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CRYOSCOPIC DATA FOR HALL-HÉROULT BATH CONTAINING MAGNESIUM FLUORIDE, CALCIUM FLUORIDE, POTASSIUM CRYOLITE, AND SODIUM CHLORIDE

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Abstract

The well-known cryoscopy equation for binary systems was extended to the ternary system NaF-AlF₃-B, where B is a substance present in small amounts. It is shown that the depression in the liquidus temperature for a given molar fraction of B depends on the direction in which B influences the activity of NaF, as well as on the NaF/AlF₃ molar ratio. This implies that it is difficult to estimate the effect on the liquidus temperature of contaminants in the Hall-Héroult bath. The three-component cryoscopy equation can be regarded as a theoretical justification of the cross-terms used in most empirical equations for calculating the liquidus temperature. New cryoscopic data are given for the system Na₃AlF₆-CaF₂ as well as for some substances that are normally present in only small amounts, and empirical equations containing cross-terms between these substances and aluminium fluoride are suggested.

Introduction

The electrolyte (bath) used in the Hall-Héroult process consists of cryolite (Na₃AlF₆) with additions of Al₂O₃, excess AlF₃, and in some cases, LiF and/or MgF₂. The bath also contains about 5 weight percent CaF₂ due to the presence of small amounts of CaO in the alumina. Empirical equations available for calculating the liquidus temperature of the bath^[1-6] typically contain terms for the components mentioned above, and in some cases, there are cross-terms between the components. It should not be forgotten, however, that “the entire periodic system” is present in the bath, since contaminants are introduced with the raw materials. The real liquidus temperature will, therefore, be somewhat lower than what can be calculated by the empirical equations. The effect of the contaminants can be estimated by the cryoscopy equation, but in its commonly known form (binary systems) it is, strictly speaking, not valid.

The main object of the present work is to present new cryoscopic data for bath components normally present in only small amounts, and to explain the findings in view of a cryoscopy equation valid for ternary systems. This equation also provides a theoretical basis for the cross-terms between components in the liquidus equations.

Theory

It is well known that the freezing point depression resulting from mixing small amounts of substance B (solute) into pure cryolite (solvent) can be calculated by

$$\frac{dT}{dx_B} = -\frac{vRT_0^2}{\Delta H_f^0} \quad (1)$$

where T is the temperature [K], x is the molar fraction, v is the number of new species formed in the mixture per molecule of B, R is the universal gas constant [8.3143 Jmol⁻¹K⁻¹], T₀ is the melting point of pure cryolite (1284 K), and ΔH_f⁰ is the heat of fusion for pure cryolite [Jmol⁻¹]. Often neglected, the equation is valid only for binary systems, in which case the solid formed has the same composition as the solvent. This is clearly not the case in the aluminium electrolysis. A typical bath with 11 wt% excess AlF₃, 5 wt% CaF₂, and 3 wt% Al₂O₃ contains only 63 mol% cryolite, while almost pure cryolite is the primary crystallisation product.

The cryoscopy equation can be extended to the ternary system NaF-AlF₃-B. Starting from the Gibbs-Duhem equation

$$x_{\text{NaF}} d \ln a_{\text{NaF}} + x_{\text{AlF}_3} d \ln a_{\text{AlF}_3} + x_B d \ln a_B = 0 \quad (2)$$

where a is activity, we introduce the molar ratio $r = x_{\text{NaF}}/x_{\text{AlF}_3}$ and differentiate with respect to x_B, remembering that $dx/x = d \ln x$ and $x_{\text{AlF}_3} = (1-x_B)/(1+r)$,

$$r \cdot \frac{d \ln a_{\text{NaF}}}{dx_B} + \frac{d \ln a_{\text{AlF}_3}}{dx_B} + \frac{(r+1) d \ln a_B}{(1-x_B) d \ln x_B} = 0 \quad (3)$$

We assume that one unit of B forms v units of “new” or “foreign” species in the melt. Furthermore, we assume that the concentration of B is very low and that Henry’s law is valid,

$$\frac{d \ln a_B}{d \ln x_B} = v \quad \text{and} \quad 1-x_B \approx 1 \quad (4)$$

which gives

$$r \cdot \frac{d \ln a_{\text{NaF}}}{dx_B} + \frac{d \ln a_{\text{AlF}_3}}{dx_B} = -v(r+1) \quad (5)$$

Provided that there is no solubility of B in solid cryolite, the relationship between activity and liquidus temperature is given by

$$\begin{aligned} \frac{d \ln a_{\text{Na}_3\text{AlF}_6(l)}}{dx_B} &= 3 \frac{d \ln a_{\text{NaF}}}{dx_B} + \frac{d \ln a_{\text{AlF}_3}}{dx_B} \\ &= \frac{\Delta H_f}{R} \cdot \frac{1}{T^2} \frac{dT}{dx_B} \end{aligned} \quad (6)$$

Combination of Eqs. (5) and (6) now gives the cryoscopy equation for the ternary system NaF-AlF₃-B,

$$\frac{dT}{dx_B} = -\frac{RT^2}{\Delta H_f} \left\{ v(1+r) + (r-3) \cdot \frac{d \ln a_{\text{NaF}}}{dx_B} \right\} \quad (7)$$

If the melt contains only cryolite ($r = 3$), Eq. (7) becomes identical with Eq. (1) except a factor of 4, because the molar fractions in Eq. (7) are based on NaF-AlF₃-B instead of Na₃AlF₆-B.

The heat of fusion for cryolite is given in JANAF [7], and the data can be represented by

$$\Delta H_f \approx 21709 + 68.66T \quad [\text{Jmol}^{-1}] \quad (8)$$

The magnitude of $RT^2/\Delta H_f$ becomes 124.76 K in pure cryolite at 1284 K, leading to a theoretical freezing point depression of -4.99 K/mol% B in the system NaF-AlF₃-B if $v = 1$. For all other NaF-AlF₃ compositions, the freezing point depression (strictly, the liquidus temperature depression) also depends on how the substance B influences the activity of NaF. This is normally not known. In an acidic melt ($r < 3$), the liquidus temperature depression becomes larger than in cryolite, if the addition of B decreases the activity of NaF. Therefore, in industrial baths containing excess AlF₃, addition of an acid substance (F-acceptor) gives larger liquidus temperature depression than in pure cryolite. Correspondingly, there will be a negative cross-term between AlF₃ and component B in the empirical liquidus equation.

The theoretical freezing point depression for some substances (small concentration in pure cryolite) is shown in Table I. It should be noted that neither NaF nor AlF₃ form new or "foreign" species when added to molten cryolite, since these substances are already present in cryolite.

It should be mentioned here that the cryolite formed during freezing is not strictly stoichiometric; it contains some AlF₃ in solid solution. It has been suggested that cryolite should be treated as a non-stoichiometric compound Na_bAlF_(3+b) where b varies from 2.876 at 1011 °C to 3.000 at 890 °C [8]. These numbers can be used in Eq. (7) instead of 3, in combination with a revised Eq. (8) where the non-stoichiometry is taken into account. This would only bring about minor changes in the calculated freezing point or liquidus temperature depression, however.

Experimental

Principle

Liquidus temperature determination by thermal analysis (TA) is based on recording the temperature course during cooling. When the first solid precipitates, there will be a more or less distinct

break in the temperature curve ("thermal arrest") because the system gives off heat during solidification.

Table I. Theoretical freezing point depression for some substances in pure cryolite. M – molar weight, v – number of new species formed per molecule added.

Substance	M kgmol ⁻¹	v	-dθ/dm °C/wt%
NaF	0.0420	0	0
AlF ₃	0.0840	0	0
CaF ₂	0.0781	1	3.30
Al ₂ O ₃	0.1020	3	7.63
MgF ₂	0.0623	1	4.11
LiF	0.0259	1	9.43
KF	0.0581	1	4.40
NaCl	0.0585	1	4.37

Apparatus. Experimental Procedure

The experimental apparatus is shown in Figure 1. A crucible containing 150 g of melt was placed in a closed laboratory furnace with argon atmosphere. The crucible lid and the tube containing the thermocouple were made of graphite, while the stirrer and the radiation shields were made of nickel.

The crucible and its contents were heated up and stabilized at about 20 °C above the expected liquidus temperature, followed by a controlled temperature reduction. Thermocouples of type S (Pt-Pt10Rh) were used; these were calibrated against the melting point of pure silver (961.93 °C). The cooling rate was 0.65 °C/min. Vigorous stirring was applied, and when approaching the expected liquidus temperature, small amounts of solid cryolite were added each 30 seconds through a sintered alumina tube (seeding), all this in order to avoid supercooling. In the majority of the measurements, two readings were performed, *i.e.*, the melt was heated up again and cooled in a new run (denoted 1st and 2nd run in the subsequent tables).

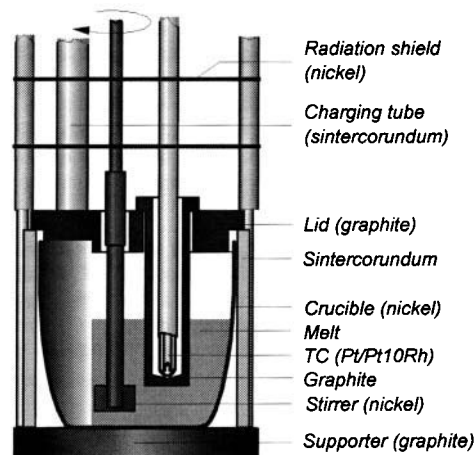


Figure 1. The experimental set-up.

Chemicals

Cryolite. Two types of cryolite were used, 1) selected lumps of natural Greenland cryolite with a melting point of 1009.6 °C, or 2) synthetic cryolite from Cerac (No. S-1176), which had a melting point of 1009.1 °C. Pure cryolite melts at 1011.0 °C [6], and the temperature readings were corrected accordingly (see below).

Aluminium Fluoride. The AlF₃ used was made from technical grade AlF₃ by vacuum sublimation at 1000 °C in our own laboratory. From analyses of the product, the average purity was estimated to be 99.5 percent.

Alumina. Al₂O₃, Merck No. 1095, calcined at 1100 °C.

Calcium Fluoride. CaF₂, Merck No. 2840.

Magnesium Fluoride. MgF₂ "Stücke", Merck No. 5821.

Potassium Fluoride. KF *p.a.*, Merck No. 1.04994

Sodium chloride. NaCl *p.a.*, Merck No. 1.06404

Aluminium carbide. Al₄C₃, Alfa Aesar No. 14038.

Treatment of Data. Corrections

A typical cooling course is shown in Figure 2 a). The recorded temperature curve (θ_{meas}) shows a thermal arrest at about 940 °C. The following procedure, which was developed to increase the accuracy in the reading of the thermal arrest, may be of some general interest:

- An auxiliary line was applied "on top of" the first part of the cooling curve (θ_{aux} in Figure 2a).
- The difference between θ_{meas} and θ_{aux} was plotted as a function of θ_{meas} , as shown in Figure 2b).

The above procedure has proved particularly helpful when there is some supercooling (not a problem in the present work), or when the thermal arrest is indistinct, which is the case in very acid bath.

The recorded temperatures (raw data) were corrected due to the calibration of the thermocouple and due to the impurities present in the cryolite. The cryolite correction factor was calculated by

$$\Delta\theta_{cry} = (1011 - \theta_{cry}) \cdot x_{cry} \quad [^{\circ}\text{C}] \quad (9)$$

where θ_{cry} is the recorded melting point for pure cryolite and x_{cry} is the molar fraction of cryolite in the melt. Furthermore, a correction was applied for the change in bath composition during the experiment. The evaporation loss from the bath was checked by weighing the crucible and its contents before and after the experiment. The evaporation loss, counted as NaAlF₄, was normally 0.6-0.9 g. The cryolite applied for seeding was also weighed (typically, 0.5 g). Based on these numbers, a corrected bath composition was calculated. The measured temperatures were then adjusted by computing the difference in liquidus temperature between the nominal (weighed-in) bath composition and the corrected bath composition, adjusted for the time of recording the thermal arrest. The resulting correction in the liquidus temperature was in the range 0.2-0.6 °C downwards.

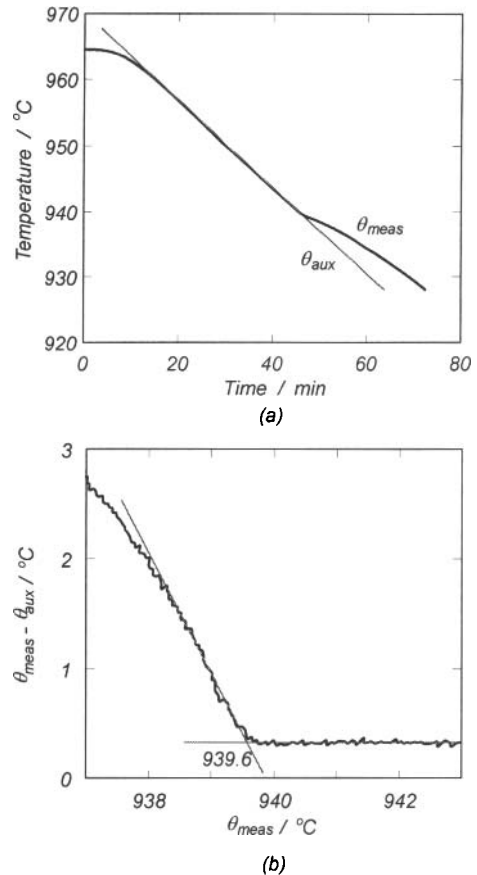


Figure 2. a) – Recorded cooling curve and b) – Plot for improving the reading of the thermal arrest (see the text).

Results and Discussion

Melts Containing Magnesium Fluoride

The results are given in Table II and in Figure 3. In one of the experiments (14 wt% AlF₃, 6.1 wt% MgF₂), a second thermal arrest was detected at 875.8 °C. This can probably be attributed to a peritectic line separating the fields for primary formation of the phases Na₃AlF₆ and NaMgF₃ [9], as indicated by the thin lines in Figure 3. It should be mentioned, however, that this second thermal arrest was very indistinct.

The results were fitted to an empirical equation [6], adding a new cross-term between AlF₃ and MgF₂. The equation is as follows,

$$\Delta\theta = -3.95[\text{MgF}_2] - \frac{0.400[\text{MgF}_2] \cdot [\text{AlF}_3]}{1 - 0.002[\text{MgF}_2] \cdot [\text{AlF}_3]} \quad (10)$$

where $\Delta\theta$ is the change in liquidus temperature [°C] and the brackets denote concentration in weight percent. The standard deviation between Eq. (10) and the 7 new experimental points in the field for primary crystallization of Na₃AlF₆ is 0.8 °C.

The liquidus curves in Figure 3 become steeper when the bath becomes more acid; the initial liquidus temperature depression (small amounts of MgF_2) increases from 3.95 °C/wt% in pure cryolite to 9.75 °C/wt% in melts containing 14.5 wt% excess AlF_3 . This can be explained by the fact that MgF_2 is an acid substance, *i.e.*, an F-acceptor; MgF_2 probably dissolves in the melt according to the scheme



This leads to a relatively large reduction of the NaF-activity and a corresponding decrease in the activity of cryolite.

Table II. Experimentally determined liquidus temperatures in melts containing magnesium fluoride.

AlF_3 wt%	CaF_2 wt%	Al_2O_3 wt%	MgF_2 wt%	1 st run °C	2 nd run °C	Average °C
7.0	5.0	3.5	0.0	970.0	970.1	970.0
7.0	5.0	3.5	2.0	956.5	956.8	956.6
7.0	5.0	3.5	4.0	942.1	942.2	942.1
7.0	5.0	3.5	6.0	926.8	926.9	926.8
14.0	5.0	3.5	0.0	940.0	940.1	940.1
14.0	5.0	3.5	2.0	919.3	919.7	919.5
14.0	5.0	3.5	4.0	897.8	897.9	897.9
14.0	5.0	3.5	6.0	878.2	-	878.2

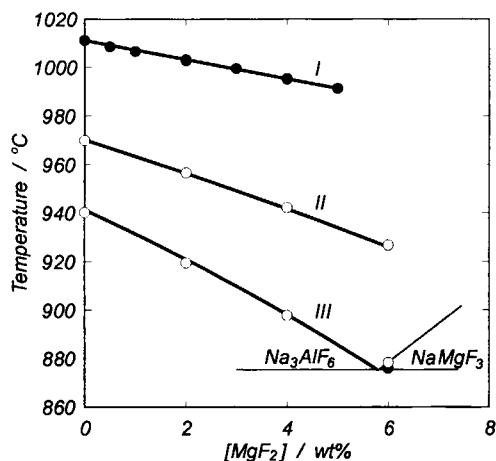


Figure 3. Liquidus temperature as a function of the concentration of MgF_2 for different melt compositions. Symbols – experimental data, curves – Eq. (10). I – pure cryolite [6], II – 7 wt% AlF_3 , 5 wt% CaF_2 , and 3.5 wt% Al_2O_3 , III – 14 wt% AlF_3 , 5 wt% CaF_2 , and 3.5 wt% Al_2O_3 .

The System Cryolite-Calcium Fluoride

According to Chrenkova *et al.* [10], eight phase diagram studies have been carried out in the system Na_3AlF_6 - CaF_2 . Four of these studies (including Chrenkova *et al.*) concluded that CaF_2 has solid

solubility in cryolite, while five studies concluded that there is no solid solubility. This, therefore, appears to be an unresolved issue.

Generally, the activities of molten and solid cryolite and the liquidus temperature are related by (see also Eq. (6))

$$d \ln \left(\frac{a_{Na_3AlF_6(l)}}{a_{Na_3AlF_6(s)}} \right) = \frac{\Delta H_f}{R} \cdot \frac{dT}{T^2} \quad (12)$$

If there is solid solubility, the activity of solid cryolite will be smaller than unity, and this leads to a smaller freezing point depression than what can be calculated from Eq. (1).

The data shown in Table III and in Figure 4 were fitted by the equation

$$\Delta \theta = - \frac{2.55 [CaF_2]}{1 + 0.003 [CaF_2]} \quad (13)$$

At low concentration of CaF_2 , the freezing point depression is -2.55 °C/wt%, which is considerably less than the calculated -3.30 °C/wt% (see Table I). This indicates solid solubility of CaF_2 in cryolite, but it can not be regarded as a final proof.

Table III. Experimentally determined liquidus temperatures in the system Na_3AlF_6 - CaF_2 .

CaF_2 wt%	θ_{liq} °C
0.80	1009.0
4.77	999.2
4.77	998.5
8.74	990.0
8.74	989.6

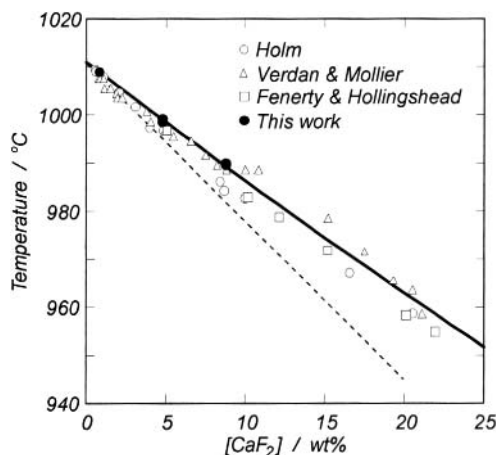


Figure 4. Liquidus temperature in the system Na_3AlF_6 - CaF_2 , including data from Holm [11], Verdan and Mollier [12], and Fenerty and Hollingshead [13]. Symbols – experimental data, full curve – Eq. (13), dotted line – theoretical freezing point depression (see Table I).

Melts Containing Potassium Fluoride

Potassium fluoride is generally avoided in aluminium electrolysis, since it is anticipated that it would lead to excessive swelling of the cathode due to C_xK intercalation compounds. Still, potassium is one of the major contaminants in Hall-Héroult bath, and it was recently suggested^[14] to modify the electrolyte by adding LiF, MgF_2 , and rather large amounts of KF (4.7 wt%) in order to increase the alumina solubility as well as the electrical conductivity.

Several authors have studied the system Na_3AlF_6 - K_3AlF_6 , as summarized in "Aluminium Electrolysis"^[15]. The investigators seem to agree that there exists a "mixed cryolite" K_2NaAlF_6 that divides the phase diagram in two parts, and that there are two eutectica in the system.

The results from the present investigation are shown in Table IV and in Figure 5. No second thermal arrests could be detected. The eutectic points were therefore estimated from the course of the liquidus temperatures,

$$e1: x_{K_3AlF_6} = 0.330, t = 944.2 \text{ } ^\circ C$$

$$e2: x_{K_3AlF_6} = 0.712, t = 953.8 \text{ } ^\circ C$$

The liquidus diagram shown in Figure 5 does not differ very much from the one given by Chin and Hollingshead^[16].

Since KF is a basic compound, one would expect that the empirical liquidus equation should contain a positive cross-term between KF and AlF_3 . Based on the experimental data the following term was derived,

$$\Delta\theta = -3.95[KF] + 0.106[KF] \cdot [AlF_3] \quad (14)$$

The experimental freezing point depression of KF in pure cryolite is somewhat smaller than what was calculated in Table I, which may be due to solid solubility of KF (K_2NaAlF_6 ?) in cryolite.

Melts Containing Sodium Chloride

Chlorides are among the most important contaminants that are normally not accounted for in empirical liquidus equations. In the present experiments, NaCl was added together with AlF_3 to keep the Na/Al molar ratio constant. The results are shown in Table V and in Figure 6, together with some older data by Holm^[17] (who added NaCl to cryolite, implying that the Na/Al ratio varied).

Based on experimental data the following equation was derived,

$$\Delta\theta = -4.8[NaCl] - 0.00047[NaCl] \cdot [AlF_3]^P \quad (15)$$

Table IV. Experimentally determined liquidus temperatures in melts containing potassium fluoride.

K_3AlF_6 mol%	1 st run °C	2 nd run °C	Average °C
10	986.0	-	986.0
15	972.4	972.4	972.4
23	955.2	955.2	955.2
28	947.9	947.8	947.9
30	945.4	945.4	945.4
32	944.5	-	944.5
35	944.3	944.2	944.2
40	946.4	-	946.4
45	949.8	-	949.8
50	952.3	952.2	952.3
56	955.9	-	955.9
56	955.7	-	955.7
61	956.6	-	956.6
67	955.2	955.3	955.3
70	954.7	-	954.7
72	955.1	-	955.1
80	966.5	966.5	966.5
90	982.6	-	982.6
100	998.9	-	998.9

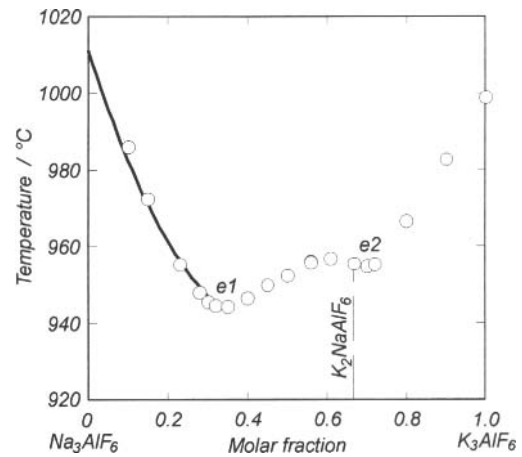


Figure 5. Symbols – experimentally determined liquidus temperatures in the system Na_3AlF_6 - K_3AlF_6 , curve – Eq. (14).

Table V. Experimentally determined liquidus temperatures in melts containing sodium chloride.

NaCl wt%	AlF ₃ wt%	Na/Al mol/mol	θ_{liq} °C
3.00	1.44	3.0	995.1
6.00	2.87	3.0	981.8
9.00	4.31	3.0	967.4
0.00	12.70	2.2	982.6
3.00	14.03	2.2	955.3
6.00	15.36	2.2	927.4
9.00	16.69	2.2	892.8

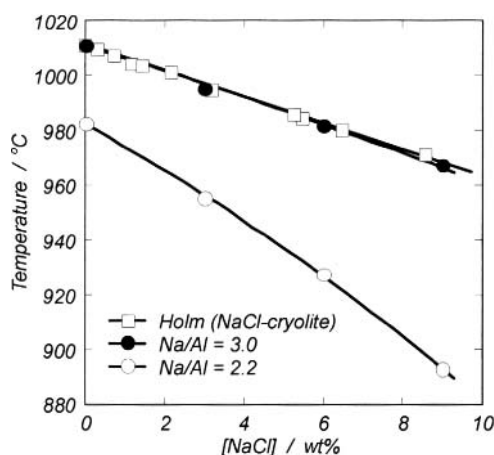


Figure 6. Symbols – experimentally determined liquidus temperatures in the system Na₃AlF₆-K₃AlF₆, curves – Eq. (15). Data from this work and from Holm^[17].

Concluding Remark

As a general advice, it should be kept in mind that the industrial Hall-Héroult bath is very different from pure cryolite. This can be exemplified by the fact that the activity of AlF₃ is about 4-5 times higher in a NaF-AlF₃ melt with molar ratio 2.2 than in cryolite. Much of the physical data and other information obtained in laboratory experiments are based on cryolite, particularly in the older literature. While old data is not necessarily bad data, the relevance of measurements made in pure cryolite and concepts derived for binary systems can be questioned in some cases.

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