Physical Chemistry

L. L. Makarov and Yu. G. Vlasov

1958

SovietRxiv

Abstract

Full Text

Physical Chemistry

L. L. Makarov and Yu. G. Vlasov

Thermodynamics of Solid Solutions CsCl–RbCl at 25°

(Presented by Academician A. N. Terenin, 27 XII 1957)

X-ray structural studies ([1]) and crystallographic characteristics (lattice type, ion sizes) make it possible to expect limited miscibility of CsCl with RbCl at low temperatures. In the present work, in order to determine the limits of existence of the CsCl–RbCl solid solution and to study its thermodynamic properties, the system CsCl–RbCl–H_2O at 25° was investigated. The experimental data and the results of thermodynamic calculations carried out in accordance with the relations of A. V. Storonkin–M. M. Shul' ts ([2]) are presented in Table 1, where m denotes the concentration in moles per 1000 g of water; x is the mole fraction; P_{H_2O} is the vapor pressure of water over the solution, in mm Hg; f is the rational activity coefficient in the solid phase, $\lim_{x\to 1} f \to 1$; $\gamma_{\pm}$ is the mean ionic activity coefficient in the aqueous solution at the indicated concentrations m_{CsCl} and m_{RbCl}; $D_{2,1}$ is the crystallization coefficient, determined from the relation: $D_{2,1}\frac{x_2}{1-x_2} : \frac{m_1}{m_2}$, where the subscripts 1 and 2 refer, respectively, to the solvent substance and the dissolved substance in the solid phase (the solvent in the solid solution will be called the substance present in the larger amount).

To attain the state of equilibrium between the liquid and solid phases, the method of isothermal

Table 1

Composition of the liquid phase m_{RbCl}	Composition of the liquid phase m_{CsCl}	Composition of solid phase x_{RbCl}	$D_{2,1}$	F_{H_2O}	f_{CsCl}	$\gamma_{\pm CsCl}$	f_{RbCl}	$\gamma_{\pm RbCl}$
7,78	10^{-3}	1,000	0,05	17,82	8,6	0,496	1,00	0,573
7,46	0,66	0,996	0,05	17,60	7,3	0,41	0,99	0,571
7,06	1,60	0,985	0,06	17,27	6,7	0,505	1,00	0,566
6,76	2,26	0,982	0,05	17,04	8,9	0,516	0,99	0,566
6,45	2,87	0,977	0,05	16,83	8,6	0,512	1,00	0,568
6,17	3,49	0,970	0,05	16,61	8,9	0,519	0,99	0,570
5,91	4,04	0,966	0,05	16,41	9,1	0,518	0,99	0,571

Figure 1

Figure 1: Figure 1

Composition of the liquid phase m_{RbCl}	Composition of the liquid phase m_{CsCl}	Composition of solid phase x_{RbCl}	$D_{2,1}$	$F_{\mathrm{H_2O}}$	f_{CsCl}	$\gamma_{\pm\mathrm{CsCl}}$	f_{RbCl}	$\gamma_{\pm\mathrm{RbCl}}$
5,54	5,01	0,956	0,05	16,07	9,2	0,517	0,99	0,570
5,02	6,16	0,944	0,05	15,66	9,5	0,516	0,99	0,576
4,56	7,79	0,914	0,05	15,08	8,6	0,516	1,00	0,570
4,35	8,36	0,891	0,06	14,88	7,4	0,512	1,01	0,571
4,14	9,10	0,789	0,12	14,62	8,6	0,514	0,99	0,573
4,09	9,02	0,094	0,22	14,65	0,98	0,514	13,3	0,574
3,23	9,55	0,037	0,12	14,65	0,98	0,517	21,3	0,615
2,65	9,86	0,042	0,16	14,81	0,99	0,517	14,8	0,615
1,28	10,76	0,012	0,10	15,28	0,98	0,512	15,7	0,490
10^{-3}	11,41	0,000	0,16	15,61	1,00	0,516	13,3	0,573

of removing supersaturation, followed by prolonged (10 h) stirring. The solid phase was analyzed by the Schreinemakers method. Radioactive isotopes Rb^{86} and Cs^{134} were used for the purposes of the analysis. The vapor pressure of water over the solutions was determined by an isopiestic method. The experimental results (Table 1) show that CsCl and RbCl form solid solutions with a miscibility gap from 10.7 to 93.3 mol. % CsCl (these limits of existence of the CsCl–RbCl solid solutions are calculated from the value $D_{2,1}$ and the composition of the liquid phase at the ternary point).

Fig. 1. Free energy of formation of CsCl–RbCl solid solutions at 25°. a–$x\Delta\mu_{\mathrm{CsCl}}$, b–$(1-x)\Delta\mu_{\mathrm{RbCl}}$, v–$\Delta\Phi$

As is seen from Table 1, the activity coefficients in saturated aqueous solutions, within the limits of experimental error, remain constant over the entire length of the solubility isotherm. In the case of limiting dilution with respect to one of the components, the following relations hold:

$$\gamma_{\pm\mathrm{CsCl}(\mathrm{RbCl}\ m=7.78)} = \gamma_{\pm\mathrm{CsCl}\ m=7.78},$$

$$\gamma_{\pm\mathrm{RbCl}(\mathrm{CsCl}\ m=11.4)} = \gamma_{\pm\mathrm{RbCl}\ m=7.78}.$$

In the solid phase, the activity coefficients of the solvent component determining the crystal structure of the solid solution are, with high accuracy, equal to

unity. The activity coefficients of the dissolved substance retain a constant value, different from unity, but with large deviations from the mean, which is a peculiarity of the calculation method employed.

The results of the final calculations of the changes in chemical potentials $\Delta\mu_{\mathrm{CsCl}}$ and $\Delta\mu_{\mathrm{RbCl}}$ and of the change in free energy upon formation of the CsCl–RbCl solid solution are presented in Table 2* and in Fig. 1.

The form of the obtained curve for the dependence of $\Delta\Phi$ on composition (Fig. 1) shows that formation of the solid solution occurs under the condition

$$\frac{\partial\Delta\Phi}{\partial x_2} < 0,$$

where x_2 is the mole fraction of the dissolved substance.

Table 2

x_{CsCl}	$-\Delta\mu_{\mathrm{CsCl}}$	$-\Delta\mu_{\mathrm{RbCl}}$	$-\Delta\Phi$
	cal. per 1 mole of ion pairs	cal. per 1 mole of ion pairs	cal. per 1 mole of ion pairs
0.000	∞	0.0	0.0
0.020	1037	12.0	32.5
0.040	626	24.2	48.2
0.060	383	36.7	57.5
0.080	215	49.4	62.6
0.090	145	56.0	64.0
0.095	113	59.2	64.3
0.100	82.6	62.5	64.5
0.107	41.1	67.0	64.2
Miscibility gap	Miscibility gap	Miscibility gap	Miscibility gap
0.933	41.1	67.0	42.8
0.935	39.9	87.4	43.0
0.940	36.7	134	42.5
0.960	24.2	374	38.2
0.980	12.0	783	27.5
1.000	0.0	∞	0.0

Near the stability boundary of the solid solution the following relations hold:

$$\left(\frac{\partial\Delta\Phi}{\partial x}\right)_{\simeq x^{\mathrm{sat}}} = 0,$$

* In calculating $\Delta\Phi$, the values of the activity coefficients of the dissolved substances at the ternary point wer

or

$$\Delta\mu_1 \cong \Delta\mu_2,$$

whence

$$x_1^{\text{sat}} = \frac{f_2}{f_1 + f_2}$$

$$x_2^{\text{sat}} = \frac{f_1}{f_1 + f_2}$$

Consequently, the composition of saturated solid solutions x^{sat} is determined through the activity coefficients of both components.

Leningrad State University
named after A. A. Zhdanov

Received
24 XII 1957

References Cited

1. R. J. Havighurst, E. Mack, Jr., F. C. Blake, J. Am. Chem. Soc., **47**, 1 (1925).

2. A. A. Storonkin, M. M. Shults, Vestn. LGU, No. 11 (1954).

3. V. G. Khlopin, Tr. gos. radiev. inst., **4** (1938).

Note: Figure translations are in progress. See original paper for figures.