PROPERTIES OF SYSTEM Al–Zn–Sn AT 700°C AS STUDIED WITH USE OF ELECTRON CHARACTERISTICS

F. MOLNÁR

Department of Chemistry,
Institute of Technology, 043 85 Košice

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The electron characteristics of systems Al–Zn, Zn–Sn, and Al–Sn at 700°C have been calculated with use of data experimentally found for the effective charge, specific electric resistance, and molar volume of these systems. The solutions of these systems may be considered monogenous, making use of electron characteristics as well as of principle of "mutual accordance" for the three binary systems. On the basis of this principle a statement can be made that the values of real ion charges in the melts of the given systems are equal to the group numbers of elements in the Mendeleev periodic system.

The present paper aims at showing on an example of molten metallic system Al–Zn–Sn at 700°C the usefulness of the principle of "mutual accordance", a term introduced by Belashchenko[1] in the study of properties of molten metallic systems. On the basis of experimentally established values of the effective charge and calculated electron characteristics, it is possible to determine with help of the principle mentioned, whether monogenic or polygenic metallic solutions are involved.

Solution of the problem, what is the state in which particles of a particular component occur in a metallic solution, has a great importance for the theory of liquid metallic or semiconductive solutions as well as for practical questions. It is well-known that there are several states of such nature for the given component, for example, in systems Tl–S and Tl–Se, thallium may occur, in addition to Tl^+ and Tl^{3+} ions, in the form of neutral atoms. In accordance with the electroneutrality principle, atoms or groups of atoms in various states, differing in their electrical or kinetic properties (mobility, diffusion), must occur in solutions of such type. Belashchenko suggested to call such solutions polygenic[2]. It follows from this that monogenic are the solutions, where particles of the same component take place in one state only. Condition of monogenity of the solution assumes all the particles of the given component to occur in equal equivalent states, scattering of electrons and diffusion being taken into account.

THEORETICAL

Belashchenko[3,4] starting from the Mott–Faber theory[5,6] and using relations for electric conductivity and electrodiffusion in metallic melts showed that the important characteristics of electron gas on the Fermi level, *i.e.* the g factor defined in the following way: $g = N(\varepsilon_F)/N(\varepsilon_F)_{FEM}$, may be calculated, where $N(\varepsilon_F)$ is the real density of energetic states on the Fermi level for a real metal, and $N(\varepsilon_F)_{FEM}$ is the density of energetic states on the Fermi level for a free electron model (FEM). The g factor then denotes a measure of a deviation of the behaviour of electrons in real metallic systems from the free electron model. For a binary system at constant temperature, Belashchenko derived for monogenic solutions relationship

$$\ln \frac{Z_2 \varrho V (k_F^2 g^2)}{\bar{Z} \varrho_2 V_2 (k_F^2 g^2)_2} = \int_0^{N_1} \frac{Z_2^*}{\bar{Z} N_1'} \, dN_1' , \qquad (1)$$

where ϱ is the specific electric resistance of the melt, V is the molar volume of the melt, Z_2^* the effective charge of the second component (established from electrodiffusion), N_1 the molar fraction of the first component; $\bar{Z} = Z_1 N_1 + Z_2 N_2$ is the mean charge of ions, where Z_1 and Z_2 are real charges of ions, consistent with the group number of element in the Mendeleev periodic system, and k_F is the absolute value of the wave vector of an electron on the Fermi level. Symbols with indexes 1 and 2 relate to the properties of the first and second pure components, whereas symbols having no index to the properties of the solution. The effective charges in binary systems Al–Zn (ref.[7]), Zn–Sn (ref.[8]), and Al–Sn (ref.[9]) at 700°C were determined by means of the high-temperature alternative of the stationary method[10,11]. Equation (*1*) allows to determine electron characteristic $k_F^2 g^2/(k_F^2 g^2)_2$ of an arbitrary solution of the binary system with respect to the pure second component, if dependence of effective and real charges of the solution upon concentration is known. Let us denote ratio $k_F^2 g^2/(k_F^2 g^2)_2$ as Θ_2. If we introduce $N_1 = 1$, then starting from equation (*1*) we can according to [ref.[12]] write

$$\Theta_2^1 = \frac{(k_F^2 g^2)_1}{(k_F^2 g^2)_2} = \frac{Z_1 \varrho_2 V_2}{Z_2 \varrho_1 V_1} \exp \left[\int_0^1 \frac{Z_2^*}{\bar{Z} N_1'} \, dN_1' \right]. \qquad (2)$$

Let us assume that at the same temperature the experimentally found effective charge is Z_2^*, specific electric resistance ϱ, the molar volume of solution V, for three binary systems consisting of components A, B, C. Using equation (*2*), magnitudes Θ_B^A, Θ_C^B, Θ_A^C may be determined for three systems. By writing equation (*1*) three times for systems A–B, B–C, and C–A, we after summation obtain zero for right

sides of equation (*1*)

$$\int_0^1 \frac{Z_B^*}{\bar{Z}N_A}\,dN_A + \int_0^1 \frac{Z_C^*}{\bar{Z}N_B}\,dN_B + \int_0^1 \frac{Z_A^*}{\bar{Z}N_C}\,dN_C = 0 \qquad (3)$$

so that

$$\Theta_B^A \,.\, \Theta_C^B \,.\, \Theta_A^C = 1\,. \qquad (4)$$

This is a principle of "mutual accordance" in a ternary system A–B–C, introduced by Belashchenko[1]. This equality must be necessarily fulfilled for monogenic solutions. If the solutions studied were not monogenic, the equality presented could not be fulfilled. The principle quoted then gives the possibility of checking values of anticipated real charges Z_i in binary systems A–B, B–C, and C–A.

RESULTS AND DISCUSSION

Results of electron characteristics of the Al–Zn, Zn–Sn, and Al–Sn systems calculated for 700°C from equation (*1*) are summarized in Table I. For the Al—Zn system, specific electric resistance ϱ and molar volume V were taken from the literature[13,14]. Numerical values of the integral of equation (*1*) were obtained by graphical integration of function $Z_2^*/\bar{Z}N_1 = f(N_1)$. The values of $k_F^2/(k_F^2)_2$ were calculated for the free electron model from relation[15]

$$k_F^2/(k_F^2)_2 = (\bar{Z}V_2/Z_2V)^{2/3}\,. \qquad (5)$$

TABLE I
Values of Ratio $k_F^2 g^2/(k_F^2 g^2)_2$

N_1	Al(1)–Zn(2)	Zn(1)–Sn(2)	Al(1)–Sn(2)
0·0	1·0	1·0	1·0
0·1	1·0284	0·984	1·069
0·2	1·0504	0·960	1·121
0·3	1·1804	0·939	1·198
0·4	1·1582	0·925	1·285
0·5	1·2554	0·915	1·375
0·6	1·3268	0·906	1·466
0·7	1·4202	0·900	1·488
0·8	1·5194	0·879	1·534
0·9	1·5933	0·847	1·463
1·0	1·7178	0·770	1·271

For the Zn—Sn and Al—Sn systems[13,16], specific electric resistance ϱ was taken from the literature. Molar volume V of the alloys was for both systems calculated additively from specific density for pure components, provided that the given systems behave at 700°C as ideal solution.

By introducing for $N_1 = 1$ values from Table I for systems Al—Zn, Zn—Sn, and Al—Sn into equation (*1*) we obtain $1{\cdot}7178 \times 0{\cdot}770 \times 1/1{\cdot}271 = 1{\cdot}040$. The deviation from unity is associated with inaccuracy of experimental values of the effective charge, specific electric resistance, and molar volume of the melts. For the ternary system Al—Zn—Sn, the assumption of monogenity of the solutions of melts as well as assumption of real ion charges in the solution, equal to the group number of elements in the periodic system, are fulfilled. If the real ion charges were in the molten solutions different from those considered for the calculation of $k_F^2 g^2/(k_F^2 g^2)_2$, equation (*4*) would not be then fulfilled.

In general, the value of real ion charges in the melts of monogenic solutions of metals can be considered as being equal to the group number of elements in the Mendeleev periodic system. To understand better properties of the solutions as well as to solve the problem of preparing solutions with required properties, it is important to know the state in which particles of the solution components are present.

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