

# THE LIMIT SOLUBILITY RELATIONSHIPS BASED ON FRENKEL'S HETEROPHASE FLUCTUATIONS THEORY

*R. V. Shapovalov*<sup>1\*</sup> and *O. A. Osmayev*<sup>2,1</sup>

<sup>1</sup>National Science Center "Kharkov Institute of Physics and Technology", 61108, Kharkov, Ukraine

<sup>2</sup>Ukrainian State Academy of Railway Transport, 61050, Kharkov, Ukraine

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For a weak one-component solution, in which the solvent and dissolved substances are not chemically bound, a simple analytical approximation was found for temperature dependence of limiting solubility of the dissolve substance. The derivation of the approximation is based on the Frenkel theory of heterophase fluctuations. It was shown how the parameters of this analytical approximation can be related to experimental data.

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## 1. INTRODUCTION

It is known that generally the quantity of solute which can be dissolved in a solvent under given temperature is limited. As a rule the solvent capability to dissolve grows together with temperature. The system, where solute fraction is less or equals the corresponding limit, is in equilibrium state under unchangeable environment. In 1939 it was pointed out by Frenkel [1] that in general case in the equilibrium solution along with monomers there are clusters of two and more solute atoms. Starting from the above mentioned paper these clusters are considered as heterophase fluctuations. The cluster's size distribution function was obtained in paper [1] from the principle of thermodynamic potential minimum. In paper [2] much more simple way was proposed for obtaining the distribution function. The method was based on the stationary solution of the system of Becker-Döring equations. In paper [2] it was demonstrated also a causal relationship between heterophase fluctuations and the characteristic times of successive stages of nucleation in a supersaturated solution. The method of study was numerical solution of the Fokker-Plank equation.

In the present work the authors attempt to carry the Frenkel's idea of heterophase fluctuations through to its logical completion. We choose the simplest kind of such systems – a weak perfect single component solution where solute and solvent do not react chemically. This simplest system is still a good approach to e.g. inorganic water dissolved salts.

## 2. BASIC EQUATIONS

It is known that the time evolution of solute clusters size distribution function is described by a system of

Becker-Döring kinetic equations

$$\frac{\partial f(x, t)}{\partial t} = I(x-1, t) - I(x, t), \quad x \geq 1 \quad (1)$$

$$I(x, t) = W(x, x+1) f(x, t) - W(x+1, x) f(x+1, t). \quad (2)$$

Here the value  $f(x, t)$  is the number of clusters consisting of  $x$  monomers normalized to the number of atoms/molecules of solvent in unit volume in the present moment of time  $t$ ,  $I(x, t)$  is the cluster flux in cluster size space,  $W(x, x+1)$  is the rate of adsorption of monomers by solute cluster consisting of  $x$  monomers,  $W(x+1, x)$  is the rate of desorption of monomers off the solute cluster consisting of  $x+1$  monomers.

Equation (1) takes into account the fact of polymer cluster immobility in physical space (at any case the cluster mobility has to be much less than the monomer mobility) and their interaction only by adsorption or emission of mobile monomers. At the same time the probability of an elementary process with two and more monomers is negligibly small. This is an analogy of the mean field approximation. Analytical form of transient rates is given as a rule by the following expressions

$$W(x, x+1) = \frac{3D}{a^2} x^{1/3} c(t), \quad (3)$$
$$W(x, x-1) = \frac{3D}{a^2} c_e x^{1/3} \exp\left(\frac{\beta_1 \cdot x^{-1/3}}{T}\right).$$

Here  $D$  is the diffusion coefficient of monomer in solution,  $a$  is the lattice parameter of a cluster or, that is the same, of a solute matter in parent phase,  $c(t)$  is the monomers concentration,  $c_e$  is it equilibrium value,  $\beta_1 = \frac{8\pi a^2 \gamma}{3k_B}$  is the cluster surface energy in

\*Corresponding author E-mail address: r\_v\_shapo@kipt.kharkov.ua

temperature units,  $\gamma$  is the specific surface energy,  $k_B$  is Boltzmann constant, and  $T$  is the temperature.

There is an evident and conventional approach to the study and solution of equation (1). It consists in the transformation of discrete variable into its analog quantity and solving the corresponding Fokker-Plank equation thus obtained from equation (1). The parabolic differential equation can be solved analytically only approximately for some initial conditions and certain supplementary considerations. The process of its treatment becomes much more complicated if the solute conservation law is taken into account. In that case one can use numerical methods. It is also known that studying relatively small time interval one needs no conservation law and that the asymptotic solution results from arbitrary physical reliable initial conditions [3].

### 3. EQUILIBRIUM DISTRIBUTION

It is evident that the above equations can be applied to the stable state of the system. In this case the initial conditions are at once the solution of equation (1). If one considers a liquid in condition of limiting saturation then there is no need in conservation law. Actually the most evident way to obtain the saturated solution is to bring into contact some quantity of solvent with an a priori excess of solute substance. It is evident that some time later the system comes to equilibrium state. Due to excess in advance of sol-

vent the equilibrium system will consist of totally saturated liquid solution being in thermodynamic balance with the residuum of solute substance. Without loss of generality let us consider a flat interface of a cluster. For weak perfect solutions it yields

$$\psi_s + T \ln c_e = \psi_b .$$

Therefore

$$c_e = \exp(-\Delta\psi/T) , \quad (4)$$

where  $\psi_s$  is the specific thermodynamic potential of solute in liquid and  $\psi_b$  is the specific thermodynamic potential of solute in parent phase. The difference  $\Delta\psi = \psi_s - \psi_b$  is the variation of specific thermodynamic potential under dilution.

Equations (1) with fluxes (2) have an evident implication for equilibrium state. It is a coupling between distribution function values for different cluster sizes,

$$f(x+1) = \frac{W(x, x+1)}{W(x+1, x)} f(x) .$$

By means of the explicit form of transient rates (3) some evident conclusions from this equation can be received. First a coupling of distribution functions for two values,  $x+1$  and  $y$  respectively can be established, and after simple transformation one obtains the expression for distribution function of arbitrary size expressed in terms of the stationary monomers concentration  $c$

$$f(x+1) = \frac{W(x, x+1)}{W(x+1, x)} f(x) = \frac{\prod_{k=0}^{x-y} (x-k)^{1/3}}{\prod_{k=0}^{x-y} (x-k+1)^{1/3} \exp\left(\frac{\beta_1}{T} (x-k+1)^{-1/3}\right)} \left(\frac{c}{c_e}\right)^{x-y+1} f(y),$$

$$f(x+1) = \exp\left(-\frac{\beta_1}{T} \sum_{k=3}^{x+1} k^{-1/3}\right) \frac{2^{1/3}}{(x+1)^{1/3}} \left(\frac{c}{c_e}\right)^{x-1} \frac{W(1, 2)}{W(2, 1)} f(1).$$

A probability of association of monomers into dimers can have a different form in general case. Let us suppose that

$$W(1, 2) = \frac{3D}{a^2} \cdot B \cdot c(t) , \quad (5)$$

where value  $B$  is a coefficient which defines an efficiency of monomer collision. The coefficient modifies the rate of monomer association. In paper [2] it was accepted  $B = 2$ . In the present paper its numerical value is not considered.

$$\begin{aligned} \frac{W(1, 2)}{W(2, 1)} &= \frac{\frac{3D}{a^2} \cdot B \cdot c}{\frac{3D}{a^2} c_e \cdot 2^{1/3} \cdot \exp\left(\frac{\beta_1}{T} \cdot 2^{-1/3}\right)} \\ &= \frac{c}{c_e} 2^{-1/3} \cdot B \cdot \exp\left(-\frac{\beta_1}{T} \cdot 2^{-1/3}\right). \end{aligned}$$

Since  $f(1) \equiv c(t)$ , then

$$f(x) = \exp\left(-\frac{\beta_1}{T} \sum_{k=2}^x k^{-1/3}\right) \frac{B c_e}{x^{1/3}} r^x , \quad (6)$$

where  $r = c/c_e$  is a ratio of monomer concentration to its equilibrium value. Since in the case of limiting saturation  $c(t) = c_e$ , therefore, cluster distribution function can be written in the form

$$f(x) = \exp\left(-\frac{\beta_1}{T} \sum_{k=2}^x k^{-1/3}\right) \frac{B c_e}{x^{1/3}} . \quad (7)$$

Total value of solute  $q(T)$  is defined either as the number of impurity atoms/molecules relative to the number of solvent atoms/molecules or as volume spe-

cific value. It is defined by the next expression

$$q(T) = \sum_{x=1}^{\infty} x \cdot f(x). \quad (8)$$

As it follows from equations (6) and (8) the limit saturation is given by

$$q_{\text{lim}}(T) = c_e \left[ 1 + B \sum_{x=2}^{\infty} x^{2/3} \exp \left( -\frac{\beta_1}{T} \sum_2^x k^{-1/3} \right) \right]. \quad (9)$$

Just the same expression was obtained in papers [1] and [2]. Strictly speaking the main purpose of the present paper is to transform relationship (9) into more convenient form and to show the association of its parameters with experimental data.

#### 4. APPROXIMATION

Let us come over to summation of heterophase fluctuation. It is necessary to find out a sum of the next series

$$S(\beta) = \sum_{x=2}^{\infty} x^{2/3} r^x \exp \left( -\beta \sum_2^x k^{-1/3} \right). \quad (10)$$

Here the ratio  $\beta = \beta_1/T$  is a dimensionless coefficient.

The method of summation used for calculation of the sum consists in step-by-step application of Euler-MacLoren formula. As it is known [4] for arbitrary function, thrice differentiable on a segment  $M \leq x \leq N$   $F(x)$ , the next relationships is valid

$$\sum_{i=M}^{i=N} F(i) = F(M) + \frac{F(N) - F(M)}{2} + \int_M^N F(x) dx + \frac{F'(N) - F'(M)}{12} + R_3, \quad (11)$$

$$R_3 \leq \frac{1}{120} \int_M^N |F'''(x)| dx, \quad (12)$$

$$\sum_2^x k^{-1/3} = a(x) = 3 \frac{x^{2/3} - 2^{2/3}}{2} + \frac{x^{-1/3} + 2^{-1/3}}{2} - \frac{x^{-4/3} - 2^{-4/3}}{36} + \delta_1(x), \quad (13)$$

where  $R_3$  is the reminder.

The obtained relationship (13) shows that the sought-for series (10) is convergent under condition  $r \leq 1$ . The limit saturation corresponds to the case  $r = 1$ . Further argumentation is related to this case. By means of formula (13) it is easy to show that the absolute error is  $\delta_1 < 3 \cdot 10^{-3}$ . At the same time one can expect that obtained formula is too complicated if it will be repeatedly used in Euler-MacLoren form. It can be shown the penultimate item in expression (13) is not negative and its absolute value could not exceed  $1/90$ . Taking this fact into account one obtains an approximate reduced formula providing a good accuracy.

$$a(x) \approx 3 \frac{x^{2/3} - 2^{2/3}}{2} + \frac{x^{-1/3} + 2^{-1/3}}{2}.$$

In that way expression (10) can be written with a good accuracy in the next form

$$S(\beta) \approx \tilde{S}(\beta) \exp \left( \beta \cdot 5 \cdot 2^{-4/3} \right), \quad (14)$$

$$\tilde{S}(\beta) = \sum_{x=2}^{\infty} x^{2/3} \exp \left( -\beta \frac{3x^{2/3} + x^{-1/3}}{2} - \lambda x \right).$$

Here value  $\lambda = -\ln r = \ln c_e/c$  is nonnegative one. In the received expression slowly increasing power function is multiplied by fast decreasing exponent. Let us transform formula (14) in the same way as (10) but with some simplifications. In expression (11) one keeps only two first terms and retains first term in (14) with unchangeable form to compensate inaccuracy. In that way one gets

$$\begin{aligned} \tilde{S}(\beta) &\approx 2^{2/3} \exp \left( -\beta \cdot 7 \cdot 2^{-4/3} - \lambda \cdot 2 \right) + \\ &+ \frac{3^{2/3}}{2} \exp \left( -\beta \cdot 5 \cdot 3^{-1/3} - \lambda \cdot 3 \right) + \\ &+ \int_3^{\infty} x^{2/3} \exp \left( -\beta \cdot \frac{3x^{2/3} + x^{-1/3}}{2} - \lambda \cdot x \right) dx. \end{aligned}$$

The integral in the obtained relationship plays the main role in the region of small values  $\beta$ . For region  $\beta \leq 10$  one can use a good approximation for involved integral in the next form

$$\begin{aligned} I(\beta) &\approx 3 \exp \left( -\frac{3^{-1/3}\beta}{2} \right) \\ &\times \int_{3^{1/3}}^{\infty} z^4 \exp \left( -\frac{3z^2\beta}{2} - \lambda \cdot z^3 \right) dz. \end{aligned} \quad (15)$$

As the purpose of the work is an investigation of the case of the limit saturated solution it is sufficient to find out the value of expression (14) subject to conditions that  $r = 1 \rightarrow \lambda = 0$ . With that the right side of (15) could be calculated in accordance with the exact formula. This calculation allows us to obtain the unknown sum  $S(\beta)$ .

$$\begin{aligned} &\int_{z_{\min}}^{\infty} z^4 \exp(-b \cdot z^2) dz \\ &= \frac{z_{\min} (3 + 2bz_{\min}^2)}{4b^2} e^{(-bz_{\min}^2)} + \frac{3\sqrt{\pi}}{8b^{5/2}} \operatorname{erfc} \left( b^{1/2} z_{\min} \right), \end{aligned}$$

$$\begin{aligned} S(\beta) &\approx 2^{2/3} \exp \left( -2^{-1/3}\beta \right) \\ &+ \frac{2 \cdot 3^{1/3} + 6\beta + 3^{2/3}\beta^2}{2\beta^2} \exp \left( -5\beta \left( 3^{-1/3} - 2^{-4/3} \right) \right) \\ &+ \frac{\pi^{1/2}}{6^{1/2}\beta^{5/2}} \exp \left( \frac{5\beta}{2^{4/3}} - \frac{3^{-1/3}5\beta}{2} \right) \operatorname{erfc} \left( \frac{3^{5/6}\beta^{1/2}}{2^{1/2}} \right). \end{aligned} \quad (16)$$

It is rather difficult to get an analytical estimate of the error of this expression, but numerical calculation has shown that in a segment  $10^{-2} \leq \beta \leq 10^2$  the given formula provides an accuracy not less than 96%, minimal one has place at  $\beta \approx 0.49$ . The calculations assumed that the upper limit of the sum 10

is  $10^8$ . It can be shown that in this range of  $\beta$  this value of upper limit provides sufficient accuracy.

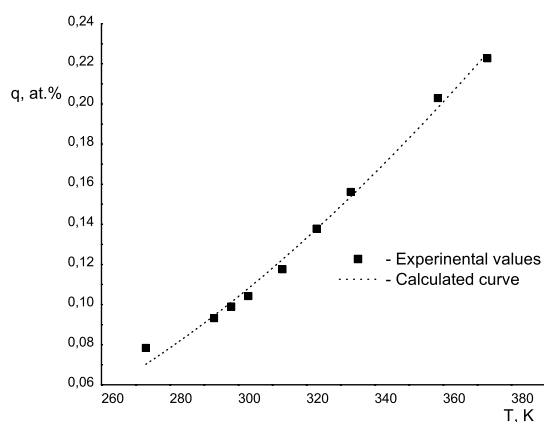
The above calculations allow to write down the maximum concentration of the equilibrium solution at given temperature in the following simple form

$$q_{\text{lim}}(T) = c_e [1 + B \cdot S(\beta)]. \quad (17)$$

For example, consider a water solution of nickel nitrate  $\text{Ni}(\text{NO}_3)_2$ , it has a molecular mass 182.

*The limit concentration of  $\text{Ni}(\text{NO}_3)_2$  in aqueous ammonia [5]*

T, K	273	293	298	303	313
$q \cdot 10^{-2}$	7.84	9.326	9.9	10.425	11.76
T, K	323	333	358.5	373	
$q \cdot 10^{-2}$	13.78	15.61	20.295	22.275	



*The fitting curve for data in the table*

Using data from the table one can construct the fitting curve by means of Levenberg-Marquardt algorithm.

The figure illustrates the fact that the equation (17) quite satisfactory describes the dependence of limit solubility on temperature.

## 5. CONCLUSIONS

1. In the framework of a simple thermodynamic model an analytical expression is obtained which allows to determine the maximal quantity of solute that can be dissolved in a solvent as a function of temperature.
2. By an example of a water solution of nickel nitrate it is shown a good agreement of the found approximation with experimental data.

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## СОТНОШЕНИЕ ДЛЯ ПРЕДЕЛЬНОЙ РАСТВОРИМОСТИ, ПОЛУЧЕННОЕ НА ОСНОВЕ ТЕОРИИ ГЕТЕРОФАЗНЫХ ФЛУКТУАЦИЙ ФРЕНКЕЛЯ

*Р.В. Шаповалов, О.А. Осмаев*

Для слабого однокомпонентного раствора, в котором растворитель и примесь не образуют химического соединения, получено аналитическое приближение, позволяющее найти предельное количество растворенного вещества в зависимости от температуры. Вывод приближения основан на теории гетерофазных флуктуаций Френкеля. Показано, как параметры аналитического выражения могут быть связаны с экспериментальными данными.

## СПІВВІДНОШЕННЯ ДЛЯ ГРАНИЧНОЇ РОЗЧИННОСТІ, ОТРИМАНЕ НА ОСНОВІ ТЕОРІЇ ГЕТЕРОФАЗНИХ ФЛУКТУАЦІЙ ФРЕНКЕЛЯ

*Р.В. Шаповалов, О.А. Осмаев*

Для слабого однокомпонентного розчину, у якому розчинник та домішка не створюють хімічної сполуки, отримано аналітичне наближення, яке дозволяє знайти граничну кількість розчиненої речовини в залежності від температури. Наближення знайдено на базі теорії гетерофазних флуктуаций Френкеля. Показано, як параметри аналітичного співвідношення можуть бути пов'язані з даними експериментів.