CHEMICAL SCIENCES

THERMODYNAMIC CHARACTERISTICS OF NON-REGULAR CONDENSED SYSTEMS WITH IMPURITY POLYATOMIC PARTICLES

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https://doi.org/10.5281/zenodo.13325895

Abstract

The paper considers the problems of changing the thermodynamic characteristics of a system when dissolving polyatomic particles in a condensed medium. It is shown that the complete measurement of the free energy of a system includes the following main components: 1) Changes associated with the formation of a cavity in the medium in which the impurity particle is located, 2) Free energy associated with the translational and rotational motion of the particle as a whole, 3) The electrostatic part associated with the interaction of the particle with the medium.

The paper presents the results of calculations of the thermodynamic characteristics of condensed systems with polyatomic impurity particles, taking into account the effects of frequency and spatial dispersion of the medium.

Keywords: condensed systems, polyatomic particles, thermodynamic characteristics, free energy, Green functions.

1. Introduction

When polyatomic particles dissolve in a condensed medium, a number of characteristics of the system change, including thermodynamic ones [1, p. 859; 2, p.1181; 3, p.8095; 4, p.293]. A complete change of the free energy of a system includes the following components: 1) The work connected with the formation of a cavity in the medium in which the impurity particle is located, 2) Free energy associated with the translational and rotational motion of the particle as a whole, 3) The electrostatic part connected with the interaction of the particle with the medium.

The first part of the change in the free energy of the system can be calculated for a specific medium, taking into account its structure, chemical bonds between the molecules of the medium (for liquid media); the lattice structure for solid crystalline media, and the molecular structure for solid amorphous media.

The second part of the change in the free energy of the system can also be calculated for specific systems, for a specific model of the environment.

The third part of the change in the system's free energy, the electrostatic part connected with the interaction of a particle with a condensed medium, usually makes the main contribution to the total change in the system's free energy. The presence of electrostatic interaction between an impurity particle (generally having a charge and a dipole moment) and the medium leads to polarization of the medium, a change in the distribution of charges and dipole moments of the molecules of the medium [5, p.1; 6, p. 362; 7, p. 2; 8, p. 530; 9, p. 425; 10, p. 54]. The latter leads to additional polarization of the particle.

2. Hamiltonian of the system

The Hamiltonian of the system — a condensed medium with an impurity particle, can be represented as:

$$H = \delta\Omega_0 + H^P + H^m + H_{int}^S + H_{int}^Q \quad (1)$$

Where, H^P is the Hamiltonian of the polarized particle, H^m is the Hamiltonian of the polarized medium, and H_{int}^S and H_{int}^Q are the Hamiltonians of the interactions of the polarization fluctuations of the medium with the static field of the impurity and intramolecular vibrations of impurities, respectively:

$$H_{int}^S = -\int d\vec{r}\delta\vec{P}\,(\vec{r})\overrightarrow{E_0}(\vec{r});\ \overrightarrow{E_0}(\vec{r}) = \vec{E}(\vec{r}, Q = Q_0) \quad (2)$$

$$H_{int}^Q = -\sum_n \int d\vec{r}\,\delta\vec{P}\,(\vec{r})V_n(\vec{r})(Q_n + Q_{n0})$$

Here $\delta\vec{P}$ is the operator of fluctuations in the polarization of the medium, $\overrightarrow{E_0}$ is the electric field intensity of a charged impurity particle, $V_n(\vec{r})$ is the derivative of the electric field intensity of the particle along the normal coordinate at the point Q_{n0} of equilibrium value of the coordinate Q_n

$$V_n(\vec{r}) = \frac{\partial\vec{E}(\vec{r})}{\partial Q_n}, Q_n = Q_{n0} \quad (3)$$

In formula (1) $\delta\Omega_0$ is the free energy of solvation, equal to

$$\delta\Omega_0 = \frac{1}{2}\int E_\alpha(\vec{r}, Q = Q_0) G_{P_\alpha P_\beta}\left(\vec{r}, \vec{r'};\ \omega = 0\right) E_\beta\left(\vec{r'}, Q_n = Q_0\right) d\vec{r} d\vec{r'} \tag{4}$$

Here $\vec{E}$ is the electric field intensity of the impurity at equilibrium values Q_0 of the intramolecular coordinates Q. $G_{P_\alpha P_\beta}$ is the Green's function of the polarization operators of the medium at zero frequencies $\omega = 0$.

Hamiltonian H^m differs from the Hamiltonian of nonpolarized medium by the magnitude:

$$\delta F^m = \frac{1}{2}\int d\vec{r} \langle \vec{P}(\vec{r}) \rangle \vec{E}(\vec{r}, Q) \tag{5}$$

In the last formula, the quantum statistical average polarizations of the medium are calculated from the states of the Hamiltonian without impurity particles.

Within the framework of linear response theory, the average polarization of a medium can be expressed in terms of the electric field intensity created by a polarized particle. As a result, for the magnitude δF^m we obtain:

$$\delta F^m = \frac{1}{2}\int E_\alpha(\vec{r}, Q) G_{P_\alpha P_\beta}\left(\vec{r}, \vec{r'};\ \omega = 0\right) E_\beta\left(\vec{r'}, Q\right) d\vec{r} d\vec{r'} \tag{6}$$

Free energies $\delta\Omega_0$ and δF^m differ by the difference of the free energies of impurity particle in solvated state and in vacuum:

$$\delta\Omega_0 - \delta F^m = kTln \prod_{n=1}^{N} 2sh\frac{\omega_n}{2kT} - kTln \prod_{n=1}^{N} 2sh\frac{\omega_{n0}}{2kT} + J_0 \tag{7}$$

Where ω_n and ω_{n0} are the frequencies of n-th intramolecular vibration of the particle in the solvated state and in vacuum, J_0 is the difference of the minimal values of the energies of the impurity particle in the solvated state and in vacuum, N is the number of intramolecular degrees of freedom of the particle:

We write the electrostatic part of the change in the system's free energy connected with the introduction of a polyatomic polarizable impurity particle into the condensed medium in the form

$$\delta\Omega = \delta\Omega_0 + \delta F^m + \delta\Omega_1 + \delta\Omega_2 \tag{8}$$

Where $\delta\Omega_1$ and $\delta\Omega_2$ are changes in the free energy of the system associated with interaction H_{int}^S and H_{int}^Q.

3. System's free energy change when uncharged non-dipole particles are introduced into the condensed medium

For uncharged non-dipole particles, the change in the free energy of the system can be calculated in a model in which H_{int}^S is equal to zero, and, accordingly, $\delta\Omega_1 = 0$.

To calculate the change in the free energy of a system associated with the presence of interaction $\delta\Omega_2$ between systems and an external source, you can use the relationships between the free energy of the system and S_2 the matrix of interaction with an external source:

$$\delta\Omega_2 = -kTln\langle S_2 \rangle \tag{9}$$

where averaging is carried out over the states of the Hamiltonian $H_0 = H^P + H^m$, and S_2 matrix is determined by the relation

$$S_2 = Texp\left[\int_0^{1/kT} d\tau \int d\vec{r} \delta\vec{P}(\vec{r}, \tau) \vec{V_s}(\vec{r}) Q_s(\tau)\right] \tag{10}$$

Let us introduce formally $S_2(\lambda)$ matrix, which differs from the matrix S_2 by replacing $\vec{V_s}$ with $\vec{V_s}\lambda$. After simple transformations we get

$$\delta\Omega_2 = -kT\int_0^1 \frac{d\lambda}{\lambda}\int_0^{1/kT} d\tau \int d\vec{r}\, \lambda \vec{V}_{s\alpha}(\vec{r})\, G_{P_\alpha Qs}(\vec{r}, \lambda, \tau = 0) \tag{11}$$

In the Fourier representation by time, the last relation takes the form

$$\delta\Omega_2 = -kT\int_0^1 \frac{d\lambda}{\lambda}\int d\vec{r}\, \lambda V_{s\alpha}(\vec{r}) \sum_{n=-\infty}^{\infty} G_{P_\alpha Qs}(\vec{r}, \lambda, \omega_n) \tag{12}$$

Expanding the S_2-matrix into a series in formula (10), we obtain quasi-statistical averages from the operators $\delta\vec{P}$ and Q_s under the sign of the T - product over the states of the Hamiltonian H^P. In accordance with Wick's theorem, such averages are decoupled into paired averages, since the Hamiltonian H^P is quadratic over Q_s. As for the quantum statistical averages of the operators $\delta\vec{P}$, it is possible, to a certain approximation, to decouple them into paired averages. In this case, we will obtain a system of linear algebraic equations for determining the Green's functions G_{QQ}, which will have the form

$$G_{Q_s Q_l}(\lambda; \omega_n) = G_{Q_s Q_l}^0 + \sum_P G_{Q_s Q_s}^0(\omega_n) U_{sp}(\lambda; \omega_n) G_{Q_p Q_l}(\lambda; \omega_n) \tag{13}$$

Where U_{sp} is the renormalized interaction of normal oscillators (of intramolecular vibrations) with each other through the medium

$$U_{sp}(\lambda; \omega_n) = \lambda^2 U_{sp}(\omega_n) \tag{14}$$

In the last formula G_{QQ} is the temperature Green function of the harmonic oscillator. At the same time, for $\delta\Omega_2$ we have:

$$\delta\Omega_2 = -kT\int_0^1 \frac{d\lambda}{\lambda}\sum_{n=-\infty}^{\infty} U_{sp}(\lambda; \omega_n) G_{P_s Qp}(\vec{r}, \lambda, \omega_n) \tag{15}$$

Having determined the components G_{QQ} from system (13), by the corresponding summation over n and integration over λ in formula (15), we can calculate the magnitude of the change in the free energy of the system $\delta\Omega_2$.

If an impurity particle has one intramolecular degree of freedom, then to calculate the change in the free energy of the system we obtain (for simplicity, let's write it in operator form):

$$\delta\Omega_2 = \frac{kT}{2}\sum_{n=-\infty}^{\infty} Spln\left|G_{QQ}^0 G_{QQ}^{-1}\right| = \frac{kT}{2}\sum_{n=-\infty}^{\infty} Spln\left|1 - G_{QQ}^0 U\right| \tag{16}$$

In the polar approximation model [11, p. 43] in the Green function of the medium polarization fluctuation operators, the renormalized interaction $U(\omega_n)$ takes the form:

$$U(\omega_n) = \sum_{i=1}^{m} \frac{u_i}{\omega_i - |\omega_n|} \tag{17}$$

Where u_i and ω_n are experimental constants of medium spectrum, m – is the number of poles of the Green function of the polarization operators of the medium.

As a result, for the change in the free energy of the system we obtain:

$$\delta\Omega_2 = \frac{kT}{2} ln \prod_{n=1}^{\infty}\left\{\left|1 - \sum_{i=1}^{m} \frac{u_{i\omega_s}}{(\omega_n^2 + \omega_s^2)(\omega_i - |\omega_n|)}\right|\right\} + ln\left(1 - \frac{U(0)}{\omega_s}\right) \tag{18}$$

Let's represent the expression in curly brackets in the last formula as a ratio of two polynomials ${P_1}/{P_2}$:

$$P_1 = \left[\left(\frac{\omega_s}{2\pi kT}\right)^2 + n^2\right] \prod_{i=1}^{m}\left(\frac{\omega_i}{2\pi kT} - n\right) - \sum_{i=1}^{m} \frac{u_i \omega_s}{(2\pi kT)^2} \prod_{k \neq i}^{m}\left(\frac{\omega_i}{2\pi kT} - n\right) \tag{19}$$

$$P_2 = \left[n^2 + \frac{{\omega_s}^2}{(2\pi kT)^2}\right]\prod_{i=1}^{m}\left(\frac{u_i}{2\pi kT} - n\right)$$

From the theory of Γ-functions it is known [12, p.16] that if the condition of equality of sums of coefficients in the form

$$a_1 + \ldots + a_l = b_1 + \ldots + b_l \quad (20)$$

is satisfied, then the product of ratios of polynomials can be reduced to Γ-functions using the following formula

$$\prod_{n=1}^{\infty}\frac{(n-a_1)\ldots(n-a_l)}{(n-b_1)\ldots(n-b_l)} = \prod_{i=1}^{l}\frac{\Gamma(1-b_i)}{\Gamma(1-a_i)} \quad (21)$$

Within our model, condition (20) is satisfied.

As a result, the change in the free energy of the system can be represented as:

$$\delta\Omega_2 = kTln\frac{kT}{\omega_s} + kTln\left(2sh\frac{\omega_s}{2kT}\right) + \frac{kT}{2}ln\left(1 - \frac{U(0)}{\omega_s}\right) + kTln\prod_{i=1}^{m+2}\Gamma\left(1 - \frac{\mu_i}{2\pi kT}\right) - kTln\prod_{i=1}^{m}\Gamma\left(1 - \frac{\omega_i}{2\pi kT}\right) \quad (22)$$

Where μ_i are the roots of the equation:

$$\left[\left(\frac{\omega_s}{2\pi kT}\right)^2 + n^2\right]\prod_{i=1}^{m}\left(\frac{\mu_i}{2\pi kT} - n\right) - \sum_{i=1}^{m}\frac{u_i\omega_s}{(2\pi kT)^2}\prod_{k\neq i}^{m}\left(\frac{\mu_i}{2\pi kT} - n\right) = 0 \quad (23)$$

From relation (22) it is clear that if the condition $U(0) \to \omega_s$ is satisfied, then the change in the free energy of the system tends to infinity, which corresponds to the dissociation of a particle in a polar medium.

In the literature, approximate models are often used to describe the absorption spectra of a medium: Debye G_{PP}^{D} and resonant G_{PP}^{R}:

$$G_{PP}^{D}\left(\vec{r}, \overrightarrow{r'}; \omega\right) = \frac{C_0}{4\pi}\frac{\gamma_0}{\gamma_0 + i\omega} \quad (24)$$

$$G_{PP}^{R}\left(\vec{r}, \overrightarrow{r'}; \omega\right) = -\frac{C}{8\pi}\frac{\omega_r^2 + \gamma^2}{\omega_r}\left[\frac{1}{\omega - \omega_r + i\gamma} - \frac{1}{\omega + \omega_r + i\gamma}\right] \quad (25)$$

Here C_0, C, γ_0, γ, ω_r are spectra parameters.

For the Debye absorption spectrum of the medium for the change in free energy, we obtain:

$$\delta\Omega_2 = \frac{1}{2}kTln(1 - \text{ǽ}) + kTln\frac{\Gamma_1}{\Gamma_2} \quad (26)$$

Where Γ_1 and Γ_2 - can be reduced to Γ-functions

$$\Gamma_1 = \Gamma\left(1 - \frac{\mu_1}{2\pi kT}\right)\Gamma\left(1 - \frac{\mu_2}{2\pi kT}\right)\Gamma\left(1 - \frac{\mu_3}{2\pi kT}\right)$$

$$\Gamma_2 = \Gamma\left(1 - \frac{\gamma_0}{2\pi kT}\right)\Gamma\left(1 - \frac{i\omega_s}{2\pi kT}\right)\Gamma\left(1 + \frac{i\omega_s}{2\pi kT}\right) \quad (27)$$

Here the values of μ_1, μ_2, μ_3 are determined from the solution of the equation

$$(\omega^2 + \omega_s^2)(\omega + \gamma_0) - \omega_s^2\gamma\,\text{ǽ} = (\omega - \mu_1)(\omega - \mu_2)(\omega - \mu_3) \quad (28)$$

The coefficient of connection strength with the medium ǽ is equal to:

$$\text{ǽ} = -\frac{C_0}{4\pi}\int d\vec{r}d\overrightarrow{r'}V_\alpha(\vec{r})\,G_{P_\alpha P_\beta}\left(\vec{r}, \overrightarrow{r'};\ \omega = 0\right)V_\beta(\vec{r}) \quad (29)$$

At a weak connection with the medium, under which the condition ǽ ≪ 1 is satisfied, we get

$$\delta\Omega_2 = -\frac{1}{2}\,\text{ǽ}kT - \frac{\text{ǽ}}{2\pi}\frac{\gamma_0\omega_s^2}{\omega_s^2 + {\gamma_0}^2}\left[\frac{\pi\gamma_0}{2\omega_s}cth\frac{\omega_s}{2kT} - \pi kT\frac{2\omega_s^2 + {\gamma_0}^2}{\gamma_0\omega_s^2} - \Psi\left(\frac{\gamma_0}{2\pi kT}\right) + Re\Psi\left(\frac{i\omega_s}{2\pi kT}\right)\right] \quad (30)$$

Here Ψ-functions (logarithmic derivatives of the corresponding Γ-functions) have certain approximate representations [12, p. 31].

For the resonant approximation of the Green functions of the polarization operators of the medium in the form (25) for the change in the free energy of the system, we obtain:

$$\delta\Omega_2 = -\frac{1}{2}\,\text{ǽ}kT - \text{ǽ}kT\frac{\omega_s^2(\omega_r^2 + \gamma^2)}{\left(\omega_r^2 + \gamma^2 - \omega_s^2\right)^2 + 4\gamma^2\omega_s^2}\cdot\left[\frac{\omega_r^2 + \gamma^2 - \omega_s^2}{4kT\omega_s}\left(cth\frac{\omega_s}{2kT} - \frac{2kT}{\omega_s}\right) + \frac{\gamma}{\pi kT}Re\Psi\left(\frac{i\omega_s}{2\pi kT}\right) - \frac{\omega_s^2 + 3\gamma^2 - \omega_r^2}{\omega_r^2 + \gamma^2} - \frac{\gamma}{\pi kT}Re\Psi\left(\frac{\gamma + i\omega_r}{2\pi kT}\right) + \frac{\omega_r^2 + \gamma^2 - \omega_s^2}{2\pi kT\omega_s}Im\Psi\left(\frac{\gamma - i\omega_r}{2\pi kT}\right)\right] \quad (31)$$

When using the obtained theoretical results for specific systems, it is necessary to consider a number of approximate results.

First of all, this concerns the use of Γ-functions and Ψ-functions, which can be expressed through approximately calculated expressions.

Depending on the required accuracy of calculations, various integral representations of these functions can be used [12, p. 16]. In this case, integral expressions allow approximate calculations with the required accuracy. In particular, for the Γ-function, its integral representation has the form:

$$\Gamma(z) = \frac{1}{z}\int_0^\infty e^{-t}t^z dt = \frac{1}{z}\Gamma(1 + z) \quad (32)$$

For the Ψ-function, one can use the integral representation in the form [12, p. 31]:

$$\Psi(z) = -\gamma + \int_0^\infty\frac{e^{-t} - e^{-tz}}{1 - e^{-t}}dt;\ \text{Re z>0}$$

$$\Psi(z) = -\gamma - \pi ctg(z\pi) + \int_0^1\frac{1 - t^{-z}}{1 - t}dt;\ \text{Re z<1} \quad (33)$$

4. Change in the free energy of the system when introducing charged non-dipole particles into the condensed medium

The above results allow us to calculate the energy parameters of the system when introducing uncharged non-dipole particles into the condensed medium.

When introducing charged non-dipole particles into the condensed medium, we can calculate the change in the free energy of the system

$\delta\Omega_1 = -kTln\langle S_1\rangle_0$ (34)

Using the above calculation methods, it is easy to show that

$$\delta\Omega_1 = \frac{1}{2}\int d\vec{r}\,d\overrightarrow{r'}E_i(\vec{r})G_{\delta P_i\delta P_k}\left(\vec{r}, \overrightarrow{r'}; \omega = 0\right)E_k\left(\overrightarrow{r'}\right) \quad (35)$$

Numerical calculations for specific models of condensed medium can be carried out using the above formulas for the Green's function of the medium polarization operators for these specific models.

5. Conclusion

The paper considers the problems of changing the thermodynamic characteristics of a system

when dissolving polyatomic particles in a condensed medium. It is shown that the complete measurement of the free energy of a system includes the following main components: 1) Changes associated with the formation of a cavity in the medium in which the impurity particle is located, 2) Free energy associated with the translational and rotational motion of the particle as a whole, 3) The electrostatic part associated with the interaction of the particle with the medium.

It is proposed to calculate the first part of the change in the free energy of the system for specific media: for liquid media, taking into account the structure of the medium and the chemical bonds between the molecules of the medium; for solid crystalline media, taking into account the lattice structure; and for solid amorphous media, taking into account the molecular structure of the medium. It is proposed to calculate the second part of the change in the free energy of the system for a specific model of the medium. In the third part of the change in the free energy of the system, which, as a rule, makes the main contribution to the total change in the free system, calculations are carried out for specific models of polarization of the medium, changes in the distribution of charges and dipole moments of the molecules of the medium.

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