

Research Article

Comparison of Model Systems $(M^+)_n \cdot [CrX_6^{3-}]$ and $M_3CrX_6 + 18MX$ Based on Quantum-Chemical Calculations (X: F, Cl)

Vyacheslav Kremenetsky and Sergey Kuznetsov

*IV Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,
Russian Academy of Sciences, Akademgorodok 26a, Apatity, Murmansk Oblast 184209, Russia*

Correspondence should be addressed to Vyacheslav Kremenetsky; kreme_vg@chemy.kolasc.net.ru

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On the basis of quantum-chemical calculations the most stable particle compositions are estimated in such model systems as $(M^+)_n \cdot [CrCl_6]$ and $M_3CrCl_6 + 18MCl$ ($M = Na, K, \text{ and } Cs$). In all systems these particles are positively charged. For systems $(M^+)_n \cdot [CrCl_6]$, $(M^+)_n \cdot [CrF_6]$, $M_3CrF_6 + 18MCl$, $M_3CrF_6 + 18MF$, and $M_3CrCl_6 + 18MCl$ ($M = Na, K, \text{ and } Cs$) a number of energy parameters characterizing the state of the system before and after electron transfer are calculated. The results indicate the possibility of electron transfer from the cathode to the melt system, which is in the initial state. However, this possibility cannot be realized in systems where LUMOs (lowest unoccupied molecular orbitals) have purely ligand character. In this case, the preliminary deformation of a cationic shell of electroactive species is required; it transforms the initial system to the transition state. However, in all considered systems the search of the transition state should be carried close to the initial state P_i . This greatly simplifies a problem and transforms it from a purely theoretical sphere to the field of practical tasks that do not require exceptional cost of computer time.

1. Introduction

Previously [1–4], quantum-chemical calculations of such model systems as $(M^+)_n \cdot [NbF_7]$, $(M^+)_n \cdot [NbCl_6]$, and $(M^+)_n \cdot [CrCl_6]$ ($M = Na, K, Cs$; $n = 1 \div n_{lim}$) were carried out. These systems contain a complex anion with a cation outer-sphere (OS) shell. It was found that compositions with an intermediate number of OS cations $m < n_{lim}$, where n_{lim} is the limiting number of OS cations bound to a given complex, are thermodynamically most stable. Such systems (designating them as the type I system) are often used for modeling of the charge transfer process in melts [5–9]. The activation energy of electron transfer is estimated here based on Marcus theory [10]. These systems are suitable for express-evaluation of the charge transfer parameters, because it does not require large expenditures of computer time. However, it is clear that such simple systems can have only limited application. In particular, the effect of the anion composition of the electrolyte cannot be incorporated in the type I systems.

To verify the main findings for model systems I quantum-chemical computations of some parameters have been carried out in extended model systems of type II $M_3CrX_6 + 18MX$ ($M = Na, K, \text{ and } Cs$; X: F, Cl).

Some results for the CrF_6 -containing systems I and II were given previously [11–13]; for $CrCl_6$ -containing systems I and II calculations were made in the nonrelativistic basis sets for M: Na and K in the main [2, 4, 14, 15]. Here we provide data for the systems $(M^+)_n \cdot [CrCl_6]$ and $M_3CrCl_6 + 18MCl$ in a quasi-relativistic ECP basis for M: Na, K, and Cs and an additional analysis of all these systems.

2. Computational Methods

The quantum-chemical calculations were performed with the Firefly program package [16], partially based on the codes of the GAMESS (US) program [17], by the density functional theory methods (DFT/UHF). The spin-polarized version of the Kohn-Sham equations and the B3LYP hybrid functional were used. All calculations are made with the

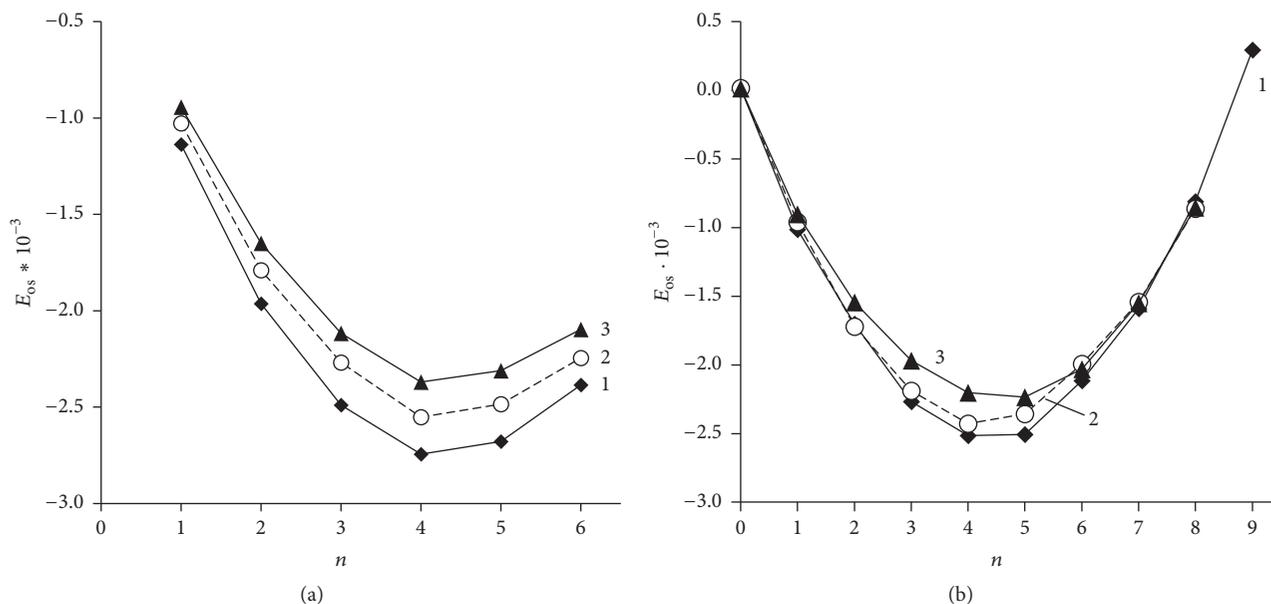


FIGURE 1: Energy of formation of the complex cationic OS shell E_{os} (kJ/mol) versus the number of OS cations (n) in systems I (M^+) $_n \cdot [CrCl_6]^{3-}$ (a) and systems II $M_3CrCl_6 + 18MCl$ (b) for (1) Na, (2) K, and (3) Cs.

quasi-relativistic ECP basis set of Stuttgart/Dresden groups [18–20], more exactly, with Stuttgart RSC 1997 ECP for Cr, K, and Cs and Stuttgart RLC ECP for F, Cl, and Na. In addition Na-systems in some cases used CRENBL ECP basis set [20]. The energy values correspond to true minima of the potential energy surface (the imaginary frequencies are absent). In all complexes chromium is in a high-spin state: $s = 3/2$ for Cr(III) and $s = 2$ for Cr(II). Spin contamination can be ignored: for the Cr(III) and Cr(II) particles, the S^2 values were 3.76–3.82 and 6.01–6.03, respectively (3.75 and 6.00 in the ideal case).

3. Results and Discussion

3.1. Composition of the Most Stable Particles. In systems II calculation of the interaction energy of the second coordination sphere fragments (M^+) $_n$ with both the complex and the external environment of a given fragment can be made. Figures 1(a) and 1(b) show the plots of the energy of cationic OS shell formation E_{os} in systems I (M^+) $_n \cdot [CrCl_6]^{3-}$ (Figure 1(a)) and II $M_3CrCl_6 + 18MCl$ (Figure 1(b)) calculated by

$$E_{os} = E_p - E_{fc} - nE_M, \quad (1)$$

where E_p , E_{fc} , and E_M are the energies of systems I (or an equivalent fragment of systems II), free $[CrCl_6]^{3-}$ complex, and free M^+ cation, respectively. The energy value E_{os} reflects the total effect of the interaction of OS cations M^+ with the complex $[CrCl_6]^{3-}$ and with each other.

Dependence of this type always has a minimum at some intermediate n_{min} value. The existence of the minimum is mainly caused by an increase in the repulsion between OS

cations as their number increases. The composition of the system at point n_{min} is the most stable. In the case of systems I $n_{min} = 4$ for all M (Figure 1(a)). The maximal number of OS cations retained by the chromium complex in systems I is 6.

Figure 1(b) shows the energy of the OS shell formation E_{os} for analogous fragments of systems II (M^+) $_n \cdot [CrCl_6]^{3-}$. Note, in systems II, the OS cations are ranked by increasing the (Cr-M) distances (r); that is, with increase of the number n on Figure 1(b) the distance $r(\text{Cr}-M_{(n)})$ increases, too. The second coordination sphere of chromium in these systems contains 8-9 cations; however the E_{os} minimum corresponds to n_{min} equal to 4 (Na, K) or 5 (Cs) only. Figure 2 shows the examples of model structures for systems I and II.

Thus, no significant displacement of the minimum was observed during the transition from systems I to systems II. This allows considering data based on results for systems I as a valid initial estimate.

Unlike the systems I, for the systems II the interaction energy of the second coordination sphere (M) $_n$ with the complex and *the rest of the system* can be calculated directly. If the interaction energy of this shell with the complex exceeds the energy of its interaction with the outer environment, we can state that there is a dynamic equilibrium in the system responsible for the existence of rather stable complex species of definite composition [11]. Relevant data are presented below.

Figure 3 shows the $E_{int}(f)$ energy of interaction of the (M^+) $_n \cdot [CrCl_6]^{3-}$ fragment with the outer environment (the rest of the systems II) as a function of the OS cations number. The $E_{int}(f)$ values were calculated from the following equation:

$$E_{int}(f) = E_s - E_f - E_r. \quad (2)$$

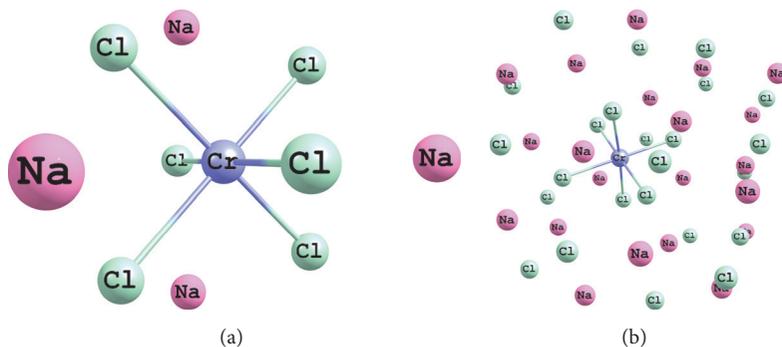


FIGURE 2: Optimized structures of (a) $4\text{Na}^+ \cdot [\text{CrCl}_6]^{3-}$ and (b) $\text{Na}_3\text{CrCl}_6 + 18\text{NaCl}$.

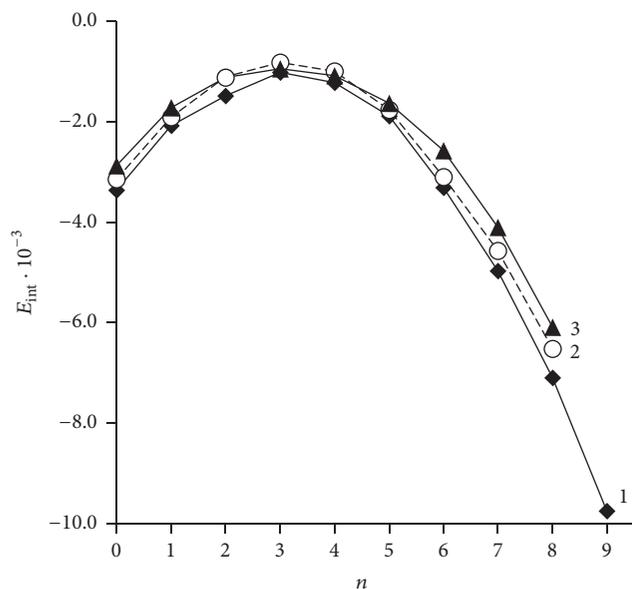


FIGURE 3: Interaction energy $E_{\text{int}}(f)$ (kJ/mol) of the $(\text{M}^+)_n \cdot [\text{CrCl}_6]^{3-}$ species in systems **II** $\text{M}_3\text{CrCl}_6 + 18\text{MCl}$ versus the number of OS cations for (1) Na, (2) K, and (3) Cs.

Here the symbols E_s , E_f , and E_r denote energies of the entire model system, its fragment $(\text{M}_n)_n \cdot [\text{CrCl}_6]^{3-}$, and the rest of systems **II**, respectively.

The maximal value of this energy is observed at $n_{\text{max}} = 3(4)$. The compositions closest in energy to the composition with the minimum energy are given in parentheses. Thus, the composition of the fragment $(\text{M}^+)_n \cdot [\text{CrCl}_6]^{3-}$ at which its interaction with the environment is minimal ($n = 3$) is close to the most stable compositions mentioned in Figure 3 ($n = 4, 5$).

Finally, let us consider the function ΔE versus n in Figure 4. It was obtained in the following way. First, two types of the interaction energy of the cation OS shell $(\text{M}^+)_n$ were calculated: (i) the energy of interaction with the complex $E_{\text{int}}(\text{M}_n \cdot \text{com})$ and (ii) the energy of interaction with the rest of systems **II** $E_{\text{int}}(\text{M}_n \cdot \text{rest})$. The ΔE value in Figure 4 is equal to the difference:

$$\Delta E = E_{\text{int}}(\text{M}_n \cdot \text{rest}) - E_{\text{int}}(\text{M}_n \cdot \text{com}). \quad (3)$$

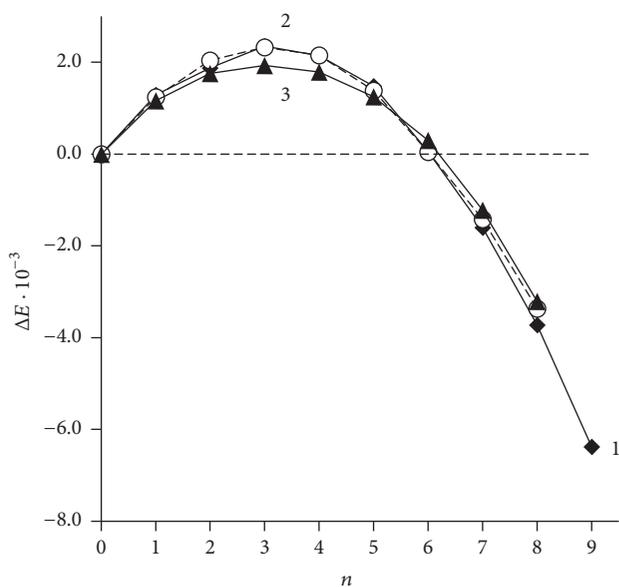


FIGURE 4: The ΔE value (kJ/mol) in systems $\text{M}_3\text{CrCl}_6 + 18\text{MCl}$ versus the number of OS cations for (1) Na, (2) K, and (3) Cs. Explanation in the text.

If we denote such fragments as $[\text{CrCl}_6]$, (M_n) , and the rest of system by characters A , B , and C , respectively, then the first energy $E_{\text{int}}(\text{M}_n \cdot \text{com})$ corresponds to equation $A + B = AB$. The second energy, that is, $E_{\text{int}}(\text{M}_n \cdot \text{rest})$, characterizes the equation $B + C = BC$, while the energy ΔE corresponds to equilibrium $(AB) + C = A + (BC)$.

As follows from Figure 4, in the range $n = 1-6$, the energy of OS shell interaction $(\text{M}^+)_n$ with the complex is larger than with the external rest of system in all model systems. Maximum of this function corresponds to the value $n_{\text{max}} = 3(4)$.

Thus, the most stable particles in systems **II** are $(\text{M}^+)_n \cdot [\text{CrCl}_6]^{3-}$ with $n = 4$ (Na, K) or 5 (Cs), as follows from Figure 1(b). According to Figure 4, such fragments can be considered as a single particle relatively weakly bound to the surroundings; they have a positive charge for all M.

3.2. Comparison of the System Energies before and after Electron Transfer. Let us introduce the following notation. P_i

TABLE 1: The energy parameters (kJ/mol) of the systems before and after electron transfer. Explanation in text.

$(M^+)_n \cdot [CrF_6]^{3-}$									
S	Na			K			Cs		
M	2	3	4	2	3	4	2	3	4
$\Delta E1$	291	14	-313	190	-31	-261	172	-51	-220
$\Delta E2$	293	17	-288	191	-29	-249	173	-33	-220
$\Delta E3$	289	10	-538	188	-34	-640	171	-28	-220
$(M^+)_n \cdot [CrCl_6]^{3-}$									
S	Na			K			Cs		
M	2	3	4	2	3	4	2	3	4
$\Delta E1$	-186	-380	-569	-133	-389	-503	-152	-351	-457
$\Delta E2$	153	-151	-462	157	-87	-375	133	-49	-303
$\Delta E3$	-257	-516	-698	-177	-489	-681	-172	-484	-628
$M_3CrF_6 + 18MCl$ $M_3CrF_6 + 18MF$ $M_3CrCl_6 + 18MCl$									
S	Na			K			Cs		
M	Na	K	Cs	Na	K	Cs	Na	K	Cs
$\Delta E1$	-265	-150	-111	-156	-67	-47	-332	-368	-354
$\Delta E2$	-43	-47	-38	-34	-34	-23	-223	-187	-122
$\Delta E3$	-428	-475	-419	-428	-91	-47	-543	-532	-495

is initial state of the system (before electron transfer); P_f is final state of the system (after electron transfer); P_{fi} is state of the system with the geometric structure P_i , but after the electron transfer (ET); P_{if} is state of the system with the geometric structure P_f , but before ET; $E(P)$ is the energy of system in state P ; $\Delta E1 = E(P_f) - E(P_i)$; $\Delta E2 = E(P_{fi}) - E(P_i)$; $\Delta E3 = E(P_f) - E(P_{if})$. Electron transfer here means the transfer of one electron in the cathode process to the complex of chromium: $[CrX_6]^{3-} + e \rightarrow [CrX_6]^{4-}$ ($X = F, Cl$).

The energy values ΔE are given in the Table 1 for systems I $(M^+)_n \cdot [CrF_6]^{3-}$ and $(M^+)_n \cdot [CrCl_6]^{3-}$ ($n = 2-4$) and systems II $M_3CrF_6 + 18MCl$, $M_3CrF_6 + 18MF$, and $M_3CrCl_6 + 18MCl$ ($M = Na, K, Cs$).

Here we should pay attention to the following. In the range of $n = 2-4$, the energy values $\Delta E2$ and $\Delta E3$ change the sign in the system $(M^+)_n \cdot [CrF_6]^{3-}$. Therefore, in this range of the n value mechanism of ET will depend on the composition of the electroactive particle. In particular for Na-system at $n = 3$ there is intermediate structure state P^* in which the intersection of the potential energy surfaces of states, before and after ET, occurs. This fact is the basis for estimation of the ET activation energy according to the Marcus theory [10]. If composition of the electroactive species in the Na-system is close to the one with n equal 4, then ET may occur directly to the complex in the initial state P_i (in case when there are no other restrictions). These considerations are also applicable to K-, Cs-systems.

In the system $(M^+)_n \cdot [CrCl_6]^{3-}$ only functions $\Delta E2$ change the sign. However, this is quite enough to use for states with $n = 3$ and 4, the conclusions obtained above in relation to the initial state P_i . Low stability of the state P_{if} in comparison with the P_f state is due to the strong influence of the Jahn-Teller effect on the structure of the $[CrCl_6]^{4-}$ complex after ET. For this reason, the state P_{if} is strongly destabilized and the $\Delta E3$ energy is less than zero for all values of n .

In the extended systems II the ΔE values are less than zero for all M. In this case, formally electron transfer can occur at the initial state P_i . Some comments on this conclusion are made in the next section.

4. Conclusions

Results of this work indicate the possibility of ET directly to the initial particle P_i , rather than through a transition state P^* . This finding needs to be clarified.

Earlier [21] analysis of the nature of frontier molecular orbitals was held in systems $M_3CrX_6 + 18MCl$ ($X: F, Cl$; $M: Na, K, Cs$) and it was shown that ET through the OS cations is only possible in system $Cs_3CrF_6 + 18CsCl$. In other systems, the nature of the LUMO (lowest unoccupied molecular orbital) requires preliminary adjustment of the OS shell to provide direct contact ligands of the first coordination sphere with the electrode surface. That is, in these systems, ET has to take place in a transition state P^* .

In work [21] it was also suggested that for the system $Cs_3CrF_6 + 18CsCl$ charge transfer takes place in a state with geometric structure which is close to the structure of the initial system. In this work we obtain confirmation of this assumption.

In the $Cs_3CrF_6 + 18CsCl$ system ET occurs with abnormally high rate and apparently is limited by diffusion. The approach of the active particles to the electrode surface requires the overcoming of the activation barrier, which depends on the particle charge. Data related to the composition and the possible charge of such particles can be obtained from data such as in Figures 1, 3, and 4. An example of use of such approach is contained in the work [22] where the abnormal rate of ET in the system $Na_2NbCl_6 + 18MCl$ in comparison with systems $M_2NbCl_6 + 18MCl$ ($M = K, Cs$) has been explained by distinction of charge of the electroactive species.

Furthermore, according to calculations, in some cases a higher rate of ET can occur for particles with less stability [13].

Thus, analysis of the mechanism of electrochemical ET in melts requires taking into account a number of factors. Nevertheless, the main conclusion of this work remains true: the search of the transition state in the considered systems should be carried close to the initial state P_i . This greatly simplifies a problem and transforms it from a purely theoretical sphere to the field of practical tasks that do not require exceptional cost of computer time.

Competing Interests

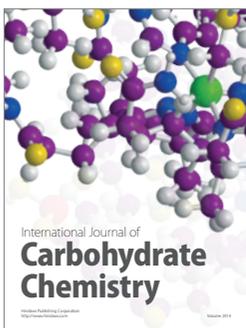
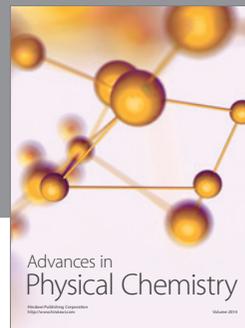
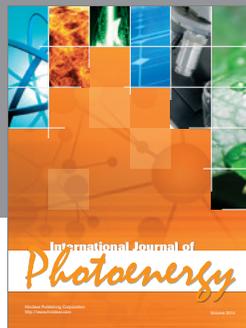
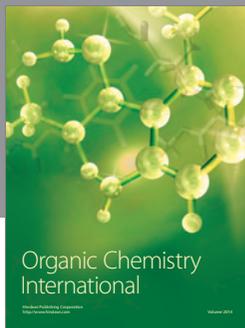
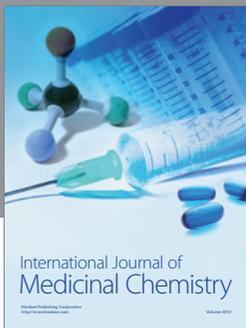
The authors declare that they have no competing interests.

Acknowledgments

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References

- [1] S. A. Kuznetsov, V. G. Kremenetskii, A. V. Popova, O. V. Kremenetskaya, and A. V. T. Kalinnikov, "Unusualeffect of the second coordination sphere on the standard charge transfer rate constants for the Nb(V)/Nb(IV) redox couple in chloride-fluoride melts," *Doklady Physical Chemistry*, vol. 428, no. 2, pp. 770–773, 2009.
- [2] V. G. Kremenetsky, O. V. Kremenetskaya, S. A. Kuznetsov, and V. T. Kalinnikov, "Quantum-chemical approach to the estimation of the composition of stable complex species in alkali metal halide melts," *Doklady Physical Chemistry*, vol. 437, part 2, pp. 75–77, 2011.
- [3] V. G. Kremenetsky, O. V. Kremenetskaya, and A. D. Fofanov, "Influence of the outer-sphere shell on the parameters of niobium complexes: quantum-chemical calculation," *Russian Metallurgy (Metally)*, vol. 2011, no. 8, pp. 748–750, 2011.
- [4] Y. V. Stulov, V. G. Kremenetsky, and S. A. Kuznetsov, "Effect of the second coordination sphere on the standard rate constants of charge transfer for the Cr(III)/Cr(II) redox couple in chloride melts," *ECS Transactions*, vol. 50, no. 11, pp. 135–152, 2012.
- [5] F. Bouyer and G. Picard, "Evidence of cations' influence for structural rearrangements in cryolitic melts," in *Proceedings of the 54th International Meeting of Physical Chemistry: Fast Elementary Processes in Chemical and Biological Systems*, vol. 364 of *AIP Conference Proceedings*, pp. 532–539, 1996.
- [6] L. Joubert, G. Picard, B. Silvi, and F. Fuster, "Topological analysis of the electron localization function: a help for understanding the complex structure of cryolitic melts," *Journal of the Electrochemical Society*, vol. 146, no. 6, pp. 2180–2183, 1999.
- [7] V. I. Shapoval, V. V. Solov'ev, and V. V. Malyshev, "Electrochemically active species and multielectron processes in ionic melts," *Russian Chemical Reviews*, vol. 70, no. 2, pp. 161–176, 2001.
- [8] V. V. Soloviov and L. A. Chernenko, "Influence modeling of cationic composition melt on structural features of the electrochemically active particles during simultaneous and sequential electron transfer," *Research & Reviews in Electrochemistry*, vol. 4, no. 5, pp. 168–173, 2013.
- [9] S. V. Volkov, I. A. Novoselova, V. V. Solovyev, and L. A. Chernenko, "Cation catalysis in high-temperature electrochemical synthesis of tungsten carbides in molten salts," *Research & Reviews in Electrochemistry*, vol. 3, no. 3, pp. 81–89, 2012.
- [10] R. A. Marcus, "On the theory of oxidation-reduction reactions involving electron transfer. I," *The Journal of Chemical Physics*, vol. 24, no. 5, pp. 966–978, 1956.
- [11] S. A. Kuznetsov and V. G. Kremenetsky, "Comparison of some structural parameters of the model systems $nM^+ [CrX_6]^{3-}$ and ${}_3M^+ [CrX_6]^{3-} + 18MCl$ ($M=Na, K, Cs$; $X=F, Cl$; $n=1-6$)," *ECS Transactions*, vol. 64, no. 4, pp. 183–188, 2014.
- [12] V. G. Kremenetsky and O. V. Kremenetskaya, "Quantum-chemical validation of the relative stability of complex species with different outer-sphere composition in the $M_3CrF_6 + 18MCl$ systems ($M=Na, K$)," *Russian Journal of Inorganic Chemistry*, vol. 58, no. 12, pp. 1523–1526, 2013.
- [13] Y. V. Stulov, V. G. Kremenetsky, and S. A. Kuznetsov, "Electrochemical and quantum-chemical studies of chromium(III,II) fluoride complexes in alkali chloride melts," *Russian Journal of Electrochemistry*, vol. 50, no. 9, pp. 815–823, 2014.
- [14] Y. V. Stulov, V. G. Kremenetsky, and S. A. Kuznetsov, "Influence of the second coordination sphere on the electrochemical behavior of chromium complexes in chloride melts: experimental and calculation methods," *International Journal of Electrochemical Science*, vol. 8, no. 5, pp. 7327–7344, 2013.
- [15] Yu. V. Stulov, V. G. Kremenetsky, O. V. Kremenetskaya, A. D. Fofanov, and S. A. Kuznetsov, "Experimental and calculation methods of studying the effect of second coordination sphere on standard rate constants of charge transfer for Cr(III)/Cr(II) redox couple in chloride melts," *Russian Journal of Electrochemistry*, vol. 47, no. 8, pp. 948–958, 2011.
- [16] A. A. Granovsky, <http://classic.chem.msu.su/gran/games/index.html>.
- [17] M. W. Schmidt, K. K. Baldridge, J. A. Boatz et al., "The general atomic and molecular electronic structure system," *Journal of Computational Chemistry*, vol. 14, pp. 1347–1363, 1993.
- [18] D. J. Feller, "The role of databases in support of computational chemistry calculations," *Journal of Computational Chemistry*, vol. 17, no. 13, pp. 1571–1586, 1996.
- [19] K. L. Schuchardt, B. T. Didier, T. Elsethagen et al., "Basis set exchange: a community database for computational sciences," *Journal of Chemical Information and Modeling*, vol. 47, no. 3, pp. 1045–1052, 2007.
- [20] EMSL Basis Set Library, <https://bse.pnl.gov/bse/portal>.
- [21] V. G. Kremenetsky and S. A. Kuznetsov, "Anomaly of the charge transfer rate in the $CsCl-K_3CrF_6$ melt: quantum-chemical analysis," *International Journal of Electrochemical Science*, vol. 10, no. 8, pp. 6164–6174, 2015.
- [22] V. G. Kremenetsky and S. A. Kuznetsov, "Quantum-chemical estimation of the temperature effect on the parameters of the model electrochemical systems containing chloride complexes of niobium," in *Proceedings of the 25th Abstracts of EUCHEM 2014 Conference on Molten Salts and Ionic Liquids*, p. 142, Tallinn, Estonia, July 2014.



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