

Reactions of Vanadium Oxide with Cryolite

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Reactions between cryolite and vanadium oxide were examined in laboratory experiments using the cryoscopic method and measuring the mass losses during heating and melting. The reaction products were identified by X-ray diffraction analysis and IR spectroscopy. The measurements were supplemented also by the thermodynamic calculation of the reaction Gibbs energies.

From the results of the cryoscopic measurements as well as on the basis of the calculated reaction Gibbs energies it may be assumed that the introduced vanadium oxide reacts in the electrolyte with cryolite under formation of volatile VF_5 , which escapes from the melt. Besides reactions with cryolite, vanadium compounds present in the electrolyte are also reduced electrochemically, which lowers the current efficiency of the process. In the presence of metallic aluminium, chemical reduction of vanadium compounds in the electrolyte is possible as well.

Impurities are introduced into the electrolyte of the aluminium cells together with raw materials, mainly with alumina. In the conditions of modern aluminium technology the prevailing part of impurities are returned back into the electrolyte by feeding using alumina from dry scrubbers, where they are adsorbed together with fluoride emissions on the alumina surface.

Several authors investigated the behaviour of impurities dissolved in the electrolyte [1]. *Bratland et al.* [2] measured the solubility of V_2O_5 in cryolite and cryolite alumina melts. They found that solubility in pure cryolite at 1030 °C was 1.1 mass % and decreased linearly with increasing alumina content in cryolite. When Al was added to the electrolyte, most of the vanadium went into the metal and only 50 ppm vanadium remained in the bath.

Goodes and Algie [3] studied the distribution of vanadium between bath and metal in graphite crucibles. The studies showed that the transfer between bath and metal was far from chemical equilibrium. The vanadium content in the bath is higher than reported in [1]. The results may depend on the experimental conditions.

Several authors have reported [4] that vanadium and phosphorus are among the most harmful impurities with respect to the current efficiency. Therefore, it would be of interest to study the influence of these impurities on the current efficiency. In the presented work the reactions between cryolite and vanadium oxide were examined in laboratory experiments using the cryoscopic method and by measuring the mass losses during heating and melting. The reaction products were identified using X-ray diffraction analysis and IR spectroscopy. The measurements were supplemented

also by the thermodynamic calculation of the reaction Gibbs energies.

THEORETICAL

Cryoscopy is an indirect experimental method frequently used to study the possible chemical reactions taking place in melts between components. For the lowering of the temperature of fusion of the solvent A, $\Delta_{\text{fus}}T_A$, caused by the addition of the solute B the following equation holds

$$\Delta_{\text{fus}}T_A = \frac{RT_{\text{fus},A}^2}{\Delta_{\text{fus}}H_A} x_B k_{\text{St}} \quad (1)$$

where R is the gas constant, $T_{\text{fus},A}$ and $\Delta_{\text{fus}}H_A$ is the temperature and enthalpy of fusion of the solvent A, respectively, x_B is the mole fraction of the solute B, and k_{St} is the correction factor introduced by Stortebeker [5], representing the number of foreign particles, which introduces the solute B into the solvent A. Differentiating eqn (1) according to x_A and setting for $x_A \rightarrow 1$ we get the relation for the tangent to the liquidus curve of the solvent A, k_0 , at the temperature of fusion of the solvent A

$$\lim_{x_A \rightarrow 1} \frac{d(\Delta_{\text{fus}}T_A)}{dx_B} = \frac{RT_{\text{fus},A}^2}{\Delta_{\text{fus}}H_A} k_{\text{St}} = k_0 \quad (2)$$

Knowing $T_{\text{fus},A}$ and $\Delta_{\text{fus}}H_A$ we can then calculate k_{St} from the tangent to the liquidus curve of cryolite, k_0 , at $x_A = 1$.

In the region of dilute solutions the following limiting law is valid

$$\lim_{x_A \rightarrow 1} \frac{\partial a_A}{\partial x_A} = k_{\text{St}} \quad (3)$$

where a_A is the activity of the solvent expressed in terms of the mole fractions x_A according to any suitable model. Eqn (3) thus defines the physical meaning of the Stortebeker factor k_{St} . If $k_{St} = 1$ the solution obeys Raoult's law and belongs to the 1st type of solutions. If $k_{St} \neq 1$, the solution belongs to the 2nd type of solutions which do not obey Raoult's law. The knowledge of k_{St} thus enables one to deduce on the possible ongoing chemical reaction between solute and solvent.

EXPERIMENTAL

For the samples preparation the following chemicals were used: Na_3AlF_6 , hand-picked Greenland cryolite, V_2O_5 , anal. grade (Aldrich).

In the cryoscopic measurements mixtures containing 0–32 mole % of the vanadium oxide were examined. 10 g of homogenized sample was placed in a Pt crucible and melted in a resistance furnace in argon atmosphere. The temperature was measured using a PtRh10—Pt thermocouple with an accuracy of ± 1 K. The heating and cooling curves were recorded using a computerized measuring device. The cooling rate did not exceed 2 K min^{-1} . The experimentally determined values of the temperatures of primary crystallization and secondary crystallization of individual samples are given in Table 1 and Fig. 1.

The mass loss measurements were studied in mixture with 5 mole % of the vanadium oxide. 10 g of mixture was melted in a platinum crucible and kept for 120 min at the temperature of 1027°C , which is 20 K above the temperature of melting point of cryolite. The mass losses were measured using the device for measurements of density in molten salt system. The detailed description of measuring device may be found in [5]. The results are given in Fig. 2.

The samples of melts for X-ray diffraction analysis and IR spectroscopy investigation were prepared from the melts after quenching, putting the melt in platinum crucible into the icy water. Such procedure may provide samples of the frozen melt with almost unchanged structure. Preparation of the melts, manipulation and weighting of chemicals were performed in a glove box filled with dry nitrogen.

The X-ray powder diffraction patterns of the samples were recorded at room temperature in the range $7\text{--}70^\circ$ (2θ). The measurements were performed on Philips PW1349/30 diffractometer using $\text{CuK}\alpha$ radiation. Identification of the present phases was done using the PDF-2 International Center for Diffraction Data database [6].

The infrared spectra were recorded on Nicole Magna FTIR 750 spectrometer in the range $400\text{--}4000 \text{ cm}^{-1}$ with the resolution of 4 cm^{-1} . The KBr pellets were prepared from the mixture of 2 mg of quenched powdered melt and 200 mg KBr.

Table 1. Measured Temperatures of Primary Crystallization, t_{pc} , and of Secondary Crystallization, t_{sc} , in the System $\text{Na}_3\text{AlF}_6\text{--V}_2\text{O}_5$

No.	$x(\text{Na}_3\text{AlF}_6)$	$x(\text{V}_2\text{O}_5)$	$t_{pc}/^\circ\text{C}$	$t_{sc}/^\circ\text{C}$
1	1.000	0.000	1008.7	—
2	1.000	0.000	1009.7	—
3	0.999	0.001	1008.6	—
4	0.999	0.001	1009.4	—
5	0.998	0.002	1007.9	—
6	0.998	0.002	1007.7	—
7	0.997	0.003	1007.6	—
8	0.997	0.003	1008.4	—
9	0.995	0.005	1007.5	—
10	0.995	0.005	1007.3	—
11	0.993	0.007	1006.9	—
12	0.993	0.007	1006.3	—
13	0.990	0.010	1005.7	—
14	0.990	0.010	1006.8	—
15	0.985	0.015	1004.6	—
16	0.985	0.015	1005.8	—
17	0.980	0.020	1004.3	—
18	0.980	0.020	1003.9	—
19	0.965	0.035	1001.5	—
20	0.965	0.035	1002.3	—
21	0.950	0.050	997.1	—
22	0.950	0.050	998.9	—
23	0.930	0.070	993.6	—
24	0.930	0.070	994.9	—
25	0.900	0.100	987.5	655.8
26	0.900	0.100	988.4	—
27	0.850	0.150	973.8	656.8
28	0.850	0.150	978.8	—
29	0.800	0.200	963.9	667.5
30	0.800	0.200	962.4	—
31	0.700	0.300	929.1	656.3

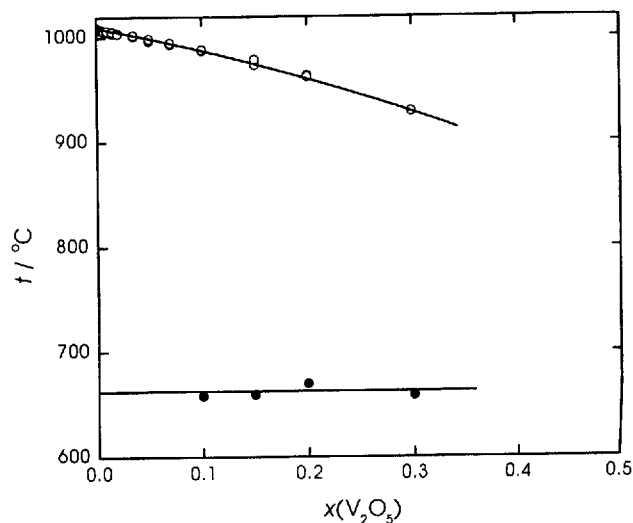


Fig. 1. Cryoscopic measurements in the system $\text{Na}_3\text{AlF}_6\text{--V}_2\text{O}_5$. \circ Temperature of primary crystallization, \bullet temperature of secondary crystallization.

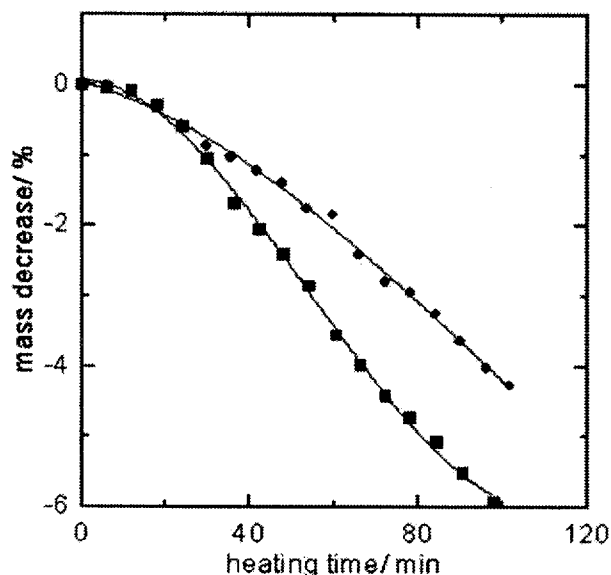


Fig. 2. Mass losses in the system $\text{Na}_3\text{AlF}_6\text{—V}_2\text{O}_5$. ● Na_3AlF_6 , ■ $\text{Na}_3\text{AlF}_6 + 5$ mole % V_2O_5 .

RESULTS AND DISCUSSION

At the cryoscopic measurements from the tangents to the experimental liquidus curves in the melting point of pure cryolite (Fig. 1) the value of the Stortebeker factor can be calculated according to eqn (2). For the enthalpy of fusion of cryolite the calorimetric value $\Delta_{\text{fus}}H_{\text{Na}_3\text{AlF}_6}^\circ = 106.75 \text{ kJ mol}^{-1}$ was used [7]. The dependence of T_{pc} on $x_{\text{Na}_2\text{AlF}_6}$ was expressed in the form of the second-order polynomial.

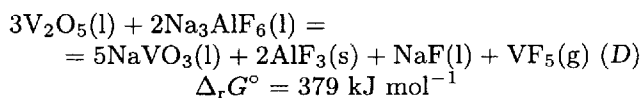
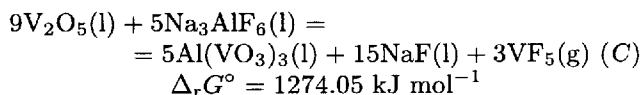
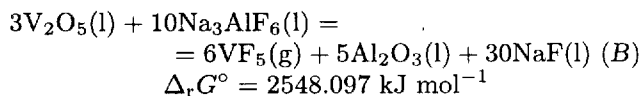
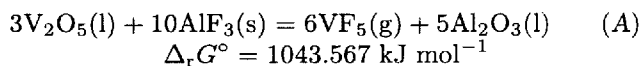
$$T_{\text{pc}}(\text{Na}_3\text{AlF}_6) = (1 - 229.48x_{\text{Na}_3\text{AlF}_6} + 227.99x_{\text{Na}_3\text{AlF}_6}^2) \text{ K} \quad (4)$$

For the constant of thermal depression, $\frac{RT_{\text{fus,cr}}^2}{\Delta_{\text{fus}}H_{\text{cr}}}$, the value 128.04 K was calculated. For k_0 and k_{St} , the values $k_0 = 226.5 \text{ K}$ and $k_{\text{St}} = 1.77$, respectively, were then calculated. From the cryoscopy in this system it follows that vanadium oxide introduces into cryolite two new species.

From the experimentally determined mass losses (Fig. 2) it follows that vanadium oxide reacts with cryolite under the formation of the gaseous products. These compounds escape from the electrolyte.

On the basis of the above-mentioned results the calculation of the reaction Gibbs energies of possible reactions of vanadium oxide with the electrolyte components, mainly cryolite, was performed. The reaction Gibbs energies in the electrolyte at the temperature of 1300 K were calculated from JANAF Thermochemical Tables data [7]. Reactions with negative or slightly positive reaction Gibbs energy are given only. On the basis of the calculated reaction Gibbs energies it may be assumed that the circulation of vanadium in the

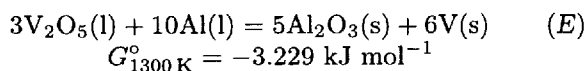
aluminium cell can be described according to the following mechanisms.



Thermodynamical probability of a given reaction is given by the value of the standard Gibbs energy of the reaction. The probability is the higher, the higher is the negative $\Delta_r G^\circ$. In the case of positive standard Gibbs energy the reaction normally does not proceed, but when one of the products is in gaseous state and it escapes from the system the reaction equilibrium is shifted to the right and the reaction may proceed. From the above listed reactions the most probable is reaction (D). In the diluted solutions of vanadium oxide in cryolite the originating VF_5 remains physically dissolved, while at higher V_2O_5 concentrations it escapes from the melt. This observation is in full agreement with the results of mass loss measurements.

For the reaction (D) 1 molecule of vanadium oxide introduces into cryolite 2 new species, 5/3 molecules of NaVO_3 and 1/5 molecules of VF_5 . This result is in good agreement with the cryoscopic measurements. The calculation of standard Gibbs energies in which oxofluorovanades take part is not possible because of lack of the needed thermodynamic data.

The reduction of vanadium oxide in the electrolyte in the presence of metallic aluminium can take place also chemically according to the reactions



X-Ray and Infrared Spectra Measurements

X-Ray powder patterns of the quenched melts of the compositions 95 % $\text{Na}_3\text{AlF}_6\text{—}5$ % V_2O_5 and 90 % $\text{Na}_3\text{AlF}_6\text{—}10$ % V_2O_5 were recorded (Fig. 3). From both patterns it is clear that only Na_3AlF_6 compound was detected in both cases and the most intensive new peak at $d = 6.92$ was observed, which indicates the formation of a new compound. Unfortunately, from the PDF-2 diffraction files it was not possible to identify the originating compound.

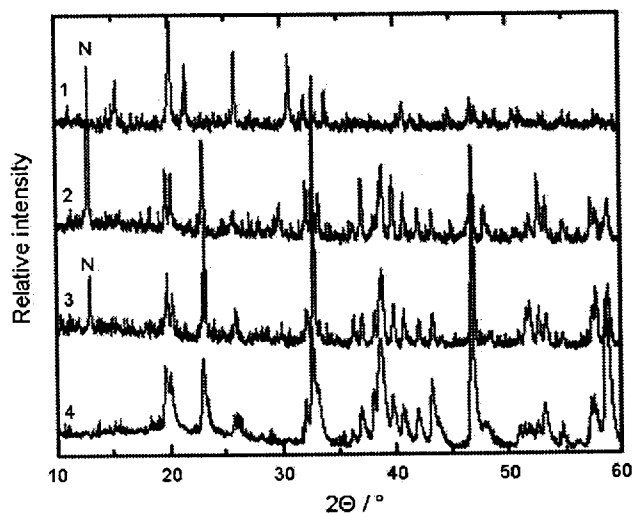


Fig. 3. X-Ray diffraction patterns of cryolite, vanadium oxide, and of quenched molten mixtures of cryolite with V_2O_5 . 1. V_2O_5 , 2. $Na_3AlF_6 + 10$ mole % V_2O_5 , 3. $Na_3AlF_6 + 5$ mole % V_2O_5 , 4. Na_3AlF_6 .

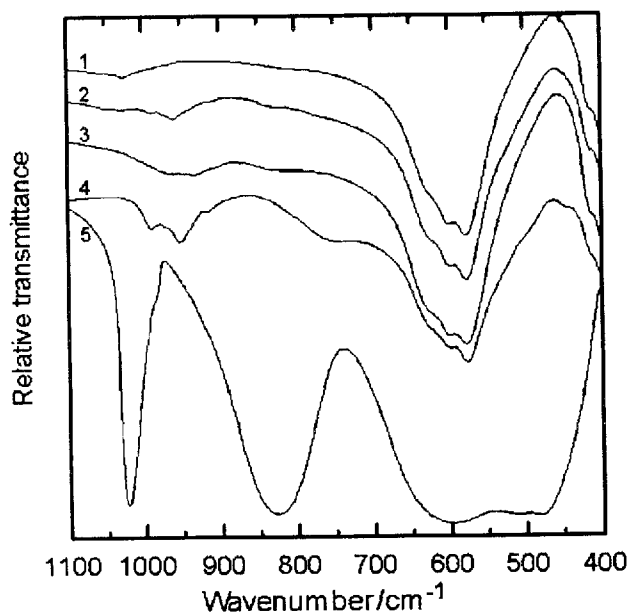


Fig. 4. Infrared spectra of cryolite, vanadium oxide, and of quenched molten mixtures of cryolite with V_2O_5 . 1. Na_3AlF_6 , 2. $Na_3AlF_6 + 5$ mole % V_2O_5 , 3. $Na_3AlF_6 + 10$ mole % V_2O_5 , 4. $Na_3AlF_6 + 20$ mole % V_2O_5 , 5. V_2O_5 .

Table 2. Infrared Spectra of Cryolite, Vanadium Oxide, $NaVO_3$, and of Quenched Molten Mixture of Cryolite with V_2O_5

Sample	Wavenumber/ cm^{-1}					
Na_3AlF_6	578	599	1026			
V_2O_5	481	596	827	1023		
$NaVO_3$	549	613	888	913	930	953
1 mole % V_2O_5	578	599	1028			
5 mole % V_2O_5	578	599	960	989		
10 mole % V_2O_5	578	599	953	990	1042	
20 mole % V_2O_5	578	599	744	915	952	989

The results of the IR spectroscopic analysis (Table 2 and Fig. 4) confirmed the results of the X-ray diffraction analysis. New bands at 915 cm^{-1} and 952 cm^{-1} , which do not belong either to the cryolite or to vanadium oxide, can be seen. It is possible to conclude that the main new structural species in the system $Na_3AlF_6-V_2O_5$ are anions $[VO_3]^-$. X-Ray and infrared spectra measurements indicate that solubility of vanadium oxide in cryolite is higher than it is reported in [2].

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