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ESTIMATION OF EXCHANGE ENERGIES IN TWO-COMPONENT MELTS OF ALKALI METALS

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Abstract

An approach allowing establishment of the relationship between the energies of mixing in binary homovalent melts of metals and the corresponding values for halide salts (chlorides or fluorides) of these metals is proposed. The procedure given as an example for estimation of the exchange energies in liquid-phase systems formed by lithium and other alkali metals allows a considerable reduction in the number of experimentally complicated definitions for thermodynamic characteristics of similar systems.

Keywords: alkali metals, binary melts, energies of mixing, halide salts,

Introduction

Alloys of alkali metals (AMs) are widely used in practice as heat-transport media in engine installations and as catalysts in various processes associated with physical and chemical phenomena. However, they fall into the category of systems whose thermal analysis is hindered because of the increased requirements of the conditions of performing the experiment. Thermodynamic properties of binary melts containing lithium have been studied less thoroughly than other AM compositions, forming disordered solutions with appreciable deviations from perfection. Experimental data on exchange energy Ω_M have been obtained for the system Li–Na alone [1], while in cases involving melts of Li and K, Rb or Cs, only tentative estimates are known [1, 2]. Since ab initio and model calculations result, as a rule, in Ω_M values for two-component AM systems that are considerably overestimated in comparison with experiment [1–3], it is a high-priority task to develop a simple and more reliable approximation of the above characteristics.

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Results and discussion

In the present paper, the Ω_M values for the compositions Li–AM were estimated from this approach, using experimental data [4] on the effective parameters of interaction Ω_S in binary melts of halide salts (chlorides or fluorides) of these metals:

$$\Omega_M = \Omega_S + \Omega_C + \Omega_p \tag{1}$$

Here, Ω_C is the energy expended to form a structure of Wigner-Seitz atomic cells of different kinds in a metal alloy and released when the latter reacts with a halogen; Ω_p is equal to the difference ΔE_p between the changes in energy of polarization of the anion by the smallest and the largest cations [4], each of which, with the results in paper [5] taken into consideration, can be presented as follows:

$$E_p \approx \frac{bi^2\alpha_{an}}{(r_k + r_{an})^4} \tag{2}$$

where b is a multiplier depending on temperature and the nature of the anion; i is the ionicity of the heteropolar chemical bond in the AM halide (in the condensed state); r_k and r_{an} are the cation and anion radii, and α_{an} is polarizability of the anion. The feasibility of such an estimate follows from a consideration of the features, comparing the energy balance of interaction between separate AMs and their compositions with non-metals [6], but the literature does not give particular examples of how this knowledge is used.

To find the contribution of Ω_C, let us consider it to increase in a linear manner as the difference between the metal atomic radii R of the separate alloy components increases [7, 8]. Further, let us take into consideration the corollary from the initial definition [9] concerning the dependence of Ω_C on the difference of cell deformabilities, specifying the value of energy consumption for the assumption of equilibrium values of volume and shape in an alloy. Accordingly assuming the relative deformability of the cell to be equal to the Herzfeld dimensionless variable $\gamma=\alpha_o/V_o$ [10] (α_o is the static dipolar polarizability; V_o is the volume per atom in a simple substance; $V_o=V_\mu/N_o$, V_μ is the gram-atomic volume, and N_o is the Avogadro number), let us suppose that

$$\Omega_C \approx \alpha\Delta\gamma\Delta R \tag{3}$$

where α is a constant proportionality coefficient, in $\Delta_\gamma=|\gamma_1-\gamma_2|$ and $\Delta R=|R_1-R_2|$, where indices 1 and 2 refer to the ingredients of the metal alloy.

Calculations with Eq. (1), with use of (2) and (3), were made by utilizing reference data on α_o [11, 12], V_o [13], R [14, 15] and α_{an}, r_{an}, r_k and i [14]. In view of the experimental dependences of Ω_M on temperature in the systems Li–Na [1] and Na–K [13, 16], for which limitations for a large molecular mass can be neglected [3, 17], we found that $a≈982.3$ kJ nm^{-1} mol^{-1}, $b≈49.64$ kJ nm^{-1} mol^{-1} (for chlorides at T=973 K) and $b≈97.33$ kJ nm^{-1} mol^{-1} (for fluorides at T=1173 K).

The Figure shows the estimates of energies of mixing of Li with K, Rb or Cs in two-component melts, derived from formula (1). For comparison, we also present the calculations made within the scope of the thermodynamic scheme [18], where Ω_M is the function of only two characteristics of the starting metals: the evaporation heat L and the electron work function Φ:

$$\Omega_M \approx 6\Xi_L - 4f\Xi_\Phi \tag{4}$$

where Ξ is a function equal to the difference between the arithmetical mean and the geometrical mean of the system parameters; f=96.485 kJ mol^{-1} eV^{-1} (quantity Φ is given in electron volts).

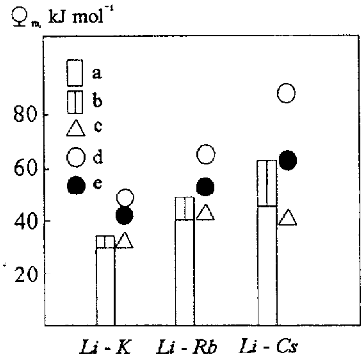

Fig. 1 Estimates of exchange energies in binary liquid compounds of lithium with potassium, rubidium and cesium, obtained within the scope of the proposed approach by means of Eq. (1), and with the values of Ω_s and Ω_p of the two-component melts of the corresponding chlorides at T=973 K (a) and the corresponding fluorides at T=1173 K (b) in comparison with the calculations of Ω_M by various methods, i.e. by formula (4) at T=973 K (c), by the pseudopotential method [1] (d) and by the procedure proposed by Miedema *et al.* [2] (e)

The latter approach was used since it appeared to be useful for the calculation of Ω_M in most binary compositions of alkali metals, system Li–Na included, and it also allows, as a first approximation the temperature relationship between the exchange energies to be taken into account [19]. In calculations with formula (4), we made use of known values of $L(T)$ [20] and $\Phi(T)$ [18, 21]. It is evident that expressions (1) and (4) yield close results for the alloys Li–K and Li–Rb. The undervalued Ω_m from (4) for the system Li–Cs is probably due to the failure in the approach [18] to take into account the characteristic properties of the repulsive interaction in compositions with Cs, which is also typical for the earlier-developed theoretical and semiempirical calculation procedures [1–3, 17]. The results obtained agree qualitatively with the known data (where one can see the analogy with the alloys formed by Na and heavier AMs), which show a considerable elevation of Ω_M with increasing temperature [13], as well as more appreciable deviations from perfection and mutual insolubility in going from the system Li–Na to the compositions Li–K, Li–Rb and Li–Cs [22, 23]. The observed tendency to an increasing role of the temperature factor in the above AM alloys can be attributed to the contribution of the positive-sign correction for heat expansion [14] (caused by the differences in coefficients of anharmonicity and tightness of bonding in the simple substances being mixed), whose role increases with the increasing atomic number of the elements in the heteronuclear couple.

The estimated energies vary in a manner similar to those calculated according to the widely-known approach of Miedeman *et al.* [2] and by the pseudopotential model [1], Ω_M being represented as a sum of electron, pseudoatomic and pair contributions. However, the Figure shows that the latter approach evidently overvalues Ω_M, not only in comparison with our own estimates, but also with the results in [2], which is characteristic of most binary AM melts containing no Li.

Conclusions

Thus, the given examples support of feasibility of establishing an analytical relationship between the exchange energies of two-component homovalent metal melts and the corresponding values for salts with the same anion. With consideration of the corrections for the formation of a structure of Wigner-Seitz atomic cells of different kinds and the changes in energy on polarization of the anion, use of this relationship allowed an estimation of the enthalpy parameters in systems with potassium, rubidium and cesium, which have not yet been determined experimentally.

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