

# Compare the Energies of Different Oxofluoro Aluminium Structures in Aluminium Electrochemical Cell

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**Abstract:** The fluoroaluminate molten salts are used in the Hall-Heroult industrial process for the production of aluminum by electrolysis. To better understand the mechanism of the dissolution of alumina ( $\text{Al}_2\text{O}_3$ ) in cryolitic melts, we have studied the structure stability of these anions. The initial structural models of  $[\text{Al}_2\text{OF}_6]^{2-}$ ,  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$ ,  $[\text{Al}_2\text{O}_2\text{F}_6]^{4-}$  and  $[\text{Al}_2\text{OF}_{10}]^{6-}$  were generated using Gauss View. Since this study attempts to compare the energies of different oxofluoroaluminum structures, the geometries should be optimized at an accurate level of theory. Therefore, geometry optimizations and energy calculations were carried out by B3LYP density functional while several basis sets including 6-31g, 6-311g\*\*, 6-311g\*\* and 6-311++g\*\* were used. Furthermore, solvent effect on structural energies was investigated through incorporation of conductor-like polarizable continuum model (CPCM) at B3LYP/6-311++g\*\* level of theory the structure was optimized at different levels by applying CPCM solvent model. Similar calculations were performed for the other complex structures and similar results were obtained for them. Based on the energy values, the following stability order is achieved:  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-} < [\text{Al}_2\text{OF}_6]^{2-} < [\text{Al}_2\text{O}_2\text{F}_6]^{4-} < [\text{Al}_2\text{OF}_{10}]^{6-}$

**Keywords:** Fluoro Aluminat molten, Hall-Heroult Industrial Process.

## INTRODUCTION

Chemical and electrochemical reactions taking place at or near the anode and cathode of Hall-Heroult cells are of great practical and theoretical importance. Although not fully understood, in spite of extensive research, enough is known to form a reasonable consistent picture. While the carbon lining of the cell is often called the cathode, the true cathode is the molten aluminium that rests on it. The prebaked carbon blocks are suspended in the electrolyte to form the anode of the cell.

Enthalpies of formation and Gibbs free energy of formation of  $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_x$  ( $x=0-6$ ),  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_4(\text{H}_2\text{O})^{2-}$  and  $\text{Al}(\text{OH})_4^-$  are calculated at B3LYP/6-31G, 6-31G and B3LYP/6-311++G(3d2p) levels respectively with Dipole&Sphere solvent model by DFT and ab initio methods.

Especially, in the process of  $\text{Al}(\text{OH})_3$  crystals precipitating from supersaturated sodium aluminate solution,  $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_x$  ( $x=0-6$ ) is the favorable growth unit,  $\text{Al}(\text{OH})_3$  is the structure unit of growth units and  $\text{Al}(\text{OH})_4(\text{H}_2\text{O})^{2-}$  is the minimum growth unit. Using DFT Method [1].

The experimentally well-known alumina solubility in the range of acid to neutral cryolite-base melts has been modeled thermodynamically in terms of several oxyfluoride solutes. For an acidic melt, cryolite ratio (CR)=.5, the dominant solute is monooxygen  $\text{Na}_2\text{Al}_2\text{OF}_6$ . In a less acidic regime, dioxygen  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$  is dominant, whereas for neutral alumina solubility in the compositions (CR=3)  $\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6$  starts to gain importance. The fit of the model to the experimental solubility data is virtually perfect. The values of the equilibrium constants for the formation of the individual solutes are reported. [2]

Cryolitic liquids ( $\text{NaF-AlF}_3$  binary system) with dissolved aluminum oxide ( $\text{Al}_2\text{O}_3$ ) are used for the production of metallic aluminum by the Hall-Heroult electrolytic process. To better understand the

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mechanism of the dissolution of alumina ( $\text{Al}_2\text{O}_3$ ) in cryolitic melts, we have studied the structure stability of these anions in electrolyte.

## THEORETICAL

### Method

A Gaussian 09 was employed to optimize the geometries and calculate energies. Also, Hyper Chem and Gauss View were used for graphical illustrations

#### Selection of the Molecular Models and Structure Optimization

The initial structural models of  $[\text{Al}_2\text{OF}_6]^{2-}$ ,  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$ ,  $[\text{Al}_2\text{O}_2\text{F}_6]^{4-}$  and  $[\text{Al}_2\text{OF}_{10}]^{6-}$  were generated using Gauss View. Since this study attempts to compare the energies of different oxyfluoroaluminum structures, the geometries should be optimized at an accurate level of theory. Former DFT based energy calculations [3] have confirmed that DFT approach can result in good agreement with experimental data. Therefore, geometry optimizations and energy calculations were carried out by  $\text{B}_3\text{LYP}$  density functional while several basis sets including 6-31g, 6-311g\*\*, 6-311g\*\* and 6-311++g\*\* were used. Furthermore, solvent effect on structural energies was investigated through incorporation of conductor-like polarizable continuum model (CPCM) at  $\text{B}_3\text{LYP}/6-311++g^{**}$  level of theory.

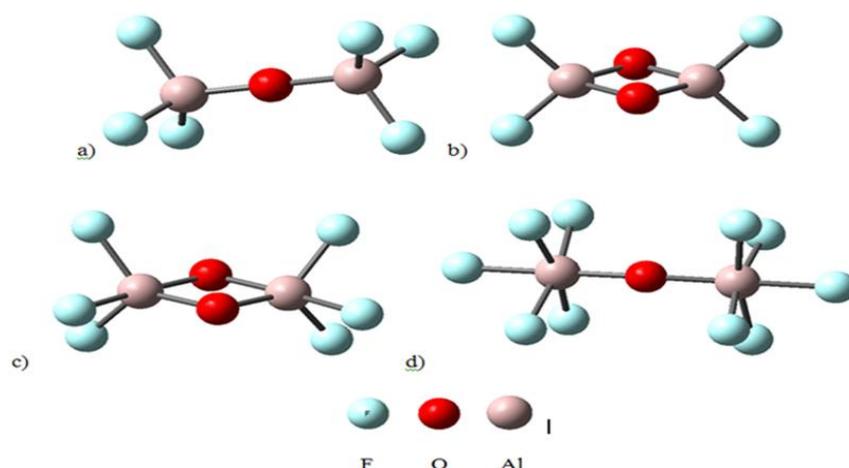


Fig. 1: Geometry optimizations structural models of  $[\text{Al}_2\text{OF}_6]^{2-}$ ,  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$ ,  $[\text{Al}_2\text{O}_2\text{F}_6]^{4-}$  and  $[\text{Al}_2\text{OF}_{10}]^{6-}$

For all structures, the initial geometries were supposed to have symmetric configurations and the oxygen atoms were considered as the structural bridges. The noticeable point is that in the  $[\text{Al}_2\text{OF}_6]^{2-}$  complex, the oxygen atom had formed a  $110^\circ$  angle bridge before optimization (Figure 2) while it forms a  $180^\circ$  bridge, after full optimization and acquiring structural stability. This finding is in good agreement with the results of Zhang et al [6]. It is noteworthy that  $[\text{Al}_2\text{OF}_{10}]^{6-}$  is unstable in gas phase and it should be concerned in solvent phase. As a consequence, the structure was optimized at different levels by applying CPCM solvent model. Similar calculations were performed for the other complex structures and similar results were obtained for them.

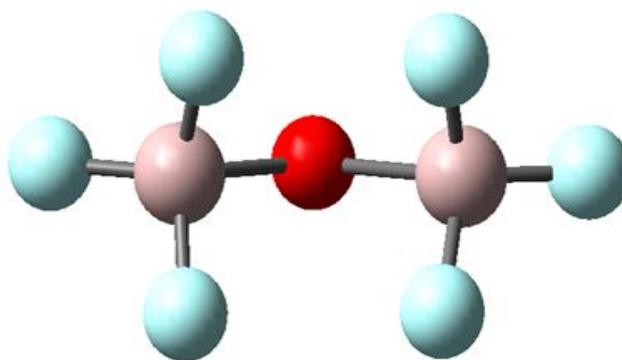


Fig. 2:  $[\text{Al}_2\text{OF}_6]^{2-}$  before optimization

## Result and Discussion

All the calculated energy values of the four complexes are reported in Table 1

Table 1: Comparison of the calculated energy values of the four complexes

	$[\text{Al}_2\text{OF}_6]^{2-}$	$[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$	$[\text{Al}_2\text{O}_2\text{F}_6]^{4-}$	$[\text{Al}_2\text{OF}_{10}]^{6-}$
B3LYP /6-31g	-1159.587	-1035.017	-1234.074	-1559.600
B3LYP /6-311g**	-1160.017	-1035.391	-1234.541	-1560.225
B3LYP /6-311+g**	-1160.081	-1035.443	-1234.673	-1560.418
B3LYP /6-311++g**	-1160.081	-1035.443	-1234.673	-1560.418
B3LYP /6-311++g** (CPCM)	-1160.358	-1035.741	-1235.789	

According to this table, moving from 6-31g to 6-311++g\*\* basis set, i.e. adding polarization and diffusion functions to the basis set, reduces the computed energy and predicts further energy stabilization. Meanwhile, the addition of the second diffuse function has no effect. Based on the energy values, the following stability order is achieved:  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-} < [\text{Al}_2\text{OF}_6]^{2-} < [\text{Al}_2\text{O}_2\text{F}_6]^{4-} < [\text{Al}_2\text{OF}_{10}]^{6-}$

One of the interesting findings of Table 1 is that the solvent affects and stabilizes  $[\text{Al}_2\text{O}_2\text{F}_6]^{4-}$  more than any other complex. Also, the solvent stabilizes the  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$  and  $[\text{Al}_2\text{OF}_6]^{2-}$  complexes by 186.62 and 173.43 kJ mol<sup>-1</sup> energy compared to the gas phase, respectively. As experiments declare, first  $[\text{Al}_2\text{OF}_6]^{2-}$  complex forms and then  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$  would generate. Moreover, higher solubility is reported for  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$  [5]. Our observations verify these statements so that the solvent stabilizes  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$  more than  $[\text{Al}_2\text{OF}_6]^{2-}$ . In order to calculate the chemical shielding tensor of 17O nuclei, GIAO approach was used. The extent of isotropic chemical shielding was calculated by Gaussian package. The chemical shift of oxygen nuclei in  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$  and  $[\text{Al}_2\text{OF}_6]^{2-}$  complexes was computed to be respectively 35.73 ppm and -7.4 ppm. Lacassagne et al. [7] have experimentally found out that the chemical shift reduces from 25 ppm to 8 ppm, for  $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$  and  $[\text{Al}_2\text{OF}_6]^{2-}$ , respectively. The differences between the experimental and theoretical values are attributed to the fact that the theoretical results are associated with gas phase calculations. Also, it should be noted that in the experimental medium, the two species coexist and the chemical shift values in the solvent phase are the average values regarding their simultaneous presence. Therefore, where X represents atomic fraction of oxygen in each complex. Further details and equations are discussed in Ref [8]

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