

Theoretical estimation of equilibrium partitioning of elements between crystals and binary melts (fluids)

V.S. Urusov

Moscow University and Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Moscow, Russia.

Long ago V.M. Goldschmidt (1937) emphasized the importance of ionic sizes in controlling element substitutions in crystal structures and the distribution of trace elements between the coexisting crystals and liquids (melts and fluids). It is well-known that Goldschmidt's rules are tentative and prone to many exceptions. The deviations from these rules have been explained in terms of differences in bond type of electronegativity of major and trace elements (Ahrens, 1953; Shaw, 1953; Ringwood, 1955) and crystal field effects for transition metal ions (Burns, 1970).

Despite the above-mentioned corrections, new strong evidence favours the dependence of partition coefficients on ionic sizes and charges. The so-called Onuma diagrams (Onuma *et al.*, 1968) do present partition coefficients for separate minerals as a function of ionic radius and charge. At the same time some workers have attempted theoretical solution of the outlined problem. Such approaches were based on either the elastic continuum model of excess (mixing) energy (Nagasawa, 1966; Brice, 1975) or on the ionic lattice energy of a doped crystal (Durham and Hawkins, 1951; Tsang *et al.*, 1978). I present here an important development with reference to the author's works since the middle 1970s.

A fundamental result of thermodynamic analysis of equilibrium between a crystal and melt is as follows:

$$R \ln K_i = R \ln(x_s/x_l) = \Delta H_{ml}(1/T - 1/T_{ml}) - (\Delta H_i^e - T\Delta S_i^e)/T \quad (1)$$

where R is the universal gas constant, K_i is the partition (distribution) coefficient, x_s and x_l are the mole fractions of i -component in solid and liquid phases, correspondingly, ΔH_{ml} and T_{ml} are the melting enthalpy and temperature of pure i -component, ΔH_i^e and ΔS_i^e are the differences of excess enthalpy and entropy of i -component in solid and liquid phases.

Both phases are taken as regular solutions

$$H_i^e = (1-x_i)^2 W_i \quad (2)$$

where W_i is the interaction parameter. In addition, if the i -component is a trace element, that is $x_i \ll 1$, then:

$$R \ln K_i = \Delta H_{ml}(1/T - 1/T_{ml}) - \Delta W_i/T + \Delta S_i^e \quad (3)$$

where W_i is the difference between interaction parameters in solid and liquid phases.

As was shown (Urusov and Kravchuk, 1976), the mixing enthalpy of ionic binary melts very simply anti-correlates with that of solid solutions

$$W_i^l \cong -0.2W_i^s \quad (4)$$

so that $\Delta W_i \cong 1.2W_i^s$. Moreover, a universal correlation between mixing enthalpy and excess (vibrational) entropy appears to be valid for ionic and metallic solids and melts (Urusov and Kravchuk, 1976; Urusov and Kravchuk, 1983):

$$\Delta S_{vib}^e \cong \Delta H_m^e/t \quad (5)$$

where the empirical parameter t is approximately equal to 2800 ± 500 k. Taking into consideration the approximations (4) and (5) Eq. (3) can be simplified to:

$$R \ln K_i = \Delta H_{ml}(1/T - 1/T_{ml}) - 1.2W_i^s(1/T - 1/2800) \quad (6)$$

When K_i is found to be markedly different from unity, then the first term on the right side of Eq. (6) is usually of minor importance. This suggests that the key to the question lies with the amount of the interaction parameter for the solid solution.

A crystal chemical way to evaluate the mixing enthalpy of solid solutions was developed in the previous author's investigations (Urusov, 1975; Urusov, 1992). According to this consideration, the interaction parameter of isovalent solid solution can be expressed in the form

$$W = mz^+z^-(b\delta^2 + a\Delta^2) \quad (7)$$

where m is the number of atoms in molecular unit,

z^+ and z^- are the valences (charges) of atoms, b is proportional to the ratio V/β (V is the molar volume, β is the compressibility), $a = a/2d_n$ (a is the reduced Madelung constant), $\delta = \Delta d/d_n$ ($\Delta d = d_i - d_n$, d_i and d_n are the interatomic distances in crystals of trace and host components, respectively), $\Delta = f_i - f_n$ is the corresponding ionicity difference. The first term in Eq. (7) is the deformation (elastic) energy due to size mismatch and the second term is the chemical one due to the bonding character mismatch. The latter is closely related to the electronegativity difference. It is notable that the size parameter δ can be expressed by means of the radii difference: $\delta = \Delta r/d_n = (r_i - r_n)/(r_n + r)$, where r_i and r_n are the ionic (or atomic) radii of trace and host elements and r is that of common structural unit. Substituting Eq. (7) into Eq. (6) one easily see that the K_i value becomes a function of the radii and the electronegativity difference.

If the electronegativity difference is small and the chemical term occurs to be negligible then calculations of the partition coefficients have been made possible by the use of Eq. (6). The results are in a good agreement with experiment for alkali metal and halogen ions in alkali halide crystals grown from binary melts or aqueous solutions, and in satisfactory accordance with scarce experimental data for some isovalent impurities in nitrates, oxides, silicates, etc.

In the case of significant chemical contribution to the interaction parameter the correlation between the mixing enthalpies in solid and liquid phases changes sign as compared to relation (4). By this it is meant that the constant in Eq. (6) becomes less than 1.2 and even less than 1. That might partly offset the high value of W_i and relatively decrease the estimated value of K_i . In general, the influence of melt (fluid) composition on K_i value should be taken properly into account by variation of the same factor. For instance, increase of silicate melt acidity (SiO_2 content) will effectually enhance the K_i values of elements characteristic of basic melts. This corresponds to significant positive value of excess free energy of such compositions in melts (fluids). Much evidence of such a behaviour comes from geochemical observations.

With respect to heterovalent element parti-

tioning, consideration must be given to the mechanism of charge compensation. In particular, in the case of vacancy formation to compensate for the excess charge of the impurity element, the corresponding energy of vacancy formation is involved in the estimation W_i and K_i values (Urusov and Dudnikova, 1987).

Partition of elements in microconcentrations is distinctive because of a commonly occurring rise in K_i in this range of melt compositions. An explanation of this so-called trapping effect has been recently made by analysis of interaction between impurity atoms and intrinsic thermal defects (Schottky and Frenkel types) of a crystal (Dudnikova and Urusov, 1992; Urusov and Dudnikova, 1993).

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