrm{A}} = -<C^*_{\mathrm{A}}>\Delta\mu_{\mathrm{A}} \cong RT\left[\sum_{i}^{l-1} C_{\mathrm{B}i}\right] \equiv RT\,C_{\Sigma}$$
$$= \boldsymbol{i}\,RT\,C^*_{\mathrm{B}}, \qquad (7)$$

where factor ***i*** is given by the $C_{\Sigma}/C^*_{\mathrm{B}}$ ratio.

Given below are several examples of how factor ***i*** can be calculated using the C^*_{B} and the C_{Σ} data (expert sample). For instance, in the above two examples we have factor ***i*** of 2.00 for sodium chloride (throughout the pressure and temperature ranges of existence of its dilute aqueous solution, a strong electrolyte) and 1.13 for ammonia [at $P = 1$ atm, $T = 298.15$ K, and $C^*(\mathrm{NH}_3) = 1.00 \times 10^{-3}$ M]. In the latter example, the calculation of the van't Hoff factor (***i***) took into

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[2] Regarding the priority of the molar concentration scale in formulations and solutions of mass balance problems for complex equilibria as related to the mass action law and standardizations of medium effects, we have addressed ourselves several times to this topic previously [2, 8, 13]. For more detailed discussion of these issues, including the relationship with the restrictions posed by the principle of macroscopic electrical neutrality of phases, see monograph by I.V. Mironov [10].

[3] This restriction was set in an attempt to avoid obscuring with unnecessary details the potential inherent in the specific applications of the three conjugate forms of the fundamental equation [3, 4]. It is quite clear, however, that the passage from (1)–(6) to (7) and (8), and the result itself, open up fresh opportunities compared to Lewis' theory [14] for taking into account the secondary medium effects [2, 3, 9].

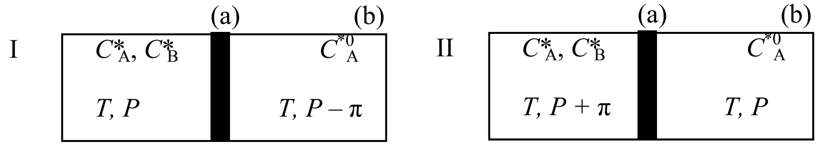

Illustration of the final states in osmotic equilibrium realizations.

account the distribution of the ammonia molecules in solution over two forms only:

$$NH_{3aq} + H_2O_{aq} \leftrightarrow NH^+_{4aq} + OH^-_{aq}$$

(based on the $\Delta_r G^0$ data from [5], the equilibrium constant was estimated at 1.85×10^{-5}). Naturally, the same result is obtained for the variant

$$NH_4OH_{aq} \leftrightarrow NH^+_{4aq} + OH^-_{aq}$$

in which it was conventionally assumed that each of the ammonia molecules that did not form $NH_4{}^+{}_{aq}$ is chemically bonded to a water molecule. In particular, the $\overline{G}^0$ value for NH_4OH_{aq}, given by Latimer [5], corresponds to specifically this variant.

Solution of the direct problem of chemical equilibrium [4] for chlorine dissolution in initially pure water up to its saturation at $P(Cl_2)$ = 1 atm and T = 298.15 K gave the following results. The gross concentration of chlorine (C^*_B, where $B = Cl_2$) was estimated at 0.093 M, and the concentrations of the detailed components $B_1 = Cl_2$, $B_2 = H^+$, $B_3 = Cl^-$, and B_4 = HClO, at 0.062, 0.031, 0.031, and 0.031 M, respectively [the thermodynamically possible decomposition of HClO ($HClO_{aq} = H^+_{aq} + Cl^-_{aq} + 1/2O_{2gas}$) was excluded for yet unknown reasons]. On this basis, we estimated factor i at 1.67. It is appropriate to note that the calculated $C^*(Cl_2)$ concentration coincides accurately to within the rounding error with the reference value of the solubility of chlorine.

The chain of equalities (7) can easily be extended to the case $k^* > 2$, if the index of summation (over i) and, correspondingly, C_Σ be attributed to the complete list of the detailed components B_i formed with participation of the entire set of gross-components $B_{(j)}$. Naturally, in the $k^* > 2$ case, factor $\boldsymbol{i}$ will be a function of not only the sum of $C^*_{B(j)}$ concentrations but of their ratios as well. However, this leaves open the possibility to represent the generalized variant in the form:

$$-\langle C^*_A\rangle\, \Delta\mu_A \cong RT\left[\sum_{i=1}^{l-1} C_{Bi}\right] \equiv RT\, C_\Sigma = \boldsymbol{i}\, RT\left[\sum_{j=1}^{k^*-1} C^*_{B(j)}\right], \qquad (8)$$

where factor $\boldsymbol{i}$ is given by the ratio

$$C_\Sigma / \sum_{j=1}^{k^*-1} C^*_{B(j)}.$$

Equations (7) and (8) clearly demonstrate the reasons for μ^*_A (and, hence, for μ_A) to decrease and provide a universal tool for estimating the decrease observed when one or several gross-components B are added to any liquid solvent A in the case that C^*_B or $\Sigma\, C^*_{B(j)}$, and correspondingly C_Σ, take values such that the system does not fall beyond the range of acceptable approximation (6) for any detailed component B_i from the complete list. Therefore, the results of the fundamental chemical-thermodynamic analysis as expressed in form (7) and (8) can provide a deeper insight into osmotic phenomena, Raoult's and Henry' laws, cryoscopy, ebullioscopy, etc., so their use can be more efficient, as briefly illustrated below.

Osmotic pressure. Schemes I and II (see figure) present the results of two slightly different realizations of the same process in the so-called van't Hoff equilibrium box [8, 15], i.e., in an abstract device with an ideal semipermeable membrane.

To obtain the desired expression for the osmotic pressure π it will be sufficient to consider the following equalities, valid under the restrictions behind relations (7):

$$(\partial\mu^*_A/\partial P)_{T,\,n^*}\, (n_B{}^* \ll n_A{}^*) = \overline{V}^*_A \cong \overline{V}_A \cong \widetilde{V}_A \cong \langle C^*_A\rangle^{-1}, \qquad (9)$$

where $\widetilde{V}_A$ is the specific molar volume of liquid A, and $\overline{V}^*_A$ and $\overline{V}_A$, partial molar volumes of the initial and detailed components, respectively.

With the differences between $\langle C^*_A\rangle$ and $C^{*\,0}_A$, the secondary medium effects, and the compressibility effects disregarded, we have:

$$\pi \cong RT\, C_\Sigma = i\, RT\, C^*_B. \qquad (10)$$

In variant I, which considers cell (a) at fixed T, P, the pressure in cell (b) should be decreased by π at the same temperature in order that membrane equilibrium in distribution of component A between these cells be reached. In variant II, by contrast, there is a need to increase by π the pressure in cell (a) when component B is added to the cell under conditions of membrane equilibrium for component A, occurring in this cell, with pure solvent A, occurring in cell (b) at fixed T, P. In the former case, μ^*_A (and, hence, μ_A) decreases by the same value in cell (a) (due to adding component B at fixed T, P) and in cell (b) (due to decrease in pressure by π). In the latter case, μ^*_A and μ_A remain unchanged in both cells: In cell (a), the effect from addition of component B at concentration C^*_B is compensated by that from increase in pressure by π in the same cell, and in cell (b) these parameters are constant. Naturally, for systems with

$$C_\Sigma / \sum_{j=1}^{k^*-1} C^*_{B(j)}$$

[Eq. (8)] instead of C^*_B [Eq. (7)], estimation of C_Σ by solving the direct problem of chemical equilibrium requires knowledge of the entire set of the initial concentrations $C^*_{B(j)}$.

Raoult's and Henry's laws. For monomolecular dissolved individual substances at $C_B << C^{*\,0}_A$ the following relationship was experimentally established:

$$\Delta P_A/P^0_A = (P^0_A - P_A)/P^0_A \cong N_B \cong C_B/C^{*0}_A, \qquad (11)$$

where P^0_A and P_A are the partial pressures of the monomolecular component A in saturated vapor of pure solvent and solution, respectively.

The chemical-thermodynamic interpretation of this empirical law (Raoult's law) can be provided with the use of the universal relation for such systems:

$$<C^*_A> \Delta\mu_A + RT\, C_B = 0. \qquad (12)$$

This expression represents a special case of a more general relationship (7). Considering another well-known relation

$$\Delta\mu_A \cong RT \ln (P_A/P^0_A)$$
$$= RT \ln [(P^0_A - \Delta P_A)/P^0_A] \cong -RT\, \Delta P_A/P^0_A, \qquad (13)$$

we obtain from (12) the following expression:

$$\Delta P_A/P^0_A \cong C_B/<C^*_A> \cong N_B. \qquad (14)$$

Obviously, Raoult's law also applies to cases that require replacing C_B in Eq. (12) and, correspondingly in Eq. (14), by C_Σ [in interpretations, referring to (7) and (8)].

Along with derivation on the basis of relations (12) and (13) [Eq. (14)], Raoult's law can be "derived" as a form of appearance of another well-known empirical law, Henry's law. Specifically, for monomolecular dissolved gases there exists a proportionality between their partial pressures P_B and molar fractions N_B in solutions saturated at T, P_B:

$$P_B \cong (K^0_{H,N})_B\, N_B, \qquad (15)$$

where $K^0{}_{H,N}$ are the empirically determined Henry's law constants for $N_B \le 0.001$ in the ideal gas approximation.

In deriving (14) from (15), the applicability of (15) to component A is also presumed:

$$P_A \cong (K^0_{H,N})_A\, N_A. \qquad (16)$$

Expression (16) leads to $K^0_{H,N} \cong P^0_A$ at $N_A = 1$ and, further, to Eq. (14). However, in view of the restrictions behind Eqs. (1)–(6) and, correspondingly Eq. (12), component A (whose source is the solvent) and B (whose source is the solute, which is added to the solution in relatively small amounts) are clearly differentiated between the two initial component considered. Therefore, no changes are inacceptable for the addresses in the terms of Eq. (12). Among the six above-mentioned equations, the justification of Henry's law employs the last-named one solely. To demonstrate this, we will consider the equilibrium for the process:

$$B_{solv}\ (\text{chem. form in soln})$$
$$\leftrightarrow B_{gas}\ (\text{indiv. subst. or chem. form B in gas}). \qquad (17)$$

The following known characteristics correspond to this process:

$$\Delta_r G = \tilde{G}_B\,(\text{gas}) - \bar{G}_B\,(\text{soln})$$
$$= \bar{G}_B\,(\text{gas}) - \bar{G}_B\,(\text{soln}) = \Delta_r\mu, \qquad (18)$$

where $\tilde{G}_B$(gas) is the specific molar Gibbs energy of the gas formed by detailed component B, and $\bar{G}_B$(gas) and $\bar{G}_B$(soln), partial molar Gibbs energies of detailed component B in the gaseous and liquid solutions, respectively.

The equilibrium condition implies $\Delta_r G = \Delta_r\mu = 0$, from whence, considering (6), it follows:

$$\Delta_r\mu^0 = \mu^0_{B,C}\,(\text{gas}) - \mu^0_{B,C}\,(\text{soln})$$
$$= -RT \ln K^0_{H,C}, \qquad (19)$$

where

$$(K^0_{H,C})_B \cong C_B(\text{gas})/C_B(\text{soln}). \qquad (20)$$

The mass action law for the equilibria of type (17) processes, written in form (20), can easily be reformulated into the common expression of Henry's law [with C_B(gas) replaced by P_B, or with C_B(soln) replaced by N_B]. It should be emphasized, however, that specifically Eqs. (19) and (20) can underlie deriving the data on how changes in the nature of single- or multicomponent solvents can influence the primary medium effects as part of μ_i^0 or $\mu_i^{\otimes}$ [8, 9] for any detailed components and as part of $\Delta_r\mu_j^0$ or $\Delta_r\mu_j^{\otimes}$ (and correspondingly K_j^0 or $K_j^{\otimes}$) for any reactions involving the forms produced by these components in the media considered. Also noteworthy is the fact that the concept of the "primary medium effect" exerted by pure solvent A (as part of μ_i^0) and by pure complex solvent (as part of $\mu_i^{\otimes}$ in a more general case) applies not only to all detailed components B_i but also to all detailed components in whose terms the composition of the solvent proper can be represented [2, 13].

Cryoscopy. Cryoscopic technique is underlain by the phenomenon of depression of the incongruent freezing (solidification) point of a liquid solution relative to the freezing point of a pure solvent. We will consider this phenomenon in the context of a generally available example:

$$H_2O_{liq} \leftrightarrow H_2O_{ice}\ (1h), \tag{21}$$

$$\Delta_r G = \widetilde{G}(1h) - \widetilde{G}(liq) = 0,$$
$$\text{at } T = 273{,}15\text{ K}, P = 1\text{ atm}. \tag{22}$$

When any individual substance is dissolved in water, a bicomponent (in terms of gross-components) solution is formed. Therefore, to describe incongruent freezing (solidification), phase reaction (21) should be replaced by a heterogeneous process with chemical form H_2O_{solv} and ice 1h acting as reactants:

$$H_2O_{solv} \leftrightarrow H_2O\ (1h), \tag{23}$$

$$\Delta_r G = \widetilde{G}\ (1h) - \overline{G}(H_2O) = 0 = \Delta_r H - T\Delta_r S, \tag{24}$$

$$\Delta_r S = \Delta_r H/T. \tag{25}$$

Using Eqs. (24) and (25), we will assess the two effects exerted on $\Delta_r G$ of reaction (23), which should cancel each other under the equilibrium conditions:

$$\Delta_1(\Delta_r G) = -\Delta\mu(H_2O) \cong C_\Sigma RT/\langle C^*(H_2O)\rangle, \tag{26}$$

$$\Delta_2(\Delta_r G) \cong -(\Delta_r H/T)\Delta T. \tag{27}$$

The approximation sign in equalities (26) and (27) is due solely to neglect of the influence exerted by the secondary medium effects on the chemical potentials of the set of the detailed components responsible for C_Σ in the former equality and of that exerted by the presence of these components in solution and by depression of the temperature on $\Delta_r H/T$, in the latter equality. Using Eqs. (26) and (27) we can easily obtain:

$$\Delta T_{freez} \cong (RT^2/\langle C^*(H_2O)\rangle\ \Delta_r H_{melt})\ C_\Sigma = K_{cr}\ C_\Sigma. \tag{28}$$

Naturally, the applicability of Eq. (28) is subject to restrictions identical to those mentioned above for relationships (26) and (27).

After substituting $R = 1.986$ cal mol^{-1} K^{-1}, $T = 273.15$ K, $\langle C^*(H_2O)\rangle \cong 55.5$ M, $\Delta_r H_{freez} = -\Delta_r H_{melt} \cong -1.44$ kcal mol^{-1} in Eq. (28) we obtain $K_{cr} = 1.86$ K L mol^{-1}.

In a similar way it is possible to substantiate the meaning and value of the ebulioscopic constant K_{eb}, which was estimated at 0.535 K L mol^{-1} for aqueous solutions.

Here, we for the first time presented the derivation of relations (7) and (8) in a consistent way, with all the necessary restrictions indicated. This task could not have been accomplished without directly referring to the specific features of the detailed components as compared to the initial components [2–4] and to the principle of universal behavior of a substance in dispersed state according to van't Hoff's theory [15]. We will emphasize the fact that, in order that relations (7) and (8) can be used effectively for any purpose, including interpretations of colligative properties of solutions, serious consideration should be given to both nontrivial relationships and differences between the terms *initial component* and *phase* and *detailed component* and *chemical form*, as well as to the notions of the primary and secondary medium effects [2–4]. Specific aspects of neglecting these issues in routine practice of studying complex equilibria in solutions were considered on a number of occasions previously [9, 11].

In our opinion, supplementing the consequences of the fundamental equations by relations (7) and (8) will offer a scope for improving the techniques for examination and description of any processes involving chemical forms in solutions, including those in areas of significant manifestation of the secondary medium effects [16].

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