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The structure and energetics of cryolite melts

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Abstract. A method of solvation energy computation is proposed for ions and molecules in the environment of an ionic melt, based on the approximation of the ionic melt as an ideal conductor. The method is used to compute equilibrium constants of some equilibria in cryolite melt. Theoretically obtained results predict that aluminium is bound in tetrafluorocomplexes AlF_4^-.

Key words: Ionic melt – Cryolite – Solvation – Density functional theory calculation

1 Introduction

The importance of cryolite in aluminium production motivates the many scientific studies of cryolite melt structure and energetics.

Most of the experimental data concerning the stepwise dissociation of hexafluoroaluminate ion is from electrochemical measurements and Raman spectra. The results of recent high temperature in situ Raman spectroscopy studies are usually interpreted by the dissociation schemes proposed by Gilbert, $AlF_6^{3-} \rightarrow AlF_5^{2-} + F^- \rightarrow AlF_4^- + 2F^-$, with a relatively high concentration of AlF_5^{2-} ion [1,2]. This conclusion is based on the decomposition of measured bands in the region of totally symmetric valence vibrations of the AlF_6^{3-} anion into components arising from supposed species present in the melt. However, the way of decomposition of vibration spectra is a critical point of the interpretation of the experimental data in this case [3]. For this reason a theoretical study is called for.

Among the theoretical methods used for the study of this problem are the Monte Carlo (MC) simulations of Qiu and Xie [4] and the molecular dynamics (MD) calculations of Liška et al. [5]. However, none of the MD and MC simulated melt structures confirm Gilbert's dissociation scheme. Unlike MC, the MD result agrees well with basic features of the equilibrium crystal structure of cryolite (six-fold Al coordination, Al-F distance).

The reasons for some failures of MC and MD are traditionally attributed to the pairwise form of the total potential and its particular parametrisation. However, a deeper analysis of whether the discrepancies between theoretical and experimental results are failures of the MC and MD schemes or whether these discrepancies are consequences of insufficiently careful interpretation is still lacking.

As far as quantum-chemical calculations are concerned, it is well known that to obtain calculated energies with so-called "chemical" accuracy methods of post Hartree-Fock (HF) level combined with relatively large basis sets are needed. The recent paper of Bock et al. [6] is such a post-HF study of halogeno-aluminate systems. In their work, the molecules and ions, approximated to be in an ideal gas phase, served as model clusters. The influence of the molten salt environment was simulated by the presence of some alkali atoms in the model clusters.

Bouyer et al. [7] studied fluoro- and chloro-aluminate anions using density functional theory. They computed vibrational frequencies in the ideal gas phase and compared the relative stabilities of individual complexes.

Having reviewed the state of the art in the topic of quantum-chemical calculations on molten salt systems, we suggest the following strategy for this work:

- Use of a quantum-chemical method providing results of post-HF accuracy;
- Choice of a proper set of quasi-species (by this term we will mean either real or hypothetical molecules or ions representing the cryolite melt) using unambiguous criteria of their suitability;

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– Inclusion of the solvation effect of the liquid environment. This is important especially for ionic melts. In this case, the interaction energy between charged quasi-species is often greater than the reaction energies of mutual transformations of quasi-species (or, at least, of comparable magnitude). This leads to qualitatively different reaction schemes than would be expected without inclusion of this effect. The effect of solvation of the ion by the melt is greater by several orders of magnitude than the effect of vibrational motion of atoms in quasi-species (zero-point correction, entropy derived from the vibration). This is why one cannot expect too much success from a simple ideal-gas scheme. The use of a more sophisticated statistical-thermodynamics method is absolutely necessary in this case.

2 Method

A quantum-chemical method based on density functional theory (DFT) and implemented in the computer codes deMon [8] and Gaussian'94 [9] was used to calculate electronic structure and total energies of the model quasi-species. This well-established method fulfils the requirement of obtaining energies of chemical accuracy and, in comparison with HF and the post-HF methods, its computational complexity is at least one order lower. A TZP basis set for all atoms and a Perdew and Wang (PW91) exchange-correlation functional [10] was used.

The existence of sufficiently deep minima on the energy hypersurface is used as the criterion for stability of individual quasi-species. To consider the quasi-species as being stable, the lowest energy barrier of transformation to another quasi-species must be, for a given temperature T, at least one order of magnitude higher than kT (k is Boltzmann's constant)

In addition, electronic stability has to be taken into account. When the absolute value of the difference between the energy of the highest occupied molecular orbital (HOMO) and the energy of solvated unit charge is too high, the quasi-species tends to stabilise by lowering the absolute value of its charge. In the case of an electronically conducting environment this would be achieved by loss or acceptance of an electron. Our case is different; the ionic melts have ionic conductivity and the stabilisation of a complex ion of a quasi-species is achieved by loss or acceptance of a cation or anion, changing in turn the chemical quality of the respective quasi-species.

The high electrical conductivity of ionic melts allows one to estimate the solvation Gibbs energy of individual quasi-species by using a continuum model of an ideal conductor. A quasi-chemical approximation is used to describe equilibria between individual particles, that is, the quasi-species, in the ionic melt:

$$\sum_j \mu_j v_j = \sum_i \mu_i \gamma_i \ \ [V, T, N_a] \tag{1}$$

where μ_j, μ_i are the chemical potentials of the respective quasi-species, v_j, γ_i are the corresponding stoichiometric coefficients and $[V, T, N_a]$ indicates an ensemble at constant volume, temperature and total number of atoms. The equilibrium constant K can be obtained if the chemical potentials $\mu_k(N_1, N_2, \ldots, N_k, \ldots, N_M, V, T)$ are known ($N_1, N_2, \ldots, N_k, \ldots$ are the numbers of particles of the 1-st, 2-nd, …, k-th type, and M is the number of various types of quasi-species, respectively). The chemical potential of the k-th quasi-species is defined as

$$\begin{aligned}\mu_k = {} & F(N_1, \ldots, N_k + 1, \ldots, N_M, V, T) \\ & - F(N_1, \ \ldots, N_k, \ldots, N_M, V, T)\end{aligned} \tag{2}$$

where the Helmholtz free energy F is defined as:

$$F(N_1, \ldots, N_M, V, T) = -kT \ln Z(N_1, \ \ldots, N_M, V, T) \tag{3}$$

and

$$\begin{aligned}Z(N_1, \ldots, N_M, V, T) = {} & \prod_{j=1}^{M} \frac{\Lambda_j^{N_j}(T)}{N_j!} \\ & \times \int \exp\left[-\frac{U(N_1, \ldots, N_M)}{kT}\right] \prod_i d\Gamma_i\end{aligned} \tag{4}$$

where Λ_j is the electron, intramolecular and translational part of the statistical sum for the j-th particle, $\prod_i d\Gamma_i$ is the volume element of the configurational space of the entire ensemble and $U(N_1, \ldots, N_M)$ is the total potential energy of the ensemble consisting of $N_1, \ldots, N_M$ particles of the 1-st, …, M-th species:

$$U(N_1, \ldots, N_M) = \frac{1}{2} \sum_{i=1}^{M} \sum_{j=1}^{M} \sum_{\alpha_j=1}^{N_j} \sum_{\beta_i=1}^{N_i} V(\alpha_j, \beta_i) \tag{5}$$

where $V(\alpha_j, \beta_i)$ is the potential energy of the interaction between the α-th particle of the type j with the β-th particle of the type i. Now, the statistical sum $Z(N_1, \ldots, N_k + 1, \ldots, N_M)$ for $N_k + 1$ particles of the k-th species will be expressed using the statistical sum $Z(N_1, \ldots, N_k, \ldots, N_M)$ for N_k particles of the k-th type:

$$\begin{aligned}& Z(\ldots, N_k + 1, \ldots) = \prod_{i=1}^{M} \frac{\Lambda_i^{N_i}(T)}{N_i!} \cdot \frac{\Lambda_k}{N_k + 1} \cdot \\ & \int \exp[-U(\ldots, N_k + 1, \ldots)/kT] \prod d\Gamma_i\end{aligned} \tag{6}$$

The configuration integral can be written in the form

$$\begin{aligned}& \int \exp[-U(\ldots, N_k + 1, \ldots)/kT] \prod_i d\Gamma_i \\ & = \int \left[\int \exp\left[-\frac{U(\ldots, N_k, \ldots)}{kT}\right] \cdot \exp\left[-\frac{\sum_{\beta_i} V(\alpha_{N_k+1}, \beta_i)}{kT}\right] \right. \\ & \quad \left. \times \prod_{i=1}^{M} \prod_{\beta_i=1}^{N_i} d\Gamma_{\beta_i} \right] d\Gamma_{N_k+1} = \int \exp\left[-\frac{U(\ldots, N_k, \ldots)}{kT}\right] \prod_{\alpha}^{N_k} d\Gamma_\alpha \\ & \times \frac{\int \left[\int \exp\left[-\frac{U(\ldots, N_k, \ldots)}{kT}\right] \cdot \exp\left[-\frac{\sum_{\beta_i} V(\alpha_{N_k+1}, \beta_i)}{kT}\right] \prod_{i=1}^{M} \prod_{\beta_i=1}^{N_i} d\Gamma_{\beta_i} \right] d\Gamma_{N_k+1}}{\int \exp\left[-\frac{U(N_k)}{kT}\right] \prod_{\alpha}^{N_k} d\Gamma_\alpha}\end{aligned} \tag{7}$$

Then one has

$$\begin{aligned}& \int \exp\left[-\frac{U(\ldots, N_k + 1, \ldots)}{kT}\right] \prod_i d\Gamma_i \\ & = \int \exp\left[-\frac{U(\ldots, N_k, \ldots)}{kT}\right] \prod_{\alpha}^{N_k} d\Gamma_\alpha \cdot V \\ & \cdot \left\langle \exp\left[-\frac{\sum_i^M \sum_{\beta_i=1}^{N_i} V(\alpha_{N_k+1}, \beta_i)}{kT}\right] \right\rangle\end{aligned} \tag{8}$$

where $\langle A \rangle$ is the thermodynamic mean value of an arbitrary quantity A. Finally,

$$\begin{aligned}& Z(\ldots, N_k + 1, \ldots) = Z(\ldots, N_k, \ldots) \ \Lambda_k(T) \frac{V}{N_k + 1} \\ & \quad \times \left\langle \exp\left[-\frac{\sum_i^M \sum_{\beta_i=1}^{N_i} V(\alpha_{N_k+1}, \beta_i)}{kT}\right] \right\rangle\end{aligned} \tag{9}$$

Then, for the chemical potential μ_k one has

$$\begin{aligned}& \mu_k = kT \ln \frac{c_k}{\Lambda_k(T)} - kT \ \ln \\ & \quad \times \left\langle \exp\left[-\frac{\sum_i^M \sum_{\beta_i=1}^{N_i} V(\alpha_{N_k+1}, \beta_i)}{kT}\right] \right\rangle\end{aligned} \tag{10}$$

or

$$\mu_k = \mu_{k,o} + \mu_{k,\mathrm{solv}} \tag{11}$$

where $c_k = N_k/V$ is the concentration of the species of k-th type, $\mu_{k,o}$ is the chemical potential of the species of k-th type in the ideal gas phase and $\mu_{k,\mathrm{solv}}$ is the solvation contribution to the chemical potential and is equal to the isothermal work needed for transfer of the particle from the melt to the vacuum.

In the case of an electrical charge or multipole, this work is equal to the difference of electrostatic energies of a particle in the melt and in the vacuum. In our model we approximate of the melt by a continuum which behaves as an ideal conductor. The solvated particle is considered to be in a cavity surrounded by the continuous environment. In the ideal conductor approximation the only assumption is that the electric field generated by the solvated ion or multipole is completely screened in the off-cavity space. The radius of the cavity R_k is computed as

$$R_k = \sup\{R_{k,i}\}_{i=1}^{n_k} \tag{12}$$

where n_k is the number of atoms in the quasi-species of the k-th type, i runs over all the atoms of the k-th type quasi-species and

$$R_{k,i} = \mid \vec{r}_{k,i} - \vec{r}_{k,o} \mid + \rho_i \tag{13}$$

where $\mid \vec{r}_{k,i} - \vec{r}_{k,o} \mid$ is the distance of the i-th atom from the centre of mass of the considered quasi-species ($\vec{r}_{k,i}$ and $\vec{r}_{k,o}$ being the radius vectors of the i-th atom and the centre of mass, respectively) and ρ_i is the ionic radius of the i-th atom of the quasi-species. The isothermal work needed for transfer of the solvated particle from the cavity in the ideal conductor to the vacuum is then

$$\begin{aligned}\mu_{\mathrm{k,solv}} = {} & \frac{1}{8\pi}\int \vec{D}_k \cdot \vec{E}_k \, dV \\ & - \frac{1}{8\pi}\int \vec{E}_{o,k} \cdot \vec{E}_{o,k} \, dV\end{aligned} \tag{14}$$

where $\vec{D}_k$, $\vec{E}_k$ and $\vec{E}_{o,k}$ are the dielectric displacement of the k-th particle, the vector of electric field generated by the k-th particle and the vector of electric field of the k-th particle in the vacuum, respectively.

In the case of ions one obtains [11]

$$\mu_{k,\mathrm{solv}} = -\frac{Q_k^2}{2R_k} \tag{15}$$

where Q_k is the charge of the ion and R_k is the radius of the cavity. In the case of a dipole we have [11]

$$\mu_{k,\mathrm{solv}} = -\frac{d_k^2}{2R_k^3} \tag{16}$$

where d_k is the absolute value of the dipole moment of the quasi-species of the k-th type.

The relation describing the equilibrium between individual quasi-species in the melt can be then rewritten in the form

$$\sum_j \nu_j \left(kT \ln \frac{c_j}{\Lambda_j} + \mu_{j,\mathrm{solv}} \right) = \sum_i \gamma_i \left(kT \ln \frac{c_i}{\Lambda_i} + \mu_{i,\mathrm{solv}} \right) \tag{17}$$

The equlibrium constant for the reaction scheme considered is then

$$\begin{aligned}K(T,V) = {} & \frac{\prod_j c_j^{\nu_j}}{\prod_i c_i^{\gamma_i}} = \frac{\prod_j \Lambda_j^{\nu_j}}{\prod_i \Lambda_i^{\gamma_i}} \\ & \times \exp\left[\frac{\sum_i \gamma_i \mu_{i,\mathrm{solv}} - \sum_j \nu_j \mu_{j,\mathrm{solv}}}{kT} \right]\end{aligned} \tag{18}$$

In our calculations we assumed that the ratio of vibrational and rotational statistical sums for the individual reactions would be close to unity (or, in other words, that the energy differences of these motions are several orders less than changes in the electronic and solvation energies). Thus, only electronic and translational degrees of freedom are included in Λ_j, Λ_i in Eq. (18).

In accordance with widely accepted opinion and the results of spectroscopic studies [1, 2] only quasi-species with at most one aluminium atom were considered in the present work. Based on elementary chemical considerations, the preliminary set of quasi-species subjected to stability testing was restricted to Na^+, F^-, and $\mathrm{Na}_x\mathrm{AlF}_y^{(3+x-y)}$, where x ranges from 0 to 6 and y ranges from 4 to 6. Note that for some of the summary formulae of the above type, one obtains more than one chemically non-equivalent quasi-species. In this case we considered the most energetically stable molecule or ion (e.g. tridentate NaAlF_4).

Of all the possible quasi-species in the cryolite melt, the subset of most probable quasi-species with at most one Al atom is shown in Table 1. Among these, the quasi-species with lower absolute value of electric charge are expected to be the most stable in an ionic environment. (Destabilisation due to high charge significantly dominates the effect of stabilisation by solvation.) This assumption was verified by computation of some highly charged quasi-species, e.g., AlF_6^{3-}. Thus, following the above electron stability criterion a subset of most stable quasi-species was selected from scheme I. Those quasi-species for which calculations were performed are indicated in bold type in Table 1. For each of these quasi-species gas-phase geometry optimization was performed. These geometries were then used for further computations. The values of 0.95 Å and 1.33 Åwere used for the ionic radii of Na^+ and F^-, respectively, in accordance with standard textbooks of inorganic chemistry.

3 Results

3.1 Structure

Computations at a similar level of theory have been reported for some of our quasi-species. The optimised geometry of the quasi-species given by our calculations is in good agreement with the gas-phase geometry of the same ions, computed by other authors. Our Al-F bond length for the octahedral anion AlF_6^{3-} is 1.900 Å, which is in excellent agreement with the value obtained using LDF [7]. The Al-F bond lengths in AlF_5^{2-} are 1.767 Å for equatorial and 1.815 Å for the axial bonds, in good agreement with the values of 1.78 Å and 1.81 Å [7]. We also calculated equilibrium geometries of selected models using other quantum-chemical methods (B3LYP, HF/MBPT2) [9]. (All aspects of these calculations will be discussed in details in a forthcoming publication). For AlF_5^{2-} with a "hybrid" HF-DFT exchange-correlation functional B3LYP [12] we obtained bond lengths of 1.780 Å for equatorial and 1.830 Å for axial bonds in AlF_5^{2-}, respectively. The B3LYP functional provides larger bond lengths than the Perdew-Wang one, as is usually the case. The type of exchange-correlation functional used in [7] was not indicated there.

Table 1. Subset of quasi-species in a cryolite melt with at most one Al atom (bold type indicates species for which calculations were performed)

$\mathbf{Na}^+$	$\mathbf{NaF}$	$\mathbf{F}^-$
$\mathrm{Na_6AlF_4^{5+}}$	$\mathrm{Na_6AlF_5^{4+}}$	$\mathbf{Na_6AlF_6^{3+}}$
$\mathrm{Na_5AlF_4^{4+}}$	$\mathbf{Na_5AlF_5^{3+}}$	$\mathrm{Na_5AlF_6^{2+}}$
$\mathbf{Na_4AlF_4^{3+}}$	$\mathrm{Na_4AlF_5^{2+}}$	$\mathbf{Na_4AlF_6^{+}}$
$\mathrm{Na_3AlF_4^{2+}}$	$\mathrm{Na_3AlF_5^{+}}$	$\mathbf{Na_3AlF_6}$
$\mathbf{Na_2AlF_4^{+}}$	$\mathbf{Na_2AlF_5}$	$\mathbf{Na_2AlF_6^{-}}$
$\mathbf{NaAlF_4}$	$\mathbf{NaAlF_5^{-}}$	$\mathbf{Na}\mathrm{AlF_6^{2-}}$
$\mathbf{AlF_4^{-}}$	$\mathbf{AlF_5^{2-}}$	$\mathbf{AlF_6^{3-}}$

Table 2. Calculated energies [SCF (DFT/pw91) solvation, total, in a.u.] and radii of cavities (in Å) of quasi-species in the ionic melt

Quasi-species	*E*(SCF)	*E*(SOLV)	*E*(TOTAL)	*R*(CAV)
Na^+	−162.0340	−0.2786	−162.3126	0.950
F^-	−99.8470	−0.1990	−100.0460	1.330
NaF	−262.1428	−0.0732	−262.216	2.089
AlF_4^-	−642.2251	−0.0883	−642.3134	2.998
$NaAlF_4$	−804.4488	−0.0051	−804.4538	3.770
$Na_2AlF_4^+$	−966.5390	−0.0569	−966.5959	4.649
$Na_4AlF_4^{3+}$	−1290.4643	−0.4992	−1290.9635	4.770
AlF_5^{2-}	−741.9992	−0.3366	−742.3358	3.144
$NaAlF_5^-$	−904.3952	−0.0764	−904.4716	3.463
Na_2AlF_5	−1066.6198	−0.0034	−1066.6232	4.575
$Na_5AlF_5^{3+}$	−1552.5711	−0.5042	−1553.0753	4.723
AlF_6^{3-}	−841.6336	−0.7372	−843.1862	3.230
$NaAlF_6^{2-}$	−1004.1751	−0.2969	−1004.472	3.565
$Na_2AlF_6^-$	−1166.5883	−0.0758	−1166.6641	3.492
Na_3AlF_6	−1328.8706	−0.0140	−1328.8846	3.376
$Na_4AlF_6^+$	−1491.0611	−0.0736	−1491.1341	3.596
$Na_6AlF_6^{3+}$	−1814.8999	−0.5034	−1815.4033	4.731

Table 3. Equilibrium constants in the melt and without accounting for the solvent effect at 1000 K (in mol/l)

No.	Reaction	*K*(melt)	*K*(gas)
1	$NaF \rightarrow Na^+ + F^-$	3.7×10^{32}	1.3×10^{-23}
2	$NaAlF_4 \rightarrow Na^+ + AlF_4^-$	9.8×10^{36}	2.4×10^{-13}
3	$Na_2AlF_4^+ \rightarrow Na^+ + NaAlF_4$	6.5×10^{36}	5.2×10^{5}
4	$AlF_5^{2-} \rightarrow F^- + AlF_4^-$	3.5×10^{16}	2.0×10^{23}
5	$NaAlF_5^- \rightarrow Na^+ + AlF_5^{2-}$	4.5×10^{37}	5.8×10^{-37}
6	$NaAlF_5^- \rightarrow F^- + NaAlF_4$	1.6×10^{17}	4.9×10^{-1}
7	$NaAlF_5^- \rightarrow NaF + AlF_4^-$	4.2×10^{21}	9.1×10^{9}
8	$Na_2AlF_5 \rightarrow Na^+ + NaAlF_5^-$	3.2×10^{35}	2.0×10^{-13}
9	$Na_2AlF_5 \rightarrow F^- + Na_2AlF_4^+$	7.9×10^{15}	1.9×10^{-19}
10	$Na_2AlF_5 \rightarrow NaF + NaAlF_4$	1.4×10^{20}	7.5×10^{9}
11	$Na_5AlF_5^{3+} \rightarrow NaF + Na_4AlF_4^{3+}$	1.2×10^{28}	5.4×10^{18}
12	$AlF_6^{3-} \rightarrow 2F^- + AlF_4^-$	2.3×10^{31}	6.0×10^{65}
13	$AlF_6^{3-} \rightarrow F^- + AlF_5^{2-}$	6.5×10^{14}	3.0×10^{42}
14	$NaAlF_6^{2-} \rightarrow Na^+ + AlF_6^{3-}$	2.7×10^{42}	6.8×10^{-57}
15	$NaAlF_6^{2-} \rightarrow 2F^- + NaAlF_4$	6.2×10^{36}	1.7×10^{22}
16	$NaAlF_6^{2-} \rightarrow F^- + NaAlF_5^-$	3.9×10^{19}	3.4×10^{22}
17	$NaAlF_6^{2-} \rightarrow NaF + AlF_5^{2-}$	4.7×10^{24}	1.5×10^{9}
18	$Na_2AlF_6^- \rightarrow Na^+ + NaAlF_6^{2-}$	9.2×10^{29}	2.7×10^{-39}
19	$Na_2AlF_6^- \rightarrow 2F^- + Na_2AlF_4^+$	8.8×10^{29}	9.0×10^{-23}
20	$Na_2AlF_6^- \rightarrow F^- + Na_2AlF_5$	1.1×10^{14}	4.8×10^{-4}
21	$Na_2AlF_6^- \rightarrow 2NaF + AlF_4^-$	4.1×10^{38}	6.6×10^{16}
22	$Na_2AlF_6^- \rightarrow NaF + NaAlF_5^-$	9.6×10^{16}	7.2×10^{6}
23	$Na_3AlF_6 \rightarrow Na^+ + NaAlF_6^-$	1.2×10^{26}	2.5×10^{-21}
24	$Na_3AlF_6 \rightarrow 2NaF + NaAlF_4$	4.8×10^{27}	6.9×10^{8}
25	$Na_3AlF_6 \rightarrow NaF + Na_2AlF_5$	3.5×10^{7}	9.2×10^{-2}
26	$Na_4AlF_6^+ \rightarrow Na^+ + Na_3AlF_6$	1.1×10^{22}	1.0×10^{-8}
27	$Na_4AlF_6^+ \rightarrow 2F^- + Na_4AlF_4^{3+}$	6.9×10^{15}	1.0×10^{-90}
28	$Na_6AlF_6^{3+} \rightarrow NaF + Na_5AlF_5^{3+}$	2.9×10^{-2}	2.0×10^{-12}

For AlF_4^- and $NaAlF_4$ we can compare our results with results of the HF 6-31G* geometry optimisation [6]. Our Al-F bond length in AlF_4^- is 1.668 Å, the HF 6-31G* result in [6] is 1.677 Å. The interatomic distances in $NaAlF_4$ with tridentate position of Na provided by our computation versus those referred to in [6] are 2.533 vs 2.583 Å for Na-Al and 1.710 vs 1.634 Å for Al-F (closer to Na), respectively. The differences can be ascribed to the fact that the geometries in [6] were obtained at the HF level of theory.

3.2 Energetics and equilibrium constants

Table 2 summarises the total SCF energies, solvation energies, total energies in the environment of the ionic melt and the radii of cavities for all the quasi-species considered.

Table 3 shows the most important reaction schemes of the type C → A + B that can be constructed from our set of quasi-species together with the values of the respective equilibrium constants at 1000 K. The effect of stabilisation of the charged particles in the melt can be seen in the difference between the equilibrium constants for the gas phase and for the melt. The energetical preference for small cavities (Table 2) is also evident in the values of the equlibrium constants (Table 3). Looking at the equilibrium constants in the melt, one can see from the values for reactions 4 and 13 (Table 3) that the equlibrium is strongly shifted to the AlF_4^- anion (note that the equilibrium constant for reaction 12 is simply a product of the above equilibrium constants). This is, however, a simple example, although quite illustrative. To take into account all the reactions considered and various possible molar ratio NaF/AlF_3, one has to express the Gibbs energy of the reaction mixture (using the known chemical potentials) as a function of concentrations of individual quasi-species. The vector of concentrations of individual quasi-species, giving the minimum Gibbs energy, is then computed under the condition of conservation of stoichiometry and material balance. (The usual methods of linear programming can be used for such a minimisation.) Our calculations of equilibrium compositions of reaction mixtures were performed for a ratio of NaF/AlF_3 ranging from 1 (corresponding to $NaAlF_4$) to 3 (corresponding to Na_3AlF_6). These calculations showed that almost all aluminium atoms are coordinated with four fluorine atoms in AlF_4^- complex ions.

4 Discussion

The equilibrium constants we obtain predict that all aluminium ions in the melt are in the form of AlF_4^- ions, for practically all common concentration ranges. The recent experimental study of Tixhon et al. [13] yields the same result for equilibrium in an NaF-AlF_3 system in an environment of molten NaCl. The Cl^- anion does not substitute the fluoride anion in the coordination sphere of Al, and the NaCl seems to be a chemically unreactive environment for fluoroaluminate ions. This situation is very close to the assumptions of our model. Thus one can conclude that the model of solvation of ions by an ideal conductor continuum works well for ionic melts.

For pure xNaF-yAlF$_3$ systems, interpretation of experimental data of the same kind as in [13] does not show that the major component of the melt is AlF_4^- [1, 2]. The conclusion of Refs. [1, 2] that the AlF_5^{2-} ions are the most significant components of the melt contradicts our result. Moreover, in Ref. [3] serious arguments against such conclusion are presented. A possible source of error in the interpretation of the spectral data may be the neglect of contributions by dialumino (or oligoalumino) complexes. Our theoretical study carries the same limitation. Consideration of, at least, dimers will probably better describe the pure fluoride melt.

Another approximation of the present method is that the influence of the reaction field on the equilibrium geometry of the molecule or ion is not taken into account. For reactions in which the reactants have small energy differences the errors caused by this approximation may be significant. Including this effect will improve mainly the liquid/gas equilibrium constants and will enable prediction of the equilibrium gas pressure over the melt.

Two ways of further development of our model should be investigated. First, the set of model quasi-species should be extended to include oligo-aluminium species. This is strongly supported by the results of MD simulations [5]. The Al-Al partial radial distribution functions obtained in [5], and the Al-Al coordination numbers derived from them, indicate the possible existence of dimers for a melt composition of Na_3AlF_6, possible linear chains in the case of Na_2AlF_5 and a possible tetrahedral Al-Al network in case of $NaAlF_4$. One does not necessarily need to believe that there really exists a chain or a three-dimensional network in the melt, but the motivation for extending our model for quasi-species with more than one Al atom is strong.

The second direction is the methodological improvement of the solvation models used for ionic melts. Among the most promising possibilities one can mention direct inclusion of the electrical field of the environment into the Hamiltonian of the quasi-species; construction of quasi-species which include the second, third, etc. coordination spheres; and the combination of both.

5 Conclusions

The combination of sufficiently accurate quantum-chemical methods with the correct choice of quasi-species and with appropriate description of the solvation effect enables a qualitatively correct description of molten salt structure. It should be emphasised that the choice of the quasi-species is crucial to the success of this method.

The qualitatively correct results obtained using our very simple solvation model are encouraging. More accurate predictions (at least at the semiquantitative level) can be expected after minor improvements of this model.

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