

Thermodynamics of the Solid Solutions of Isomorphous Substances

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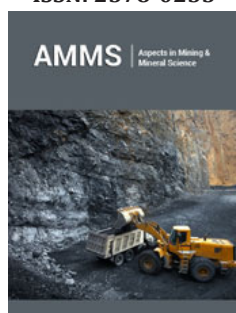
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Abstract

The article described the thermodynamics of binary solid solution of isomorphous inorganic compounds and their influence on the co-crystallization of substances from solutions.

Keywords: Activity coefficient; Chemical potential; Co-crystallization coefficient

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Introduction

The study of the conditions and characteristics of the formation of solid solution play an important role in research the processes of formation of mineral and the technology of processing mineral raw materials. The thermodynamics characteristics of the formation of binary solid solutions of isomorphous substances can be calculated using the classical expression for the crystal lattice energy associated with determination of the Coulomb potential and repulse potential in a form acceptable for both components. At the same time this problem can be solved in a more convenient way, using general relations characterizing the dependence of thermodynamics functions on the volume of the system, which leads to an adequate description of the experimental data.

Theory

Let us consider binary solid solutions of substitution when an impurity component is embedded in the crystal lattice of the main component without the formation of defects. In addition, we use the so-called quasi-harmonic approximation where it is assumed that the vibrations of atoms around the middle equilibrium positions correspond to vibrations of simple harmonic oscillators and the potential energy has a minimum value in these positions. Quantum theory says that the possible levels of the oscillator are defined as

$$\varepsilon_n = \varepsilon_0 + \left(n + \frac{1}{2}\right)h\omega \quad (1)$$

where ε_0 is the potential energy in equilibrium, h is the Plank constant, ω is the vibrational frequency and n_i are integers from zero to infinity. Summing Eq.(1) over all states from the lowest vibrational level at $n_i=0$, we can determine the partition function [1]

$$Z = \sum_0^n e^{-nh\omega/kT} = \left(1 - e^{-nh\omega/kT}\right)^{-1} \quad (2)$$

where T is a temperature and k is the Boltzmann constant ($h\omega/k$ is the Einstein temperature). The total free Helmholtz crystal energy for $3vN$ oscillators, where N is the number of atoms and v is a stoichiometric coefficient, can be determined as

$$A = U - 3vN \ln Z = U + 3vN \ln \left(1 - e^{-nh\omega/kT}\right) \quad (3)$$

where $U = 3vN \left(\varepsilon_0 + \frac{1}{2}h\omega\right)$ is the energy of the fundamental quantum state, which includes the energy of zero vibrations of atoms $1/2 h\omega$. At high temperatures we can expansion of the expression

$$\ln \left(1 - e^{-nh\omega/kT}\right) \approx \ln \left(\frac{h\omega}{kT} - \frac{1}{2} \left(\frac{h\omega}{kT}\right)^2 + \dots\right) \approx \ln \frac{h\omega}{kT} - \frac{1}{2} \frac{h\omega}{kT} + \dots \quad (4)$$

and convert Eq.(3) to the form of classical energy

$$A = U_0 + 3vNkT \ln \frac{h\omega}{kT} \quad (5)$$

where $U_0 = 3vN\epsilon_0$ is the potential energy when all atoms are in equilibrium. Differentiating Eq. (5), we can determine the pressure

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial U_0}{\partial V}\right)_T + \frac{3vNkT}{V} g \quad (6)$$

where V is the volume of system and g is the Gruneisen constant is the same for all normal vibrations [2]

$$g = -\frac{d \ln \omega}{d \ln V} \quad (7)$$

Eq.(7) shows that the vibrational frequency varies depending on the volume as

$$\frac{\omega_i}{\omega_0} = \left(\frac{V_0}{V_i}\right)^g \quad (8)$$

where ω_i is the frequency when the volume is V_i and ω_0 is the frequency when the volume is V_0 . The volume of a solid solution, according Retgers rule, can be represented as

$$V_0 = y_1V_1 + y_2V_2 \quad (9)$$

where y_1, y_2 are the mole fractions of the components ($y_1 + y_2 = 1$) and V_1, V_2 are the volumes of pure components having the common atom in its structures. When a common atom is surrounded by atoms of various species, this atom is shifted towards the atom having a high charge density. It leads to a local change in volume [3]

$$V_{01} = V_0 - \lambda(V_2 - V_1); V_{02} = V_0 + \lambda(V_2 - V_1) \quad (10)$$

where λ is the value characterizing the displacement of atoms from ideal crystallographic positions in solid solution, subject to equality $\frac{1}{2}(V_{01} + V_{02}) = V_0$.

Differentiating Eq.(5), we can determine the entropy of system

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = -3vNk \ln \frac{h\omega}{kT} + 3vNk \quad (11)$$

The change in entropy during the formation of a solid solution associated with a change in the vibrational frequencies of the atoms can be defined as

$$\Delta S_v = S_0 - y_1S_1 - y_2S_2 \quad (12)$$

where the subscript "1", "2" and "0" refer to pure components and the solid solution, respectively. Substitution Eq.(11) into Eq.(12), we have

$$\Delta S_v = 3vNk \ln \frac{\omega_1^{y_1} \omega_2^{y_2}}{\omega_0} \quad (13)$$

Given the different configurations of the surrounding of the common atom by different or identical species of atoms, for example, halogen atoms around the potassium atom in a solid solution KCl-KBr, the average vibrational frequency can be represented in the form

$$\omega_0 = \omega_{11}^{W_{11}} \omega_{12}^{W_{12}} \omega_{21}^{W_{21}} \omega_{22}^{W_{22}} \quad (14)$$

where ω_{ii}, ω_{ij} are the frequencies corresponding to the surrounding of the common atom by identical and different species of atoms and W_{ii}, W_{ij} are probabilities of these combinations

$$W_{11} = y_1^2; W_{12} = W_{21} = y_1y_2; W_{22} = y_2^2 \quad (15)$$

The mechanical theory of vibrations shows that in discrete systems waves with a frequency exceeding a certain final value

cannot propagate. For a selected pair of atoms this value can be determined as [2]

$$2\pi\omega = \left(2\frac{c}{M}\right)^{1/2} \quad (16)$$

where C is the force constant and M is the reduced mass of atoms. Using Eq.(16), the vibrational frequencies for various configurations can be expressed as

$$2\pi\omega_{11} = \left[2C_0\left(\frac{1}{M_1} + \frac{1}{M_0}\right)\right]^{1/2} \quad (17)$$

$$2\pi\omega_{12} = \left[2C_{01}\left(\frac{2}{M_1+M_2} + \frac{1}{M_0}\right)\right]^{1/2} \quad (18)$$

$$2\pi\omega_{21} = \left[2C_{02}\left(\frac{2}{M_1+M_2} + \frac{1}{M_0}\right)\right]^{1/2} \quad (19)$$

$$2\pi\omega_{22} = \left[2C_0\left(\frac{1}{M_2} + \frac{1}{M_0}\right)\right]^{1/2} \quad (20)$$

where M_1, M_2 are the masses of replaced atoms and M_0 is the mass of common atom (or a group of atoms for complex compounds). For each of the individual components, we can also write

$$2\pi\omega_i = \left[2C_i\left(\frac{1}{M_i} + \frac{1}{M_0}\right)\right]^{1/2} \quad (21)$$

Combining Eq.(8) and Eq.(16), we can determine the ratio

$$\left(\frac{c_0}{c_i}\right)^{1/2} = \left(\frac{V_i}{V_0}\right)^g; \left(\frac{c_{0i}}{c_i}\right)^{1/2} = \left(\frac{V_i}{V_{0i}}\right)^g \quad (22)$$

Then, using Eq.(17)-(22), the average frequency of atomic vibration in a solid solution according Eq.(14) can be determined as [3]

$$\ln \omega_0 = y_1 \ln \omega_1 + y_2 \ln \omega_2 - y_1y_2j - y_1y_2p \quad (23)$$

where
$$j = \frac{1}{2} \ln \frac{(M_1 + M_2)^2 (M_1 + M_0)(M_1 + M_0)}{M_1M_2 (M_1 + M_2 + 2M_0)^2} \quad (24)$$

and
$$p = g \left(\frac{y_1}{y_2} \ln \frac{V_0}{V_1} + \ln \frac{V_{01}}{V_1} + \frac{y_2}{y_1} \ln \frac{V_0}{V_2} + \ln \frac{V_{02}}{V_2} \right) \quad (25)$$

Using Eq.(9), (10) and expansion $\ln(1+x) = x$, we have

$$p = g(1-\lambda) \frac{(V_2 - V_1)^2}{V_1V_2} \quad (26)$$

Here, as a first approximation, we can put $\lambda=1/2$, whence

$$p = \frac{1}{2} g \frac{(V_2 - V_1)^2}{V_1V_2} \quad (27)$$

Substitution Eq.(23) into Eq.(13), we have

$$\Delta S_v = 3vNky_1y_2q \quad (28)$$

where $q = j + p$.

A complete change of entropy during solid solution formation can be defined as

$$\Delta S = -R(y_1 \ln y_1 + y_2 \ln y_2) + 3vRy_1y_2q \quad (29)$$

where the first term is the entropy of ideal mixing S_{id} and R is the gas constant $R=Nk$, where N is the Avogadro number.

At high temperature (here we consider an approximation where the remaining terms of expansion (4) can be neglected) the total energy of a solid can be determined according to Eq.(5) and Eq.(11) as

$$U = A + TS = U_0 + 3vRT \quad (30)$$

where the last term is the same for both the solid solution and the components forming it, so the change in energy during the formation of a solid solution can be represented as

$$\Delta U = U_0(V_0) - y_1 U_1(V_1) - y_2 U_2(V_2) \quad (31)$$

where the functional dependence of energy on volume is emphasized. Function $U_0(V_0)$ can be represented as a hybrid function of the original components [3]

$$U_0(V_0) = y_1 U_1(V_0) + y_2 U_2(V_0) \quad (32)$$

Take into account the probabilities of various configurations, Eq.(32) should be written as

$$U_0(V_0) = W_{11} U_1(V_0) + W_{12} U_1(V_{01}) + W_{22} U_2(V_0) + W_{21} U_2(V_{02}) \quad (33)$$

where V_{01} and V_{02} are defined by Eq.(10). Substituting Eq.(33) into Eq.(31), we have

$$\Delta U = y_1^2 (U_1(V_0) - U_1(V_{01})) + y_1 y_2 (U_1(V_{01}) - U_1(V_1)) + y_2^2 (U_2(V_0) - U_2(V_2)) + y_1 y_2 (U_2(V_{02}) - U_2(V_0)) \quad (34)$$

The functions $U_1(V_0)$ and $U_1(V_{01})$ for each of the components can be expanded into Taylor series keeping only the quadratic terms in it, since $dU/dV=0$ in equilibrium. Then, using Eq.(9), we can write, for example, for the first component

$$U_1(V_0) = U_1(V_1) + \frac{1}{2} y_2^2 u_1 (V_2 - V_1)^2 \quad (35)$$

$$U_1(V_{01}) = U_1(V_1) + \frac{1}{2} (y_2 - \lambda)^2 u_1 (V_2 - V_1)^2 \quad (36)$$

where

$$u_1 = \frac{d^2 U_1(V_1)}{dV_1^2} \quad (37)$$

Similar expressions when replacing subscripts can be written for another component. Further, combining Eq.(34)-(36), we have

$$\Delta U = \frac{1}{2} y_1 y_2 (V_2 - V_1)^2 [u_1 (y_2 - 2\lambda y_2 + \lambda^2) + u_2 (y_1 - 2\lambda y_1 + \lambda^2)] \quad (38)$$

Using the condition of minimum energy $\frac{d\Delta U}{d\lambda} = 0$, we have

$$\lambda = \frac{y_1 u_2 + y_2 u_1}{u_1 + u_2} \quad (39)$$

Substituting Eq.(39) into Eq.(38), we obtain

$$\Delta U = \frac{1}{2} y_1 y_2 (V_2 - V_1)^2 \frac{(y_1 u_2 + y_2 u_1)(y_1 u_1 + y_2 u_2)}{u_1 + u_2} \quad (40)$$

Turning to a change in enthalpy according to Eq.(6), we have

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + 3vRT (g_0 - y_1 g_1 - y_2 g_2) \quad (41)$$

For isomorphous substances, which have a similar properties, the last term of Eq.(41) can be neglected, therefore, we can put $\Delta H = \Delta U$. Then the Eq.(40) can be transformed to the form [3]

$$\Delta H = \frac{1}{2} y_1 y_2 \Omega \quad (42)$$

where the value of Ω can be determined in good approximation as

$$\Omega = \frac{1}{4} (V_2 - V_1)^2 (u_1 + u_2) \quad (43)$$

Finally, the change of Gibbs energy during the formation of a solid solution, according Eq.(29) and (42), can be represented as

$$\Delta G = \frac{1}{2} y_1 y_2 \Omega + RT (y_1 \ln y_1 + y_2 \ln y_2) - 3vRT y_1 y_2 q \quad (44)$$

Further using condition $d\Delta G/(dy_i) = 0$, we can determine the critical temperature of the decomposition of the solid solution

$$T_c = \frac{2\Delta H_{eq}}{R \left(1 + \frac{3}{2} vp\right)} \quad (45)$$

where ΔH_{eq} corresponds to the equal molar ratio of components.

Discussion

One of the main controversial issues in the theory of the formation of inorganic solid solution is the existence of ordered structures [4,5]. To solve this problem, we consider a partially ordered solution, where probabilities of surrounding a common atom with the same and different atoms can be represented as [4]

$$w_{11}^* = y_1 (y_1 - y_2 \sigma); \quad w_{22}^* = y_2 (y_2 - y_1 \sigma);$$

$$w_{12}^* = w_{21}^* = y_1 y_2 (1 + \sigma) \quad (46)$$

where σ is a degree of local order. Then the entropy of mixing can be defined as

$$S_\sigma = -R (w_{12}^* \ln w_{12}^* + w_{22}^* \ln w_{22}^* + 2w_{12}^* \ln w_{12}^* - y_1 \ln y_1 - y_2 \ln y_2) \quad (47)$$

and Eq.(30) can be transformed to

$$U_0(V_0) = y_1 (y_1 - y_2 \sigma) U_1(V_0) + y_2 (y_2 - y_1 \sigma) U_2(V_0) + y_1 y_2 (1 + \sigma) [U_1(V_{01}) + U_2(V_{02})] \quad (48)$$

By transformations similar to Eq.(31)-(34), the change enthalpy during the formation of a solid solution can be expressed as

$$\Delta H_\sigma = y_1 y_2 \Omega [1 - \Lambda (1 + \sigma)] \quad (49)$$

where

$$\Lambda = \frac{u_1 \lambda (2y_2 - \lambda) + u_2 \lambda (2y_1 - \lambda)}{y_1 u_2 + y_2 u_1} \quad (50)$$

Using the condition of minimum Gibbs energy $d\Delta G/d\sigma = 0$, we have [6]

$$\frac{y_1 y_2 (1 + \sigma)^2}{(y_1 - y_2 \sigma)(y_2 - y_1 \sigma)} = \exp \left[\frac{\Omega}{RT} \left(\Lambda + (1 + \sigma) \frac{d\Lambda}{d\sigma} \right) \right] \quad (51)$$

Further, to simplify the view of formulas, we consider, without loss of generality, a solid solution with an equal molar ratio of components. Then the solution of differential equation (51) can be represented as

$$\Lambda = \frac{1}{1 + \sigma} \left[\Lambda_0 + \frac{RT}{\Omega} (2(1 - \sigma) \ln(1 - \sigma) + 2(1 + \sigma) \ln(1 + \sigma)) \right] \quad (52)$$

The integration constant Λ_0 can be determined from the boundary condition – for $\sigma=0$ and $\lambda=1/2$, according to Eq.(50), we have $\Lambda_0=1/2$. Substituting Eq.(52) into Eq.(49) and to make a comparison with Eq.(42), the change enthalpy when ordering the solution can be determined as

$$\delta H = \Delta H_s - \Delta H = -\frac{1}{2}RT[(1-\sigma)\ln(1-\sigma) + (1+\sigma)\ln(1+\sigma)] \quad (53)$$

The change in entropy under these conditions can be defined as $\delta S = S_\sigma - S_0$ and using Eq.(47) to determine the change in Gibbs energy as $\delta G = \delta H - T\delta S = 0$. Thus, the coupling Eq.(52) provides a minimum Gibbs energy for any conjugate values of λ and σ . The most convenient calculation is at $\sigma=0$ using Eq.(44). Note that in this case entropy takes the maximum value.

For practical calculations, we define u_i as

$$u_i = \frac{1}{\beta V_i} \left[1 + T \left(\frac{\partial \ln \beta}{\partial T} \right)_V \right] \quad (54)$$

where β is the compressibility and the last term is about 5-10% of the basic value [3]. Thus, the value of V , β and g for a pure components are required to calculate all thermodynamics characteristics of the formation of solid solutions. This data and calculation results according Eq.(42) are given in Table 1 & 2. Figure 1 shows that the change in enthalpy during the formation of a solid solution is close to a symmetric parabolic shape.

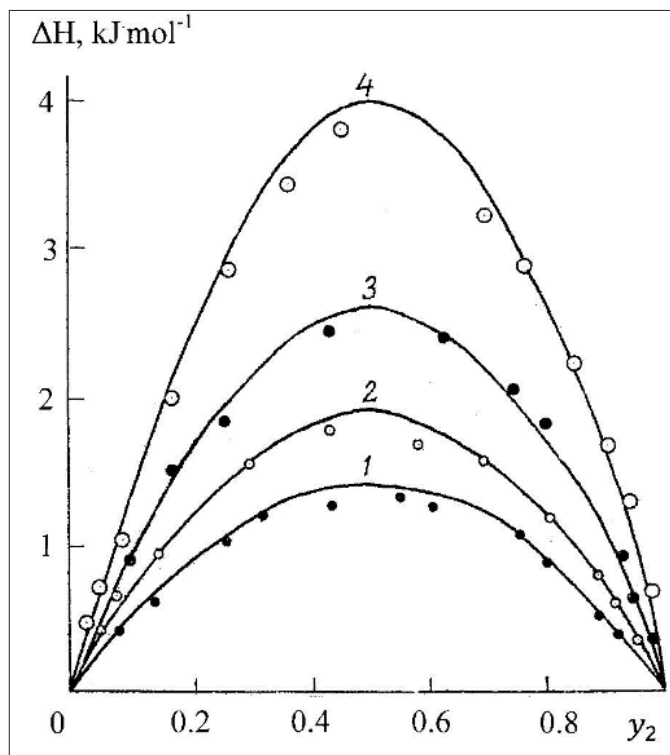


Figure 1: Enthalpy of formation of solid solutions. Calculated curve and experimental dots [7].

1: NaCl-NaBr, 2: KBr-KI, 3: NaBr-NaI, 4: NaBr-KBr.

Table 1: The properties of the individual components at 298K [3].

Substance	$V, \text{cm}^3\text{mol}^{-1}$	$10^{11} \beta, \text{Pa}^{-1}$	g
NaCl	27.02	4.11	1.62
KCl	37.54	5.62	1.58
RbCl	43.13	6.4	1.53
NaBr	32.17	5	1.66
KBr	43.17	6.59	1.58
RbBr	49.29	7.66	1.5
NaI	40.86	6.67	1.68
KI	53.12	8.31	1.63
RbI	59.59	9.28	1.73
K_2SO_4	65.34	5.23	1.07
Rb_2SO_4	73.21	5.53	1.02
Cs_2SO_4	84.94	6.02	1.15

Table 2: Thermodynamics data of solid solutions of equal molar composition at 298K. In parentheses are experimental values, Ref. [3].

System	$\Delta S_v, \text{J.mol}^{-1}\text{K}^{-1}$	$\Delta S, \text{J.mol}^{-1}\text{K}^{-1}$	$\Delta H, \text{J.mol}^{-1}$	T_c, K	$\Delta G, \text{J.mol}^{-1}$
NaCl-NaBr	0.81	6.58	1414	284	-555
			(1339)	(300)	
NaBr-NaI	0.68	6.44	2613	500	694
			(2406)	(538)	
NaCl-KCl	1.43	7.19	4719	844	2576
		(6.94)	(4393)	(773)	
NaBr-KBr	1.26	7.02	4026	670	1934
			(3724)	(668)	
NaI-KI	1.1	6.86	3127	498	1083
			(2615)	(518)	
KCl-KBr	0.86	6.62	915	183	-1057
		(6.23)	(929)		(-933)
KBr-KI	0.79	6.55	1913	387	-39
			(1830)		
KCl-RbCl	0.76	6.52	913	186	-1030
		(6.32)	(908)		(-971)
KBr-RbBr	0.93	6.69	807	159	-1189
		(6.49)	(749)		(-1184)
KI-RbI	0.96	6.72	608	119	-1395
		(6.57)	(669)		(-1289)
RbCl-RbBr	1.03	6.79	823	158	-1200
		(6.73)	(795)		(-1217)
$\text{K}_2\text{SO}_4\text{-Rb}_2\text{SO}_4$	0.53	6.29	1045	199	-829

Using Eq.(44), we can define the excess mixing energy

$$\Delta G^E = \Delta G - \Delta G_{id} = \frac{1}{2} y_1 y_2 \Omega - 3vRT y_1 y_2 q \quad (55)$$

and further, using well-known ratio, the chemical potential of the component (Gibbs partial energy), for example, with a subscript "2"

$$\Delta \mu_2 = \Delta G^E - y_1 \frac{\partial \Delta G^E}{\partial y_1} = (1 - y_2)^2 \left(\frac{1}{2} \Omega - 3vRTq \right) \quad (56)$$

This value determines the difference in the chemical potential of the component in a real and ideal solid solution, from where the activity coefficient of the component can be determined as

$$\ln f_2 = \frac{\Delta \mu_2}{RT} = (1 - y_2)^2 E \quad (57)$$

where

$$E = \left(\frac{\Omega}{2RT} - 3vq \right) \quad (58)$$

Such solutions can be called quasi-regular; their difference from regular solutions consist in taking into account the vibrational component of entropy.

Co-crystallization coefficient of any component, for example, with subscript "2", can be represented as [8]

$$D_2 = \frac{y_2 x_1}{y_1 x_2} = \frac{a_{1L}^0 \gamma_2 f_1}{a_{2L}^0 \gamma_1 f_2} \quad (59)$$

where x_1 and x_2 are relative concentrations of components of mixed liquid solution ($x = vm/W$, m is molality, W is number of moles of solvent per 1kg), γ_1 and γ_2 are activity coefficients, a_{1L}^0 and a_{2L}^0 are activity of components of saturated binary solutions, In differential form Eq.(59) can be written as

$$d \ln D_2 = d \ln L + d \ln \frac{f_1}{f_2} \quad (60)$$

where

$$L = \frac{a_{1L}^0 \gamma_2}{a_{2L}^0 \gamma_1} \quad (61)$$

The activity coefficient of component in a mixed solution, according Ref. [8], can be represented as

$$\gamma_i = \frac{a_i^*}{\sum x_i} \quad (62)$$

where a_1^* is the activity of component in an isopiestic binary solution. Using Eq.(61), (62) and the boundary conditions, we can determine the derivative function $\frac{d \ln L}{dy_2}$ as the change in value $\ln L$ in the range of concentrations from $y_2=0$ to $y_2=1$:

$$L' = \frac{d \ln L}{dy_2} \approx \frac{\Delta \ln L}{\Delta y_2} = \ln \frac{a_{1L}^0 a_{2L}^*}{a_{2L}^0 a_{1L}^*} \quad (63)$$

where a_{1L}^* is the activity of a component in its binary solution,

which is isopiestic to the saturated solution of another component. Using Gibbs-Duhem equation for solid phase

$$y_1 d \ln a_{1s} + y_2 d \ln a_{2s} = y_1 d \ln f_1 + y_2 d \ln f_2 = 0$$

where $a_{is} = y_i f_i$ is activity of component in solid phase, and Eq.(57), we have

$$\frac{d \ln \frac{f_1}{f_2}}{dy_2} = 2E \quad (64)$$

Substituting Eq.(63) and (64) into Eq.(60), we obtain to linear dependence of the co-crystallization coefficient from composition (Figure 2)

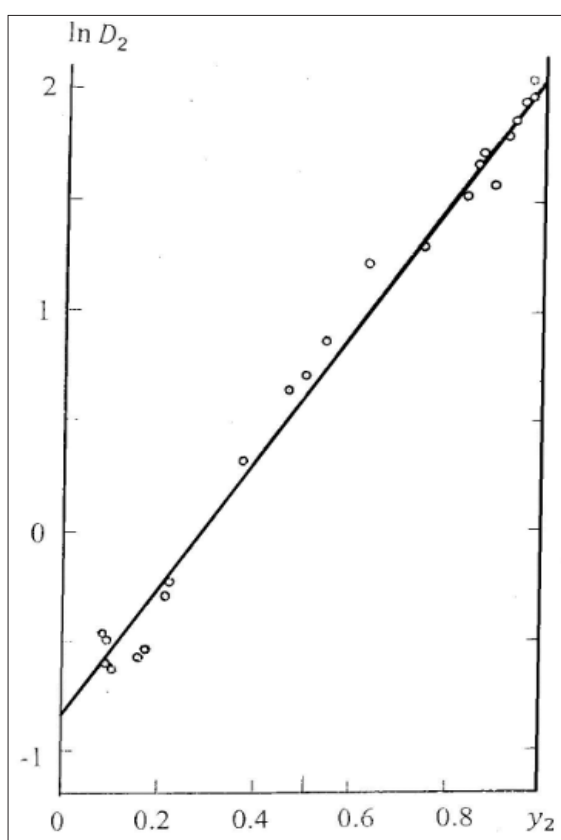


Figure 2: Co-crystallization coefficient in the system $Rb_2SO_4-K_2SO_4-H_2O$. Calculated line and experimental dots [9].

$$\ln D_2 = \ln D_2^* + (L' + 2E)y_2 \quad (65)$$

For other component, we can use definition $\ln D_1 = -\ln D_2$. Thus, according Eq.(65), the co-crystallization coefficient can be defined for any ratio of components, whence it follows that the minimum value of the co-crystallization coefficient D_2^* takes in the limiting case when $y_2 \rightarrow 0$. In this method the values a_i^* can be determined by comparing the osmotic coefficients in binary solutions of both components, using extrapolation of data for one of components to the field of supersaturated solutions [10,11]. Therefore, as a

first approximation it is possible to apply a simpler method of calculation of co-crystallization coefficients using the ratio $\frac{z_1}{z_2} \approx 1$ for a mixed solutions, which is confirmed for compounds with similar properties [12]. Then, using Eq.(57) and (59), we have

$$\ln D_2 = \ln \frac{a_{1L}^0}{a_{2L}^0} - (1 - 2y_2)E \quad (66)$$

The results of calculation according to Eq.(66) show its acceptability for the estimation of co-crystallization coefficient (Table 3); [13].

Table 3: Co-crystallization coefficient in ternary water-salt systems at 298K. Experimental data D_2^* from Ref. [13]. Impurity component is the second in writing.

System (+H ₂ O)	$\frac{a_{1L}^0}{a_{2L}^0}$	$\Delta\mu_2^*$ kJ.mol ⁻¹	D_2^* (calc.)	D_2^* (meas.)
NaCl-NaBr	0.33	4.69	5.10^{-2}	5.10^{-2}
NaCl-KCl	2.173	17.17	2.10^{-3}	5.10^{-3}
KCl-NaCl	0.461	17.17	4.10^{-4}	6.10^{-4}
KCl-KBr	0.772	2.64	0.27	0.26
KCl-RbCl	0.637	2.74	0.21	0.21
KBr-KCl	1.295	2.64	0.45	0.45
KBr-KI	0.491	6.71	3.10^{-2}	4.10^{-2}
KBr-RbBr	1.013	2.12	0.43	0.42
KI-NaI	0.064	11.2	7.10^{-4}	1.10^{-3}
KI-KBr	2.037	6.71	0.14	0.45
KI-RbI	1.83	1.29	1.09	1.02
K ₂ SO ₄ -Rb ₂ SO ₄	0.454	3.55	0.11	0.13
RbCl-KCl	1.57	2.74	0.52	0.83
RbBr-KBr	0.987	2.13	0.42	0.55
RbI-KI	0.536	1.29	0.32	0.23
Rb ₂ SO ₄ -K ₂ SO ₄	2.202	3.55	0.52	0.45

Conclusion

The considered model of the formation of solid solutions allow to determine the thermodynamics parameters of solutions based on the properties of the individual components of solution. This model is also applicable for calculating co-crystallization coefficient in the entire composition range of ternary water-salt systems, including the area of micro-concentration of the impurity component where the co-crystallization coefficient takes a minimum value.

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