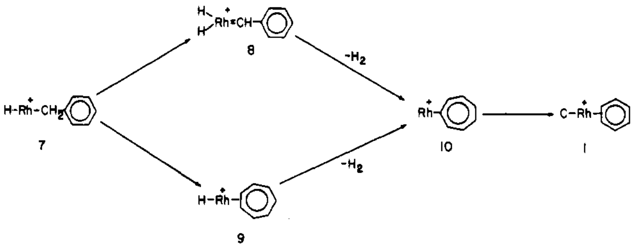
Scheme II



$RhC^+:RhC_7H_6^+$ ratio is greater for norbornadiene than for cycloheptatriene, as predicted in Figure 3, since formation of **1** is 15 kcal/mol more exothermic for norbornadiene than for cycloheptatriene.

A proposed mechanism for dehydrogenation and carbide-benzene formation is outlined in Scheme II for toluene. Initially, Rh^+ oxidatively adds to an aliphatic C–H bond,[28] generating a hydrido-benzyl complex (**7**). This is followed by an α-hydride abstraction, producing a dihydride-phenylcarbene complex (**8**), which reductively eliminates hydrogen with rearrangement to a σ-bound $c\text{-}C_7H_6$ complex (**10**). In addition, the benzyl group in complex **7** can rearrange to tropylium,[29] forming **9**. Hydride abstraction by **9** followed by dehydrogenation results in formation of **10**. Complex **10** then rearranges to the carbide-benzene complex **1**. In addition, complex **8**, after dehydrogenation, may rearrange directly to the carbide-benzene structure. Both dehydrogenation pathways are required to account for the deuterium losses observed for toluene-$\alpha,\alpha,\alpha\text{-}d_3$. In addition, the carbide-benzene formation process for all three C_7H_8 isomers may proceed through a common intermediate, probably the σ-bound $c\text{-}C_7H_6$ species (**10**).

Conclusions

In general, Rh^+ is more reactive toward these cyclic polyenes than Co^+. This is in accord with a previous study on the reactions of Rh^+ with alkanes.[26] Dehydrogenation of the three cyclic polyenes is unique for Rh^+. Structural studies indicate that the dehydrogenation product, $RhC_7H_6^+$, rearranges upon activation to a common intermediate for all three C_7H_8 isomers, presumably a carbide-benzene complex (**1**). This process is related to that reported for the surface chemistry of cycloheptatriene and norbornadiene.[6] On metal surfaces several metal centers may be involved in the dehydrogenation and benzene formation processes. However, in the gas phase, only one metal center is involved. The exact mechanism for the dehydrogenation process in the gas phase is unclear, however, and future studies call for the use of labeled compounds to help delineate this mechanism as well as the mechanisms involved for the C–C bond cleavage products observed for both metal ions.

Acknowledgment is made to the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-AC02-80ER10689), for supporting this research and the National Science Foundation (Grant CHE-8002685) for providing funds to purchase the FT mass spectrometer.

Registry No. C_7H_8, 108-88-3; Co^+, 16610-75-6; Rh^+, 20561-59-5; $c\text{-}C_7H_8$, 544-25-2; toluene-$\alpha,\alpha,\alpha\text{-}d_3$, 1124-18-1; norbornadiene, 121-46-0.

---

[28] Evidence against initial insertion into an aromatic C–H bond is that Rh^+ reacts with benzene to generate the condensation product $RhC_6H_6^+$ exclusively with no dehydrogenation observed.

[29] Rearrangement of benzyl ions to tropylium ions has been observed in the gas phase; see for examples: (a) Jackson, J. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515. (b) Kuck, D.; Grutzmacher, H.-F. *Org. Mass Spectrom.* **1979**, *14*, 86. (c) McLouglin, R. G.; Morrison, J. D.; Traeger, J. C. *Ibid.* **1979**, *14*, 014. (d) McLafferty, F. W.; Bockhoff, F. M. *J. Am. Chem. Soc.* **1979**, *101*, 1783. (e) Cone, C.; Dewar, M. J. S.; Landman, D. *Ibid.* **1977**, *99*, 372.

Contribution from Chemistry Department A,
The Technical University of Denmark, DK-2800 Lyngby, Denmark

Phase Diagram of the $NaCl\text{-}AlCl_3$ System near Equimolar Composition, with Determination of the Cryoscopic Constant, the Enthalpy of Melting, and Oxide Contaminations

ROLF W. BERG,* HANS AAGE HJULER, and NIELS J. BJERRUM*

Received March 10, 1983

The phase diagram of the $NaCl\text{-}AlCl_3$ system near the equimolar composition is reported with high precision. The freezing point of the pure, congruently melting compound $NaAlCl_4$ was determined to be 156.7 ± 0.1 °C. The molal freezing point depression constant of equimolar $NaCl\text{-}AlCl_3$ melts was estimated to be 19 ± 2 °C kg mol^{-1}. The overall enthalpy of melting for $NaAlCl_4$ given in recent literature can be divided into two parts, a premelting part ($\Delta H_p \simeq 4.5$ kJ mol^{-1}), whose origin is discussed, and a real melting part ($\Delta H_f \simeq 15.5$ kJ mol^{-1}). Oxide impurities were always found to be present in these melts. The influence of oxides, their origin, and their determination were considered, as were phase diagram corrections for the presence of oxide impurities. The freezing point depressions caused by added AlOCl showed the most likely constitution of the dissolved oxide to be $(AlOCl)_2\cdot AlCl_4^-$ in equilibrium with other species.

Introduction

Chloroaluminate melts have attracted considerable interest as high-temperature ionic solvents with low crystallization temperatures. These properties have led to applications in, e.g., the ALCOA chloride process for producing aluminum via $AlCl_3$,[1] as reaction media, and, possibly, in rechargeable high-energy-density batteries.

Considering the importance of the $NaCl\text{-}AlCl_3$ system within these respects, it is surprising to note that neither the freezing (or melting) point of the pure $NaAlCl_4$ compound nor the $NaCl\text{-}AlCl_3$ phase diagram in the vicinity of the equimolar mixture is accurately known. In addition to this, the freezing point depression (cryoscopic) constant for $NaAlCl_4$ is unknown.

The present work was started in order to compensate for these shortcomings. Detailed measurement of the phase di-

---

[1] Grjotheim, K.; Krohn, C.; Øye, H. A. *Aluminum (Düsseldorf)* **1975**, *51*, 697.

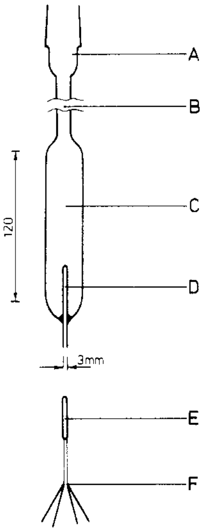


Figure 1. Cryoscopic cell of borosilicate glass: A, neck; B, sealing position; C, container; D, pocket; E, thermometer; F, leads. A and B were connected via rubber tubing during resealings.

agram near the equimolar composition is reported, as are the molar freezing point depression constant for $NaAlCl_4$ and its enthalpy of fusion. The general problem of oxide contaminations in $NaCl-AlCl_3$ melts is discussed in the light of our new results.

Experimental Section

Chemicals. Because of the cryoscopic effect of impurities, very highly purified chemicals are needed for a true determination of the phase diagram. NaCl (analytical reagent from Riedel-de Haën) was purified (in a quartz apparatus) by first passing HCl gas over the solid and then through the melt (at ca. 850 °C); flushing with pure N_2, and finally filtering the melt. $AlCl_3$ was purchased from Fluka or made from pure metal (99.999%) and HCl gas (made by reaction between hydrochloric and sulfuric acids). Both kinds of $AlCl_3$ were purified by sublimation and then by distillation twice (at ca. 205 °C) under vacuum from an Al_2Cl_6 melt in equilibrium with a $NaCl/AlCl_3$ phase containing Al metal strips (to reduce $FeCl_3$ and HCl). The final purity of the white $AlCl_3$ was checked for Na content by atomic absorption analysis and had <0.1 ppm Na by weight. Identical results were obtained independent of the kind of purified $AlCl_3$ used. CsBr (IR spectroscopic grade) was used after being dried at 150 °C for 2 days. AlOCl was synthesized from pure finely ground V_2O_5 and $AlCl_3$ according to a method by Schäfer[2] (0.7 g of V_2O_5 and 3.9 g of $AlCl_3$ in a 400-mL cell at 300 °C for 3 days followed by separation of $VOCl_3$ and excess $AlCl_3$ by condensation in liq. nitrogen twice). The AlOCl produced contained 98.5 wt % of the theoretical chlorine and no vanadium.

Technique. To prevent hydration of the chemicals, all manipulations were performed quickly in a dry N_2 glovebox and all chemicals were constantly stored in evacuated and sealed borosilicate glass containers. Grinding to powders and the use of premixed $NaAlCl_4$ were avoided to keep the moisture uptake at the lowest possible level. Initial experiments proved that these precautions were necessary to obtain reproducible results.

The cryoscopic cells were all of the kind shown in Figure 1 and similar to the type used previously in our laboratory.[3a] After addition of ca. 25 g of chemicals and sealing under vacuum, the cells were mounted in the same holder, such that the position in the furnace was the same for all experiments. All cells used the same 100-Ω platinum resistance thermometer (from Degussa, 3 mm o.d., Al_2O_3 type). The thermometer was connected to a high-precision resistance meter with digital readout via four 0.8-mm thick gold wires, to compensate for the resistance of the cables and connections. The resistance thermometer was calibrated when mounted in the holder, by using the freezing points of water and 99.999 wt % pure Sn (T_f = 231.97 °C). Calibration was done before and after the experiments, and the correction remained constant and very small (−0.02 Ω). The accuracy of the temperature calibration is estimated to be better than ±0.1 °C and the reproducibility was on the order of 0.03 °C (0.01 Ω). The rocking furnace and its regulation (±0.1 °C) was basically the same as described previously,[3b] though elongated and regulated more precisely.

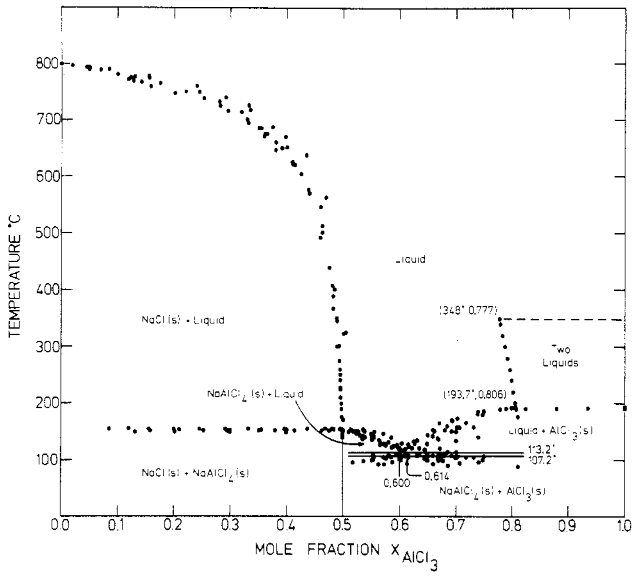


Figure 2. Phase diagram of the $NaCl-AlCl_3$ system according to information in the literature.[4-20] The acidic eutecticum occurs at X, t = ca. (0.614, 107.2 °C)[5,13,15] or at ca. (0.600, 113.2 °C).[4,8,18] The region of liquid immiscibility is from ref 14 and 20.

The determination of the liquidus temperatures was done in the following way: At first, the melt was preequilibrated in the rocking furnace heated to 175 °C to completely dissolve all crystals (a slow process in the case of NaCl). Then solidification experiments were done without rocking at furnace temperatures ca. 0.1–2.0 °C below the melting point (subcooling). The cell was taken out for a moment and locally spot cooled at the meniscus by using a thin stream of pressurized air, until crystallization started (ca. 5 s). The temperature was followed by using a recorder (Radiometer, type REC 80 servograph). A decrease of ca. 1 °C was typical, and then the temperature increased to above the furnace temperature, due to the heat of crystallization, until a stationary plateau was reached. For small subcoolings (ca. 0.1 °C), the plateau lasted several hours even without solidification of more than 10% of the melt. Several determinations were performed until the temperature remained within 0.03 °C in three successive solidifications and independent of the applied (small) subcooling.

After the measurements, the cell was normally opened (at B, Figure 1), addition of chemicals made, and the whole procedure repeated. It was checked that opening and resealing of a cell could be done without any significant change in melting point.

Compositions are generally expressed in mole fractions, e.g., X_{AlCl_3} = moles of $AlCl_3$/(moles of $AlCl_3$ + moles of NaCl). Melts with $X_{AlCl_3} > 0.5$ are referred to as acidic, those with $X_{AlCl_3} < 0.5$ are called basic, and neutral melts have $X_{AlCl_3} = 0.5$.

Results and Discussion

The $NaCl-AlCl_3$ Phase Diagram. Before we report our own results, it is worth briefly mentioning previous results. The available information[4-20] is collected in Figure 2, which shows

---

(2) (a) Schäfer, H.; Göser, C.; Bayer, G. *Z. Anorg. Allg. Chem.* **1950**, *263*, 96. (b) Schäfer, H.; Wittig, F. E.; Wilborn, W. *Ibid.* **1958**, *297*, 48. (c) Hagenmuller, P.; Portier, J.; Barbe, B.; Bouclier, P. *Ibid.* **1967**, *355*, 209.

(3) (a) Hansen, N. H.; Fehrmann, R.; Bjerrum, N. J. *Inorg. Chem.* **1982**, *21*, 722. (b) Andreasen, H. A.; Bjerrum, N. J.; Foverskov, C. E. *Rev. Sci. Instrum.* **1977**, *48*, 1340.

(4) Kendall, J.; Crittenden, E. D.; Miller, H. K. *J. Am. Chem. Soc.* **1923**, *45*, 963. Wasilewski, L.; Kaczorowski, A.; Dynkin, M. *Przem. Chem.* **1934**, *18*, 608.

(5) Shvartsman, U. I. *Zap. Inst. Khim., Akad. Nauk, Ukr. RSR* **1940**, *7(1)*, 3 (See also: Janz, G. J.; et al. *J. Phys. Chem. Ref. Data* **1975**, *4*, 920). Plotnikov, V. A.; Schvartsman, U. I. *Zap. Inst. Khim., Akad. Nauk, Ukr. RSR* **1936**, *3*, 387.

Table I. Observed Freezing Points T_f as a Function of the Mole Fractions X, Determined from Weights (the Data Fit Two Lines[a])

expt	“$AlCl_3$”,[b] mol	NaCl, mol	$X_{\text{“}AlCl_3\text{”}}$ (accuracy ± 0.00003)	$X_{\text{“}NaCl\text{”}}$ (accuracy ± 0.00003)	T_f, °C (precision ± 0.03)	regression line
A-0	0.31602	0.31098	0.50402	0.49598	155.00	A
A-1[c]	0.31602	0.31388	0.50170	0.49830	155.99	A
A-2	0.31602	0.31487	0.50091	0.49909	156.21	A
A-3	0.31602	0.31546	0.50044	0.49956	156.56	A
B-0	0.13321	0.13124	0.50373	0.49627	155.19	A
B-1	0.13321	0.13226	0.50179	0.49821	156.06	A
B-2	0.13321	0.13281	0.50075	0.49925	156.48	A
B-3	0.13321	0.13307	0.50026	0.49974	156.43	B
B-4	0.13321	0.13367	0.49913	0.50087	156.00	B
B-5	0.13396	0.13367	0.50054	0.49946	156.54	A
C-0	0.13932	0.13699	0.50420	0.49580	155.11	A
C-1	0.13932	0.13794	0.50249	0.49751	155.80	A
C-2	0.13932	0.13920	0.50021	0.49979	156.45	B
C-3	0.13932	0.13956	0.49956	0.50044	156.22	B
C-4	0.13932	0.14006	0.49867	0.50133	156.08	B
C-5	0.14030	0.14006	0.50043	0.49957	156.56	A
D-0	0.12397	0.12113	0.50578	0.49422	154.41	A
D-1	0.12397	0.12249	0.50299	0.49701	155.46	A
D-2	0.12397	0.12337	0.50120	0.49880	156.19	A
D-3	0.12397	0.12367	0.50060	0.49940	156.48	A
D-4	0.12397	0.12456	0.49881	0.50119	156.03	B
E-0	0.12719	0.12476	0.50481	0.49519	154.84	A
E-1	0.12719	0.12656	0.50123	0.49877	156.22	A
E-2	0.12719	0.12743	0.49953	0.50047	156.25	B
F-0	0.35229	0.34264	0.50694	0.49306	154.23	A
F-1	0.35229	0.35040	0.50135	0.49865	156.24	A
G-0	0.13075	0.12590	0.50944	0.49056	153.13	A
G-1	0.13075	0.13054	0.50039	0.49961	156.48	B
G-2	0.13075	0.13125	0.49904	0.50096	156.21	B
H-0	0.13703	0.13577	0.50230	0.49770	155.78	A
H-1	0.13703	0.13725	0.49960	0.50041	156.38	B
I-0	0.14253	0.14130	0.50217	0.49783	155.92	A
J-0	0.26366	0.26171	0.50186	0.49814	156.03	A
J-1	0.26366	0.26494	0.49879	0.50121	155.98	B

[a] Least-squares regression by $T_f = \alpha + \beta(X_{\text{“}AlCl_3\text{”}} - 0.5)$ with T_f in °C: regression line A, $\alpha = 156.69 \pm 0.03$ °C, $\beta = -380 \pm 7$ °C, $R^2 = 0.9925$; regression line B, $\alpha = 156.38 \pm 0.03$ °C, $\beta = 278 \pm 39$ °C, $R^2 = 0.8318$. Standard deviation on predicted T_f: 0.08 °C. [b] “$AlCl_3$” is $AlCl_3$ disregarding content of AlOCl; see text. [c] I.e., cell A with addition no. 1.

the considerable scattering that exists among the literature results. The reason for this is probably due to varying levels of impurities (especially oxides), the extensive tendency to subcooling, and limited accuracies in the temperature determinations. Also, in the acidic range (e.g., near the eutectic at approximately $X_{AlCl_3} = 0.61$), evaporation of $AlCl_3$ might easily change the composition on the order of several percent. The quoted $NaAlCl_4$ melting points vary from 151 to 156 °C. The highest values are given in ref 6–8, 10, and 15.

Our own measured melting points for the NaCl–$AlCl_3$ system as a function of composition are shown in Table I and

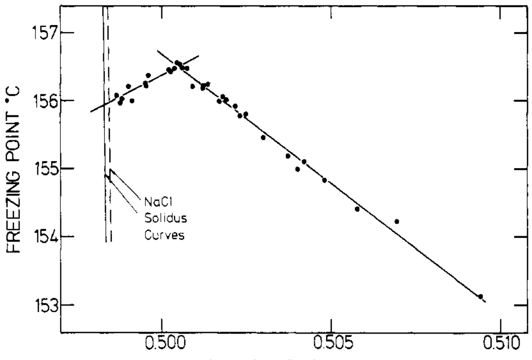


Figure 3. Observed phase diagram of the NaCl–$AlCl_3$ system near the equimolar composition. Freezing points and compositions are not corrected for AlOCl impurities in $AlCl_3$. Dashed and fully drawn NaCl solidus curves are from the work of Dewing[18] and Hjuler et al.[19] Also shown are the $NaAlCl_4$ solidus regression lines (cf. Table I).

Figure 3. The first thing to note is the existence of a maximum melting point at 156.5_6 °C at a composition near $X_{AlCl_3} = 0.50$. This maximum probably represents the melting point of the equimolar NaCl–$AlCl_3$ mixture. It shows that $NaAlCl_4$ is indeed a congruently melting compound and not a monotectic as recently claimed.[18] This melting point is the highest value ever reported. (The true melting point is higher, as discussed later on in conjunction with the small deviation from $X_{AlCl_3} = 0.50000$ caused by oxide impurities.)

$NaAlCl_4$ shares the property of being a congruently melting compound with $KAlCl_4$, $RbAlCl_4$, and $CsAlCl_4$.[9,10,21] Like

---

(6) Chrêtien, A.; Lous, E. *C.R. Hebd. Seances Acad. Sci.* **1943**, *217*, 451.
(7) Gerding, H.; Houtgraff, H. *Recl. Trav. Chim. Pays-Bas* **1953**, *72*, 21.
(8) Midorikawa, R. *J. Electrochem. Soc. Jpn.* **1955**, *23*, 72.
(9) Fischer, W.; Simon, A.-L. *Z. Anorg. Allg. Chem.* **1960**, *306*, 1 (data from Abb. 1 and 5).
(10) Semenenko, K. N.; Sorov, V. N.; Kedrova, N. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1969**, *14*, 48.
(11) Trêmillon, B.; Letisse, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1968**, *17*, 371. Trêmillon, B.; Duchange, J. P. *Ibid.* **1973**, *44*, 395; note the error in Figure 2.
(12) Torsi, G.; Mamantov, G. *Inorg. Chem.* **1971**, *10*, 1900.
(13) Levin, E. M.; Kinney, J. F.; Wells, R. D.; Benedict, J. T. *J. Res. Nat. Bur. Stand., Sect. A* **1974**, *78A*, 505.
(14) Viola, J. T.; Seegmiller, D. W.; Fannin, A. A.; King, L. A. *J. Chem. Eng. Data* **1977**, *22*, 367.
(15) Sato, Y.; Ejima, T. *J. Jpn. Inst. Met., Sendai* **1978**, *42*, 905.
(16) Bjørgum, A.; Sterten, Å.; Sørensen, V. B.; Thornstad, J.; Tunold, R. *Electrochim. Acta* **1981**, *26*, 487 and private communication.
(17) Fehrmann, R.; von Barner, J. H.; Bjerrum, N. J.; Nielsen, O. F. *Inorg. Chem.* **1981**, *20*, 1712.
(18) Dewing, E. W. *Metall. Trans., B* **1981**, *12B*, 705.
(19) Hjuler, H. A.; Mahan, A.; von Barner, J. H.; Bjerrum, N. J. *Inorg. Chem.* **1982**, *21*, 402.
(20) Fannin, A. A.; King, L. A.; Seegmiller, D. W.; Øye, H. A. *J. Chem. Eng. Data* **1982**, *27*, 114.

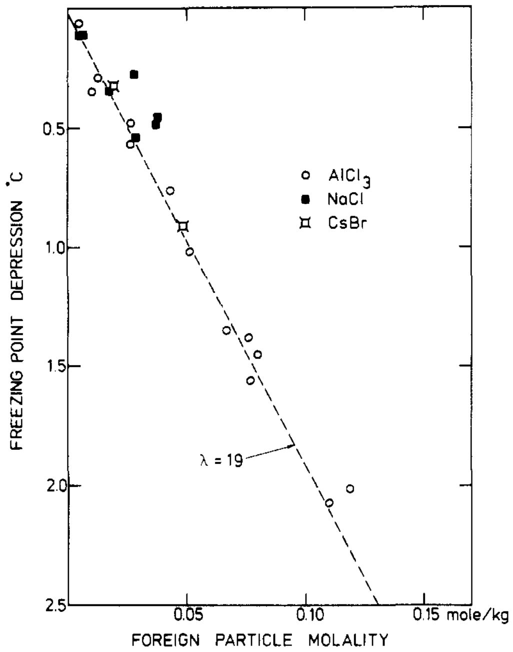


Figure 4. Freezing point depression for $NaAlCl_4$ vs. additions of foreign substances $AlCl_3$, NaCl, and CsBr, assuming ν = 1, 1, and 2. The dashed line (not a regression line) corresponds to λ = 19.

$NaAlCl_4$, $KAlCl_4$ has its basic eutecticum (at 250 °C, $X_{AlCl_3} = 0.49$) very near the equimolar mixture, which melts at 256 °C.[9] The situation for $LiAlCl_4$ is unclear[10,15,22] but it is probably similar to the one for $NaAlCl_4$.

The NaCl solidus curves in Figure 3 were obtained from Dewing[18] (dashed), and more accurately from Hjuler et al.[19] (fully drawn). On the basis of various data from the literature, Dewing showed that up to at least 475 °C the NaCl solidus curve can be reproduced by eq 1, where T is the temperature

$$\log (0.5 - X_{AlCl_3}) = 0.017 - 1214/T \qquad (1)$$

in kelvin. On the other hand, we have determined[17,19] the solubility of NaCl (solid) in molten $NaAlCl_4$ potentiometrically within the temperature range 175–300 °C. From these results, the NaCl solidus curve can be accurately calculated (see Appendix). The agreement of these two independent solidus curves is remarkably good. The eutecticum on the basic side is then at 155.9 °C with $X_{AlCl_3} = 0.4984$.

Determination of the Molal Freezing Point Depression Constant, λ. The freezing point depression of a solvent (i.e., $NaAlCl_4$) to which substances (solutes) are added in small quantitites can be expressed by the limiting Raoult–van't Hoff relation:

$$\theta \simeq \nu\lambda m \simeq \nu \frac{M}{1000} \frac{RT_f^2}{\Delta H_f} m \qquad (2)$$

Here, θ is the freezing point depression (in °C); ν is the number of foreign particles formed in the melt per mole of the added substance; m is the molality (mol per kg of solvent) of the added substance; R is the gas constant (8.3144 J mol^{-1} K^{-1}); and ΔH_f, M and T_f are the enthalpy of fusion (in J mol^{-1}), the molar weight (in g mol^{-1}), and the melting point (in K) of the pure solvent.

Table II. Experiments Used for Estimation of the Limiting Freezing Point Depression Constant λ

ref expt	obsvn expt	depres- sion[a] θ, °C	addn,[b] mol	molality increment m, mol/kg of solvent	slope θ/m, °C kg/mol
A-3	A-0	1.56	0.00449	0.0765 $AlCl_3$	20.4
A-3	A-1	0.57	0.00158	0.0262 $AlCl_3$	21.8
A-3	A-2	0.35	0.00059	0.0097 $AlCl_3$	36.1
B-5	B-0	1.35	0.00169	0.0665 $AlCl_3$	20.3
B-5	B-1	0.48	0.00067	0.0263 $AlCl_3$	18.3
B-5	B-2	0.06	0.00012	0.0045 $AlCl_3$	15.0
C-5	C-0	1.45	0.00209	0.0797 $AlCl_3$	18.2
C-5	C-1	0.76	0.00114	0.0436 $AlCl_3$	17.5
D-3	D-0	2.07	0.00254	0.1099 $AlCl_3$	18.8
D-3	D-1	1.02	0.00118	0.0510 $AlCl_3$	20.0
D-3	D-2	0.29	0.00030	0.0129 $AlCl_3$	22.5
E-1	E-0	1.38	0.00181	0.0759 $AlCl_3$	18.2
F-1	F-0	2.01	0.00779	0.1187 $AlCl_3$	16.9
A-3	G-0	3.43	0.00462	0.1917 $AlCl_3$	17.9
B-5	B-4	0.54	0.00075	0.0294 NaCl	18.4
B-5	B-3	0.11	0.00015	0.0059 NaCl	18.7
C-5	C-4	0.48	0.00100	0.0372 NaCl	12.9
C-5	C-3	0.34	0.00050	0.0183 NaCl	18.6
C-5	C-2	0.11	0.00013	0.0050 NaCl	22.2
D-3	D-4	0.45	0.00089	0.0374 NaCl	12.0
G-1	G-2	0.27	0.00071	0.0282 NaCl	9.6
A-3	J-2	0.58	0.00176	0.0349 NaCl	16.6
A-3	A-4	0.32	0.00058	0.0096 CsBr	16.7
A-3	A-5	0.91	0.00146	0.0242 CsBr	18.7
					av 18.6 ± 4.8

[a] Freezing point depression from reference composition to observation. [b] The value is calculated from Table I and refers to the relative increment in $AlCl_3$, NaCl, or CsBr from reference composition.

The freezing point depression constant λ for the solvent $NaAlCl_4$ can be estimated from our data in Table I, assuming that ν = 1 for additions of both $AlCl_3$ and NaCl. Useful combinations of experiments and the corresponding calculations are shown in Table II. The obtained values of θ and m are plotted in Figure 4. The assumption that ν = 1 for $AlCl_3$ as well as for NaCl was further confirmed by two successive additions of CsBr (0.12337 and 0.18832 g) to cell A-3. Hence, the molality was 0.00957 and 0.02418 mol of CsBr/kg of solvent, respectively, and the melting points were observed at 156.2_4 and 155.6_5 °C. It is to be assumed that ν is 2 for the dissolution of CsBr in $NaAlCl_4$, corresponding to the formation of Cs^+ and Br^- ions. These two experiments are included in Figure 4 and Table II. The agreement between the points obtained from $AlCl_3$ or NaCl and CsBr addition experiments is very good. It definitely shows that $AlCl_3$ forms one particle ($Al_2Cl_7^-$) in near equimolar acidic $NaAlCl_4$ melts. NaCl is known to dissociate into Na^+ and Cl^-. The Na^+ ions are common to the solvent (consisting of Na^+ and $AlCl_4^-$) and it has been shown repeatedly[23] that only foreign ions are cryoscopically active. In acidic melts Cl^- reacts with $AlCl_3$ or $Al_2Cl_7^-$ to produce $AlCl_4^-$. In neutral or basic melts, the Cl^- remains free. In conclusion, NaCl is cryoscopically active with ν = 1, in accordance with the results.

To determine the limiting freezing point depression constant λ, the slope of the curve in a plot like Figure 4 should ideally be evaluated at m = 0. This extrapolation is difficult because of the large relative scattering at small m. Linear regression of the θ vs. m data in Table II gives a line through the origin with a slope of 18.2 ± 0.5 °C kg mol^{-1}, but this slope is much influenced by the θ values of high m. On the other hand, linear regression of the θ/m vs. m data has an intercept of 19.2 ± 1.5 °C kg mol^{-1} (the θ/m average is 18.6 ± 4.8 °C kg mol^{-1}). The conclusion is that λ can be estimated to be 19 ± 2 °C kg mol^{-1}.

Enthalpy of Fusion of $NaAlCl_4$. The λ value may be used to obtain the enthalpy of fusion, ΔH_f, at the melting point

---

(21) van der Kamp, L. K.; van Spronsen, J. W. *Z. Anorg. Allg. Chem.* **1968**, *361*, 328.

(22) Morozov, A. I.; Kuznetsov, V. G.; Maksimova, S. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1971**, *16*, 1773.

(23) Kordes, E.; Bergmann, W.; Vogel, W. *Z. Elektrochem.* **1951**, *55*, 600.

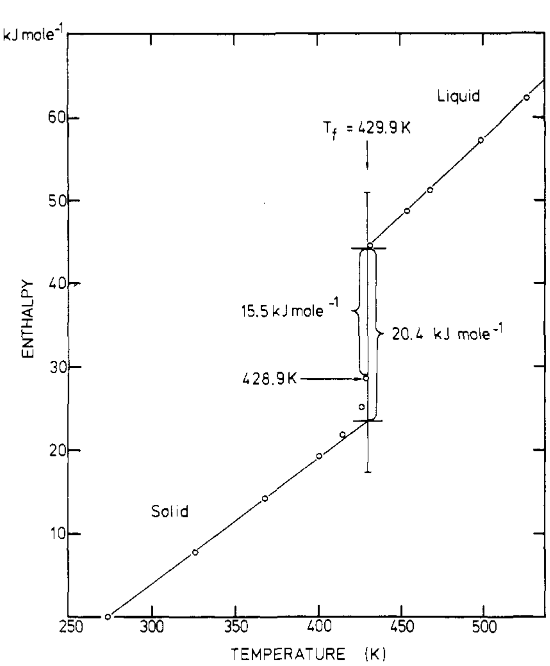


Figure 5. Enthalpy of NaAlCl$_4$ as a function of temperature ($H_{273K} = 0$). The experimental points and the ΔH_f = 20.4 kJ mol^{-1} value are due to Denielou et al.[26]

(429.8_7 K; see later), by using eq 2. The result is 15.5 ± 1.5 kJ mol^{-1}. A comparison with values in recent literature is quite interesting.

The value of 2.37 kcal mol^{-1} (=9.93 kJ mol^{-1}) reported by Godun et al.[24] is probably erroneous. Two recent papers report much higher values: Rogers,[25] 19.431 ± 0.377 kJ mol^{-1}; Denielou et al.,[26] 20.300 ± 0.500 kJ mol^{-1}. These values are so near that they are probably correct within ±2.0 kJ mol^{-1}. Also, Dewing,[18] by determining the enthalpy of the liquid NaAlCl$_4$ and obtaining a ΔH_f value of 18.4 kJ mol^{-1}, stated that no serious errors should exist in any of his final thermodynamic quantities (including ΔH_f) because of the internal overall agreement (the reader is recommended to study his paper for details).

The apparent disagreement between this established value of ΔH_f, $\simeq$20 kJ mol^{-1}, and ours may be understood from an examination of Figure 5, which is a plot of the measurements by Denielou et al.[26] near the melting point. Rogers's points[25] essentially follow the same picture but are omitted here because no point was obtained just below the melting point. Within a range of about 20 °C below the melting point a clear deviation from linearity is observed. The NaAlCl$_4$ compound absorbs ca. 4.5 kJ mol^{-1} excessive heat. If this effect is regarded as a real crystal effect (and not an onset of partial real melting started by impurities at grain boundaries), the disagreement disappears. Apparently, the NaAlCl$_4$ lattice can accommodate a part of the ~20 kJ mol^{-1} enthalpy of "melting" without losing its solid structure; it is due to either excessive Na$^+$ translations or AlCl$_4^-$ rotations. This "premelting" (or solid–solid phase transformation) requires heat, $\Delta H_p \simeq$ 4.5 kJ mol^{-1}. It should be possible to determine what cause this effect has, by means of X-ray single-crystal structure determination (like at room temperature[27]) just below the melting point. The cryoscopically observed enthalpy of fusion does not include this "heat of premelting", and hence a lower value is found. Such premelting effects (disordering) are not unique to this system.

It is quite interesting to note that Denielou et al.[26] without comments reported a "crystal-like" enthalpy at 428.9 K (even though they have T_f = 427 K) (see Figure 5). This is only 1° lower than the melting point obtained here, $T_f = 429.8_7$ K, and this indicates that their sample was relatively pure.

Influence of Oxide Impurities

General. It is well-known that oxide impurities are very difficult to avoid in tetrachloroaluminate melts. There are two fundamental reasons for the occurrence of oxide impurities in the melts:

Firstly, traces of moisture (either present as H$_2$O absorbed on the surface of glassware or present in the glove-box atmosphere) are a problem that can only be handled by working carefully and by using proper glove-box construction. To the extent that water meets with the chemicals, oxychlorides ("AlOCl") and hydrogen chloride are formed.[28-31]

$$\mathrm{AlCl_3 + H_2O \rightarrow \text{“AlOCl”} + 2HCl} \qquad (3)$$

This reaction is supported by the common observation that the addition of water to the melt (e.g., by less careful work) reduces the acidity: the water on contact with the melt forms free chloride.

$$\mathrm{AlCl_4^- + H_2O \rightarrow 2HCl + \text{“AlOCl”} + Cl^-} \qquad (4)$$

Secondly, all the experiments were carried out in contact with an oxide, borosilicate glass. It has been pointed out several times in the literature[32-34] that aluminum chloride and silicon dioxide react at elevated temperatures. There is, according to convincing evidence,[32,33] no reason to doubt that the reaction

$$\mathrm{2AlCl_3 + SiO_2 \rightarrow 2\text{“AlOCl”} + SiCl_4} \qquad (5)$$

takes place during the purification processes applied to the AlCl$_3$ (sublimation and distillation).

We examined this in two special distillations of our purest AlCl$_3$ under standard conditions. A number of long, carefully cleaned and weighed pieces of borosilicate glass tubes were placed inside the distillation containers. After the distillations (1 d at 200 °C), which left no residue, the pieces were taken out, cleaned, and reweighed. The losses in weight were significantly larger than zero (ca. 0.14 mg/cm^2). Assuming uniform etching of all internal surfaces, the AlCl$_3$ during the distillation gained an (extra) amount of oxide on the order of 0.0005 g of AlOCl per 1 g of AlCl$_3$. According to experiments reported in the literature[32,33] the etching reaction (eq 5) seems to depend on the SiCl$_4$ pressure, such that addition of SiCl$_4$ reduces the tendency of the etching. The SiCl$_4$ gas formed during one distillation (or sublimation) is lost everytime the AlCl$_3$ is transferred to another container. Hence, *several* purificational operations of AlCl$_3$, although some impurities are left behind, might not be an advantage, because new

---

(24) Godun, I. V.; Sandler, R. A.; Ivanov, I. I. *Russ. J. Phys. Chem. (Engl. Transl.)* **1977**, *51*, 760.

(25) Rogers, L. J. *J. Chem. Thermodyn.* **1980**, *12*, 51.

(26) Denielou, L.; Petitet, J.-P.; Tequi, C. *J. Chem. Eng. Data* **1982**, *27*, 129.

(27) Wallart, F.; Lorriaux-Rubbens, A.; Mairesse, G.; Barbier, P.; Wignacourt, J. P. *J. Raman Spectrosc.* **1980**, *9*, 55 and references therein. See also: Perenthaler, E.; Schulz, H.; Rabenau, A. *Z. Anorg. Allg. Chem.* **1982**, *491*, 259.

(28) Letisse, G.; Tremillon, B. *J. Electroanal. Chem. Interfacial Electrochem.* **1968**, *17*, 387.

(29) Tremillon, B.; Bermond, A.; Molina, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *74*, 53.

(30) Robinson, J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1977**, *16*, 3040. Gilbert, B.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 2725.

(31) Taulelle, F.; Piolet, C.; Tremillon, B. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *134*, 131.

(32) Polyachenok, L. D.; Dudchik, G. P.; Polyachenok, O. G. *Russ. J. Phys. Chem. Engl. Transl.* **1976**, *50*, 227.

(33) Schäfer, H.; Trenkel, M.; Peine, M. *Z. Anorg. Allg. Chem.* **1978**, *445*, 129.

(34) Bjørgum, A.; Sterten, Å.; Thonstad, J.; Tunold, R. *Electrochim. Acta* **1981**, *26*, 491.

corrosion starts after every step. Furthermore, it must be remembered that gaseous oxides (Al_4OCl_{10}, etc.) can be present under the conditions applied in the purification of $AlCl_3$.[35,36]

The ultimate lower limit of oxides in $AlCl_3$ purified in glass containers is estimated to be on the order of 0.0005 g of AlOCl/g of $AlCl_3$ found above. We reach the conclusion that $AlCl_3$ purified in glassware inevitably contains small quantities of AlOCl, even when the highest purity is claimed.[37,38]

It might be assumed that the $NaAlCl_4$ melts further reacted with the borosilicate glass containers during the experiments. This is not the case, or at least very little reaction takes place. It was investigated by weighing a number of borosilicate tube pieces before and after soaking in molten $NaAlCl_4$ for 1 week at 200 °C. No change in weights was observed within ±0.00005 g. Also the melting points observed were stable for weeks. Hence, the oxides present in the tetrachloroaluminate melts come mainly from the AlOCl content of the $AlCl_3$ used.

Behavior of Oxides in Tetrachloroaluminate Melts. The behavior of oxide ions in the melts has been the subject of much confusion.[28-31] However, it is now commonly agreed that no free oxide ion "O^{2-}" is present. Instead, oxide reacts with the melt according to eq 6 and 7. Equation 6 dominates

$$\text{"}O^{2-}\text{"} + AlCl_4^- \rightarrow \text{"}AlOCl\text{"} + 3Cl^- \qquad (6)$$

$$\text{"}O^{2-}\text{"} + AlCl_4^- \rightarrow \text{"}AlOCl_2^-\text{"} + 2Cl^- \qquad (7)$$

in slightly acidic and neutral melts, i.e., most of the range studied here. Equation 7 becomes of importance in more basic melts.[28-31] Furthermore, an equilibrium (8) is assumed to exist

$$\text{"}AlOCl\text{"} + Cl^- \rightleftarrows \text{"}AlOCl_2^-\text{"} \qquad (8)$$

in the basic range (near NaCl saturation). The exact chemical formulas of the solutes designated "AlOCl" and "$AlOCl_2^-$" are not known; it is known only that between three and two chloride ions have been detected potentiometrically per oxide ion added (i.e., oxide is tribasic to dibasic) depending on the acidity.[17,28-31]

Determination of Oxide Contaminations. The determination of the amount of oxide in tetrachloroaluminate melts is complex. Mamantov and Osteryoung[39] and also El Hosary et al.[40] have surveyed proposed methods for determination of oxide and concluded that few viable methods have been reported thus far. On the other hand, it is clear from studies on metals with high oxide affinity (Ti(IV), Se(IV), Nb(V)) in tetrachloroaluminate melts that oxide impurities really are present.[17,41,42] Fehrmann et al.,[17] from measurements of electrode potentials, determined an oxide level on the order of 0.02 mol per kg of equimolar mixture of NaCl and $AlCl_3$. Osteryoung et al.[41] claimed a ca. five times lower oxide level in their tetrachloroaluminate melts with an organic cation, and they concluded that they were unable to prepare oxide-free melts.

From measurements in our laboratory,[43] the level of oxide in a standard equimolar $NaAlCl_4$ melt (not of highest purity) could be estimated in the following way. $AlCl_3$ (72.626_1 g) was mixed with NaCl (31.828_4 g) by melting in a borosilicate cell. From these weights, X'_{AlCl_3} (i.e., mole fraction without accounting for the AlOCl presence) is calculated as 0.50003. The solidified melt was mechanically homogenized and the chloride concentration was measured in four standard potentiometric cells[43] (two cell compartments separated by a porous borosilicate disk).[44] Two of the cells had carbon electrodes (which respond to the chlorine/chloride potential after addition of Cl_2) and two had aluminum electrodes. The four electrode potentials were measured at 175 °C, relative to similar reference melts saturated with NaCl. The potentials obtained were 18.06, 17.32, 25.10, and 25.90 mV. Mole fractions, X_{AlCl_3}, were then calculated as in the Appendix. For the chlorine/chloride and aluminum/chloroaluminate cells we obtained $X_{AlCl_3} = 0.49861 \pm 0.00001$ and $X_{AlCl_3} = 0.49873 \pm 0.00001$, respectively. The slightly higher $AlCl_3$ content obtained by using aluminum as electrode material is most probably due to a small concentration of HCl in the melt, and this HCl reacts with aluminum, forming H_2 and $AlCl_3$. This shows that the HCl content in the melt is very low and that if water comes in contact with the $AlCl_3$ or $NaAlCl_4$ during glove-box manipulations, AlOCl is formed according to eq 3 and 4. The HCl is given off either immediately or during evacuation prior to sealing.

The difference between the mole fraction $X'_{AlCl_3} = 0.50003$ (determined from the weights) and the potentiometric results ($X_{AlCl_3} = 0.49861$) shows the level of AlOCl present in the $AlCl_3$. The oxide content (i.e., the AlOCl weight fraction) calculated by the method outlined in the Appendix is $W_{AlOCl}/W_{NaAlCl_4} = 0.00376$ (AlOCl molality = 0.048 mol/kg). This is a small but nonnegligible amount. Similar levels of oxide impurities (0.2–0.5 wt% AlOCl) have been found by Kühnl et al.[45] in their $NaAlCl_4$ melts, by use of precision analyses of aluminum and chloride to determine the oxide levels.

Composition Correction of Cryoscopic Experiments. The $AlCl_3$ used for the cryoscopic cells was contaminated with AlOCl to some extent. The effect of this AlOCl contamination is twofold: First, the calculated mole fractions (X_{AlCl_3} and X_{NaCl}) are biased such that the melt really is less acidic than calculated. Second, the AlOCl, even when otherwise chemically inert, acts as a cryoscopically active substance, depressing the freezing point.

Composition correction of the experiments in Table I can be done in this way. The consistency of the results (see also Figure 3) shows that the AlOCl impurity level remains constant and reproducible within this series of experiments. According to Figure 3, the maximum freezing point (and hence presumably neutrality, i.e., $X_{AlCl_3} = 0.50000$) occurs at $X'_{AlCl_3} = 0.50045$. This deviation cannot be due to the small aluminum chloride evaporation from the melts, since the pressure is less than 2 mmHg[18,19,46] and a rough calculation of the amount of $AlCl_3$ in the gas phase using the ideal gas law shows evaporation of less than 3×10^{-6} mol of $AlCl_3$ (monomer), i.e., negligible compared to the weighing accuracy.

Assuming then that the difference between X_{AlCl_3} and X'_{AlCl_3} is due to the AlOCl presence alone, and using the formulas in the Appendix, we obtain the weight ratios $W_{AlOCl}/W_{AlCl_3} = 0.0018$ and $W_{AlOCl}/W_{NaAlCl_4} = 0.0012$. On the average, an oxide molality of 0.016 mol of AlOCl per kg of $NaAlCl_4$ solvent (or a molarity of 0.026 mol of AlOCl per L) was thus present in the cryoscopic experiments. From this knowledge of the oxide content, the corrected number of moles of $AlCl_3$ for all cryoscopic experiments is obtained by multiplying the

---

(35) Eley, D. D.; Watts, H. *J. Chem. Soc.* **1952**, 1914.

(36) Schäfer, H.; Binnewies, M. *Z. Anorg. Allg. Chem.* **1977**, *433*, 58.

(37) Howie, R. C.; Macmillan, D. W. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 399.

(38) Seegmiller, D. W.; Rhodes, G. W.; King, L. A. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 885.

(39) Mamantov, G.; Osteryoung, R. A. In "Characterization of Solutes in Nonaqueous Solvents"; Mamantov, G., Ed.; Plenum Press: New York, 1978; p 231.

(40) El Hosary, A. A.; Kerridge, D. H.; Shams El Din, A. M. In Inman, D., Lovering , D. G. "Ionic Liquids"; Plenum Press: New York 1981; Chapter 16.

(41) (a) Linga, H.; Stojek, Z.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 3754. (b) Stojek, Z.; Linga, H.; Osteryoung, R. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *119*, 365.

(42) von Barner, J. H.; Bjerrum, N. J.; Smith, G. P. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 837.

(43) Zachariassen, K.; von Barner, J. H., personal communication.

(44) von Barner, J. H.; Bjerrum, N. J. *Inorg. Chem.* **1973**, *12*, 1981.

(45) Kühnl, H.; Geffarth, U. *Z. Anorg. Allg. Chem.* **1972**, *391*, 280.

(46) Linga, H.; Motzfeldt, K.; Øye H. A. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 568.

Table III. Determination of the Cryoscopic Effect of AlOCl

expts	"AlCl$_3$",[a] mol	NaCl, mol	$X_{\text{"AlCl}_3\text{"}}$[b] accuracy (±0.00003)	T_f, °C[b] (precision ±0.03)	added AlOCl, mmol	increment[c] molality, m_{AlOCl}	T_f, °C (precision ±0.03)	θ, °C	ν_{AlOCl}[d]	X_{AlCl_3}[e]
E-2, E-3	0.12719	0.12743	0.49953	156.25	0.3066	0.01256	156.11	0.14	0.59 ± 0.10	0.49908
E-4[f]	0.12940	0.12743	0.50384	~155.22[f]	0.3066	0.01241	155.10	0.12	0.51 ± 0.20	0.50339
E-5[f]	0.12940	0.12886	0.50103	~156.31[f]	0.3066	0.01237	156.18	0.13	0.55 ± 0.20	0.50058
G-2, G-3	0.13075	0.13125	0.49904	156.21	0.4335	0.01727	156.03	0.18	0.55 ± 0.10	0.49859
H-1, H-2	0.13703	0.13725	0.49960	156.38	0.2244	0.00853	156.30	0.08	0.50 ± 0.10	0.49915
I-0, I-1	0.14253	0.14130	0.50217	155.92	0.5198	0.01907	155.70	0.22	0.61 ± 0.10	0.50172
J-1, J-2	0.26366	0.26494	0.49879	155.98	0.8527	0.01684	155.82	0.16	0.50 ± 0.10	0.49834

[a] Disregarding the presence of AlOCl impurities. [b] Before addition of AlOCl. [c] Not including oxide impurities. [d] ν = number of foreign particles formed per AlOCl added = $\theta/(\lambda m_{\text{AlOCl}})$. [e] Corrected for oxide impurities; see text. [f] No reference experiment; freezing point determined from Figure 3.

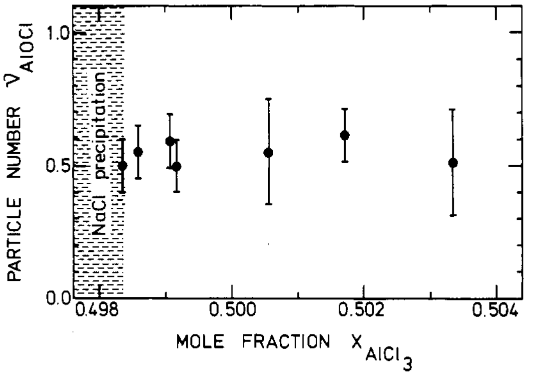


Figure 6. Number of foreign particles formed per added AlOCl particle vs. composition, expressed as the oxide-corrected mole fraction of AlCl$_3$.

number of moles of "AlCl$_3$" (in Table I) by 0.9982. Then corrected mole fractions X_{AlCl_3} and X_{NaCl} can be calculated. (Approximately 0.00045 should be substracted from $X_{\text{'AlCl}_3\text{'}}$ and 0.00045 added to $X_{\text{'NaCl'}}$ in Table I.)

Melting Point Correction of Cryoscopic Experiments. It is known that AlOCl has a certain (small) solubility in equimolar NaAlCl$_4$ melts, the extent depending on acidity and temperature.[28,45] The dissolved "AlOCl" is electrochemically inactive and acts as an inert solute in a pCl interval around neutrality,[28-31] although the limits of the interval are subject to controversy.[43] The cryoscopic action of AlOCl is unknown, and we decided to investigate this matter in detail because it would allow for melting point corrections and give valuable information on the chemical constitution of the dissolved "AlOCl".

Small quantities of pure AlOCl were added to cryoscopic cells containing NaAlCl$_4$ melts with known composition and melting points (or at least the melting points could be predicted fairly accurately from Figure 3). The experiments are reported in Table III and in Figure 6.

From these experiments we estimate that ν_{AlOCl} (i.e., the number of foreign particles formed per AlOCl) is 0.5 ± 0.1 (for the interpretation of this information see later). The cryoscopic action of AlOCl in NaAlCl$_4$ melts near neutrality is then given by

$$\theta_{\text{AlOCl}} \simeq 19 \times 0.5 m_{\text{AlOCl}} \qquad (9)$$

For the phase-diagram experiments in Table I with $m_{\text{AlOCl}} \simeq 0.016$ mol kg^{-1}, an AlOCl impurity induced depression of $\theta_{\text{AlOCl}} = 0.15$ °C is found. This means that a phase diagram corrected for oxide impurities can be constructed. It looks like Figure 3, but the coordinates are shifted by $(\Delta x, \Delta\theta) = (-0.00045, 0.15)$ and thus has its maximum freezing point at 156.7$_1$ °C for $X_{\text{AlCl}_3} = 0.50000$ and the basic eutecticum at 156.1$_5$ °C for X_{AlCl_3} = ca. 0.4984 ± 0.0001.

Verification of T_f for Pure NaAlCl$_4$. Experiments to find T_f for NaAlCl$_4$ were done by combining cryoscopy and potentiometry in one special cell equipped with Al electrodes in the compartments and a pocket for the resistance thermometer. The sample compartment was loaded with 12.31900 g of "AlCl$_3$" and 5.37865 g of NaCl (i.e., $X_{\text{'AlCl}_3\text{'}} = 0.50096$). The potential relative to the NaCl saturated reference (at 175 °C) was 162.10 mV before and 158.74 mV after the measurement of the freezing point (156.3$_8$ °C) of the sample melt was performed (1 week). The average potential (160.5 mV) corresponds to $X_{\text{AlCl}_3} = 0.49997$, $W_{\text{AlOCl}}/W_{\text{AlCl}_3} = 0.00399$, $W_{\text{AlOCl}}/W_{\text{NaAlCl}_4} = 0.00277$, and an AlOCl molality of 0.0353 mol of AlOCl/kg of solvent. (This high oxide content probably comes partly from borosilicate disk corrosion). The corresponding freezing point depression θ is then calculated from eq 9 to be 0.33 °C. This gives the corrected freezing point of 156.7$_1$ °C for the oxide-free NaAlCl$_4$ melt ($X_{\text{AlCl}_3} = 0.49997$), in accordance with the previous result in this work.

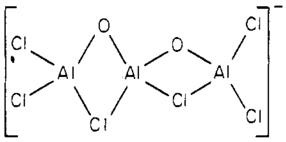
Determination of the Freezing Point of Pure NaAlCl$_4$. It was considered important to establish the reliability of the predicted freezing point, T_f = 156.7$_1$ °C. To this end, we slowly solidified ca. 40% of the (melted) content of cell F-1 and isolated the solid from the supernatant melt by turning the furnace upside down and then lowering the temperature. After transfer to an empty cell, the freezing point of the 40% first-solidified fraction was found to be 156.6$_2$ °C, i.e., higher than for any previously measured melt. This procedure was then repeated for the content of the latter cell. After isolation of an even purer fraction, the freezing point raised to 156.6$_8$ °C, i.e., only 0.0$_3$ °C lower than the freezing point predicted for pure NaAlCl$_4$, 156.7$_1$ °C. The precision is estimated to be ±0.03 °C and the absolute accuracy is ±0.10 °C.

Self-Dissociation of NaAlCl$_4$. In the considerations thus far, the self-dissociation of the AlCl$_4^-$ ions (into Al$_2$Cl$_7^-$ and Cl$^-$ ions; see eq A11 in the Appendix) has been neglected. However, it is clear that the absolute values of the freezing points are influenced by self-dissociation. The influence is largest at neutrality, where $[\text{Cl}^-] = [\text{Al}_2\text{Cl}_7^-] = K^{1/2}[\text{AlCl}_4^-]$. The magnitude of the equilibrium constant, defined in eq A12 ($K = 8.9 \times 10^{-8}$ at ca. 156 °C) may be estimated by extrapolation of the data of Hjuler et al.[19] Hence, $[\text{Cl}^-] = [\text{Al}_2\text{Cl}_7^-] = 0.0027$ mol L^{-1} = 0.0015 mol kg^{-1}. This corresponds to a maximum self-dissociation freezing point depression of $2 \times 0.0015 \times 19 = 0.06$ °C. The self-depression levels off very sharply when the composition differs from that of neutrality; hence the self-depression should cause the NaAlCl$_4$ solidi curves to meet smoothly at $X_{\text{AlCl}_3} = 0.500000$. Relative to the precision of our measurements the effect is not large enough to be seen (Figure 3). If NaAlCl$_4$ did not self-dissociate, the freezing point would probably have been 156.7$_7$ °C in the oxide-free state. This temperature is probably the melting point of the pure crystal.

On the Constitution of "Dissolved AlOCl"

The number of particles formed per added AlOCl (i.e., ν_{AlOCl}) is 0.5 ± 0.1, independent of the acidity within the range studied (see Table III and Figure 6). For virgin AlOCl particles (or for solvated AlOCl particles like $Al_2OCl_5^-$) a value of 1 for ν_{AlOCl} would have been predicted.

A value of $^1/_2$ means that two virgin particles of AlOCl on the average are needed to form one cryoscopically active particle. $Al_2O_2Cl_2$ is not a likely species from a structural point of view, since Al cannot adopt tetrahedral coordination in such a particle. The simplest satisfactory structure of "dissolved AlOCl" is the solvated dimer $Al_3O_2Cl_6^-$.



Such a formula is in accordance with similar structures seen for aluminum chlorosulfides dissolved in tetrachloroaluminate melts.[47]

The existence of dissolved species like Al_3O_4Cl or $Al_4O_4Cl_5^-$ has been reported[44] in basic $NaAlCl_4$ melts of high oxide concentration. (Also, solids like $NaAl_4O_4Cl_5$ have been prepared.)[2c,48] Such species cannot be formed to any appreciable extent in our melts, since the reaction of formation, eq 10,

$$4AlOCl + Cl^- \rightarrow Al_3O_4Cl + AlCl_4^- \rightarrow Al_4O_4Cl_5^- \qquad (10)$$

shows that ν_{AlOCl} must be zero in this case (one foreign particle, Cl^-, consumed and one, Al_3O_4Cl or $Al_4O_4Cl_5^-$, produced per four AlOCl).

Of course, the value $\nu_{\mathrm{AlOCl}} \simeq 0.5$ might result from a molecular ensemble that on the average results in this value. The following example should illustrate this point. Suppose that the added AlOCl forms a series of homologous polymers $[Al_{n+1}O_nCl_{n+4}]^-$ of structure similar to the dimer ($n = 2$; see above structural formula) and that these are mutually in equilibrium. If the molality of the n-mer is m_n, the relation given in eq 11 must be fulfilled (e.g., $m_1 = m_3$ and m_4, m_5...

$$\nu_{\mathrm{AlOCl}} = \frac{m_1 + m_2 + m_3...}{m_1 + 2m_2 + 3m_3...} \simeq \frac{1}{2} \qquad (11)$$

$= 0$ is all that is required). Of course many other ensembles can be proposed.

The following observations indicate that equilibria are indeed present. If the oxide-containing $NaAlCl_4$ melts (those in Table III, and to smaller extent all melts) were heated to 200–250 °C for a short time and the freezing points then determined as fast as possible after thermal equilibration (1–2 h, small subcooling), lower freezing points were observed, corresponding to $\nu_{\mathrm{AlOCl}} \simeq 1$. The reestablishment of the chemical equilibrium took at least 1 day (giving then again $\nu_{\mathrm{AlOCl}} \simeq 0.5$), and perhaps repeated freezing and melting (at temperatures within the range $T_f \pm 1$ °C) had a promoting effect. These nonequilibrium observations can be explained by postulating the presence of reaction 12. If the dissociation at higher temperatures is fast and the reverse reaction is slow, nonequilibrium ν_{AlOCl} values near 1 can be explained.

$$Al_3O_2Cl_6^- + AlCl_4^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftarrows}} 2Al_2OCl_5^- \qquad (12)$$

As mentioned in relation to eq 7, several authors[17,29-31,43] have presumed the formation (to some extent) of dissolved species like $AlOCl_2^-$ or $Al_2OCl_6^{2-}$ in the most basic $NaAlCl_4$ melts, i.e., near NaCl saturation. Also, solid $NaAlOCl_2$ has been prepared.[49] Taulelle et al.,[31] correcting previous errors, conclude that $AlOCl_2^-$ does not exist in appreciable amounts at 175 °C. However, the chloroacidity of AlOCl is still in question.[43]

The nature of the cryoscopic results obtained here (Table III) is such that they cannot be used to solve the problem. At first sight the value of $\nu_{\mathrm{AlOCl}} \simeq 0.5$ seemed to favor the nonexistence of $AlOCl_2^-$ (or $Al_2OCl_6^{2-}$) in our experiments. The formation of $AlOCl_2^-$ or $Al_2OCl_6^{2-}$ would require a ν_{AlOCl} value near zero (one cryoscopically active Cl^- ion is replaced with $AlOCl_2^-$ or $Al_2OCl_6^{2-}$ per added AlOCl), and polymeric versions like $(AlOCl_2^-)_n$ would give even a negative ν_{AlOCl}.

However, we cannot exclude the action of two opposite effects: monomerization and chloride uptake. Thus, the acid–base dissociation reaction (eq 13) would proceed without any change in $\nu_{\mathrm{AlOCl}} \simeq {}^1/_2$. Therefore, our ν_{AlOCl} results still leave the question of $Al_2OCl_6^{2-}$ formation unsolved.

$$Al_3O_2Cl_6^- + AlCl_4^- + Cl^- \rightarrow Al_2OCl_5^- + Al_2OCl_6^{2-} \qquad (13)$$

On the other hand, the significantly flatter slope in Figure 3 of the *basic* relative to the *acidic* solidus curves (β values 278 ± 39 and −380 ± 7, Table I) might best be explained by some mechanism which consumes Cl^- and thereby reduces the cryoscopic action of chloride added to neutral $NaAlCl_4$. Such a mechanism is the presumed formation of "$AlOCl_2^-$" via eq 8, or rather via reactions like eq 14.

$$Al_2OCl_5^- + Cl^- \rightarrow Al_2OCl_6^{2-} \qquad (14)$$

The difference in slope in Figure 3 could, to our opinion, indicate that "AlOCl" really is weakly chloroacidic in basic sodium tetrachloroaluminate.

Acknowledgment. This work was supported by the Danish Technical Science Research Foundation. We wish to thank Dr. R. Fehrmann for helpful discussions and Kim Zachariassen for performing some of the potentiometric measurements.

Appendix

Calculation of the NaCl Solidus Curve. The following thermodynamic information is available[19] for the dissolution of NaCl in basic $NaAlCl_4$ as a function of the temperature T (in kelvin),

$$NaCl(s) \rightleftarrows Na^+ + Cl^- \qquad (A1)$$

with $\Delta H°(T) = -11850 + 63.26T$ (J mol^{-1}) and $\Delta S°(T) = -352.81 + 62.26 \ln T$ (J mol^{-1} K^{-1}). The solubility product is

$$K_s = [Na^+][Cl^-] \qquad (A2)$$

where brackets denote the concentration of an ion, in mol L^{-1}, activity coefficients being assumed to be unity. It can be calculated from

$$K_s(T) = \exp\left(\frac{-\Delta H°}{RT} + \frac{\Delta S°}{T}\right) \qquad (A3)$$

In, for example, 1 g of the saturated melt, with x g of NaCl in solution and with the density $\rho \simeq 1.72$ g cm^{-3} near the melting point[50] one has

$$[Cl^-] = x\rho \times 1000/M_{\mathrm{NaCl}} \qquad (A4)$$

$$[Na^+] = x\rho \times 1000/M_{\mathrm{NaCl}} + (1 - x)\rho \times 1000/M_{\mathrm{NaAlCl_4}} \qquad (A5)$$

M = molecular weight. Hence, from the definition of K_s, x can be calculated by solving the second-order equation (A2).

---

(47) Berg, R. W.; von Winbush, S.; Bjerrum, N. J. *Inorg. Chem.* **1980**, *19*, 2688.

(48) Portier, J.; Tressaud, A.; Hagenmuller, P. *Bull. Soc. Chim. Fr.* **1966**, 551.

(49) Morozov, I. S.; Chatova, V. L.; Morozov, A. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1971**, *16*, 323.

(50) Berg, R. W.; Hjuler, H. A.; Bjerrum, N. J. *J. Chem. Eng. Data* **1983**, *28*, 251.

Finally, X_{AlCl_3} (saturated) is obtained as

$$X_{AlCl_3} = \frac{(1-x)/M_{NaAlCl_4}}{(x/M_{NaCl}) + 2(1-x)/M_{NaAlCl_4}} \qquad (A6)$$

Calculation of Oxide Contents. Suppose that the weight of impure $AlCl_3$ ($W_{AlCl_3} + W_{AlOCl}$) and the weight of pure NaCl (= W_{NaCl}) is known. From this the apparent mole fraction, $X_{\text{`}AlCl_3\text{'}}$, can be calculated.

$$X_{\text{`}AlCl_3\text{'}} = \frac{(W_{AlCl_3} + W_{AlOCl})/M_{AlCl_3}}{(W_{AlCl_3} + W_{AlOCl})/M_{AlCl_3} + W_{NaCl}/M_{NaCl}} \qquad (A7)$$

Suppose further that the true composition of the melt (formed by mixing these chemicals) is known from some experiment. As an example, it can be determined potentiometrically.[44] In this case, the melt is contained in one electrode compartment separated (by a porous borosilicate disk) from a reference melt (saturated with NaCl) in the other electrode compartment. Electrodes of aluminum or carbon are used according to the electrode processes

$$AlCl_4^- + 3e^- \rightleftarrows Al + 4Cl^- \qquad (A8)$$

$$Cl_2 + 2e^- \rightleftarrows 2Cl^- \qquad (A9)$$

The electrode potential difference, ΔE, is measured, e.g., at 175 °C. The chloride concentration, $[Cl^-]$ in mol L^{-1}, is then given by $[Cl^-] = 10^{(-pCl)}$ where

$$pCl = \Delta E/A + pCl_{satd} \qquad (A10)$$

If ΔE is expressed in mV, A can be calculated (from the Nernst equation) as $A = 3\mathcal{F}/(4RT \ln 10) = 118.559$ mV for the aluminum electrodes and as $A = \mathcal{F}/(RT \ln 10) = 88.922$ mV for the carbon electrodes ($\mathcal{F}$ = Faraday's constant). pCl_{satd} is 1.128 (6) at 175 °C.[17] The concentration of $AlCl_4^-$ can be found from the density of the melt[50] and the molar weight, $[AlCl_4^-] \simeq 8.877$ M. From the equilibrium

$$2AlCl_4^- \rightleftarrows Cl^- + Al_2Cl_7^- \qquad (A11)$$

with equilibrium constant

$$K = \frac{[Cl^-][Al_2Cl_7^-]}{[AlCl_4^-]^2} = 8.9125 \times 10^{-8} \qquad (A12)$$

at 175 °C,[17] the $[Al_2Cl_7^-]$ concentration is found.

The net excess of $[Al_2Cl_7^-]$ or $[Cl^-]$ is calculated as the difference. Assuming 100% purity of NaCl, the real amount of pure $AlCl_3$ is then found.

Finally the true mole fraction X_{AlCl_3} is calculated.

$$X_{AlCl_3} = \frac{W_{AlCl_3}/M_{AlCl_3}}{(W_{AlCl_3}/M_{AlCl_3}) + (W_{NaCl}/M_{NaCl})} \qquad (A13)$$

From eq A7 and A13 we obtain

$$\frac{W_{AlOCl}}{W_{AlCl_3}} = \frac{X_{\text{`}AlCl_3\text{'}} - 1 + (1 - X_{AlCl_3})X_{\text{`}AlCl_3\text{'}}/X_{AlCl_3}}{1 - X_{\text{`}AlCl_3\text{'}}} \qquad (A14)$$

$$\frac{W_{AlOCl}}{W_{NaAlCl_4}} = \frac{W_{AlOCl}M_{AlCl_3}}{W_{AlCl_3}M_{NaAlCl_4}} \qquad (A15)$$

The AlOCl molality is then

$$\frac{W_{AlOCl}}{W_{NaAlCl_4}}\left(\frac{1000}{M_{AlOCl}}\right) \qquad (A16)$$

Registry No. NaCl, 7647-14-5; $AlCl_3$, 7446-70-0; $NaAlCl_4$, 7784-16-9.

Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

Preparation of Well-Defined Surfaces at Atmospheric Pressure: Studies by Electrochemistry and LEED of Pt(100) Pretreated with Iodine

ANDRZEJ WIECKOWSKI,† STEPHEN D. ROSASCO, BRUCE C. SCHARDT, JOHN L. STICKNEY,
and ARTHUR T. HUBBARD*

Received May 24, 1983

Reported here are studies by LEED, Auger spectroscopy, and electrochemistry which show that Pt(100) monocrystal surfaces purposely disordered by electrochemical oxidation and reduction (as in the procedure commonly employed to clean or "activate" Pt electrodes) are restored to an ordered state by programmed heating under an Ar atmosphere containing iodine vapor. A nearly hexagonal, centered-rectangular adlattice of I atoms was formed, containing three I and five Pt atoms in the surface unit cell, $\theta_I = 0.6$, $Pt(100)[c(\sqrt{2}\times 5\sqrt{2})]R45°\text{–}I$. Programmed heating of this adlattice led to stepwise desorption of halogen and produced a series of related adlattices. One of these, $Pt(100)[(c\sqrt{2}\times 2\sqrt{2})]R45°\text{–}I$, at $\theta_I = 0.50$, is particularly amenable to identification, without LEED, by means of its characteristic cyclic voltammogram for silver electrodeposition. The behavior of each iodine adlattice toward silver electrodeposition and programmed temperature desorption is reported. These atmospheric iodine pretreatment and voltammetric procedures for preparing and verifying a well-defined electrode surface do not require vacuum equipment, although demonstration of the ordered structures in this work employed LEED and related techniques under ultrahigh vacuum. This basic approach should be applicable to a wide range of metals and adsorbates.

Introduction

Studies by LEED and electrochemistry of the molecular structure and composition of electrodeposits on platinum monocrystal surfaces pretreated with iodine vapor have been reported.[1-3] Iodine pretreatment and characterization of the monocrystal electrodes under ultrahigh vacuum allowed exploration of the effect of chemisorbed layer structure on the electrodeposition process[4] and also protected the electrode (and electrodeposit) surfaces from attack by the electrolyte and residual gases.[1-4] A number of interdependencies between surface structure and electrochemical behavior were indicated:

---

† Permanent address: Department of Chemistry, Warsaw University, Warsaw, Poland.

(1) A. T. Hubbard, J. L. Stickney, S. D. Rosasco, M. P. Soriaga, and D. Song, *J. Electroanal. Chem. Interfacial Electrochem.*, **150**, 165 (1983).

(2) J. L. Stickney, S. D. Rosasco, D. Song, M. P. Soriaga, and A. T. Hubbard, *Surf. Sci.*, **130**, 326 (1983).

(3) J. L. Stickney, S. D. Rosasco, and A. T. Hubbard, *J. Electrochem. Soc.*, in press.

(4) J. L. Stickney, S. D. Rosasco, B. C. Schardt, and A. T. Hubbard, *J. Phys. Chem.*, in press.

0020-1669/84/1323-0565$01.50/0