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METAL HALIDE-GROUP III HALIDE GAS COMPLEXES WITH EMPHASIS ON ALUMINUM CHLORIDE

by

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METAL HALIDE-GROUP III HALIDE GAS COMPLEXES WITH EMPHASIS ON ALUMINUM CHLORIDE*

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ABSTRACT

The thermodynamics of the presently known gas complexation reactions between metal halides and group III halides are treated in a self-consistant manner. By focusing on aluminum chloride as a complexing agent, certain systematic trends are revealed. The partial pressures of the gaseous complexes display shallow minima near 800° K whenever the complex molecules involve more than one molecule of $AlCl_3$. Increasing the aluminum chloride pressure from 1 atm. to 10^3 atm. decreases somewhat the differences in the partial pressures among the various gaseous complexes which span two to three orders of magnitude.

The methods developed for characterizing the complexes, and their structures as well as some applications of gas complexation are discussed.

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1. INTRODUCTION

The trivalent group IIIA chlorides, bromides and iodides are characterized by having relatively low boiling or sublimation temperatures, as illustrated by the boiling or sublimation temperatures of BCl_3: 18 (b.p.), $AlCl_3$: 183 (s.p.), $GaCl_3$: 201 (b.p.), $InCl_3$: 418 (s.p.). It has long been recognized that these compounds are Lewis acids. In particular, $AlCl_3$ has been used extensively in organic synthesis due to its Lewis catalytic activity.

High volatility at moderate temperature combined with halide acceptor ability makes these halides useful as volatilization agents for less volatile halides in the temperature range 200-1000°C.

The stability and volatility of $NaAlCl_4$ in the gas phase was recognized by Fischer and Grothe [1] in 1949, and Grothe [2] remarked that $MgCl_2$ seemed to be transported in the gas phase when binary mixtures of $AlCl_3$ and $MgCl_2$ were prepared. Dewing found high volatilities for reactions between divalent chlorides with $AlCl_3$ and $FeCl_3$ [3,4]. A dramatic example of volatility enhancement is the formation of $NdAl_3Cl_{12}(g)$ and $NdAl_4Cl_{15}(g)$ leading to an increase by a factor of $\sim 10^{13}$ in the partial pressure of $NdCl_3$ in 1 atm. Al_2Cl_6 at 600 K, relative to pure $NdCl_3$ at the same temperature [5,6].

Several review articles have appeared which have treated gas complexation by IIIA halides, notably by Novikov and Gavryuchenkov [7], Hastie [8,9], Emmenegger [10] and Schäfer [11].

The present paper is not an exhaustive review of the literature. Rather the emphasis is on experimental methods of characterization, correlations and the evaluation of thermodynamic quantities. The aim is to establish a systematics of complexation based on chemical bonding considerations.

Gas complexation between a IIIA halide and another halide may be formulated generally as follows:

$$mMX_y(s,l \text{ or } g) + nA_2X_6(g) \ (\text{or } 2nAX_3(g)) = M_mA_{2n}X_{6n+my}(g) \quad (1)$$

Such equilibria may be studied by a variety of techniques depending on whether or not MX_y is present as a condensed phase and depending as well on the magnitude of the gas pressure and the temperature. In the following discussion the advantages and disadvantages of the different techniques, and the conclusions to be drawn from pertinent examples will be detailed. Then a thermodynamic treatment of the results will be presented. Finally, the structures of the gas complexes, the stabilities of condensed versus gaseous phases and potential applications of the gas complexes will be discussed.

2. EXPERIMENTAL METHODS

Nearly every method used for determination of vapour pressures and structures of high-temperature vapours may be employed in the study of gas complexation with IIIA metal halides. The book edited by Margrave [12] may be consulted as a general reference. In the following, the methods that up to now have proved particularly useful for determination of gas complexation with IIIA metal halides will be examined.

a) Transpiration techniques

A general discussion of the transpiration method is given by Merten and Bell [13]. The method requires the salt MX_y to be in a condensed state and the vapour pressure to be from a few Torr up to 1 atm. The complexing gas A_2X_6 in a pure or dilute state is passed over the sample at the temperature, T, of investigation. The gas is saturated with the vapour of the sample and the vapour is later condensed out in a cold trap. The experiment gives information on the quantity of MX_y in the vapour phase per mol A_2X_6.

With some assumptions which will be discussed later, it is possible to calculate the pressure of the gas complex M-A-X* as a function of $P_{A_2X_6}$ and hence determine the equilibrium constant for Eqn. (1). A typical example of an application of this method is the study of gas complexation between $CaCl_2$, $CoCl_2$, $MgCl_2$, $MnCl_2$, $NiCl_2$ and $CdCl_2$ with Al_2Cl_6 and Fe_2Cl_6 gas [4].

b) Near IR-UV visible absorption spectroscopy

Many of the gas complexes encountered contain metal ions with unfilled d- or f- shells which absorbs light in the wavelength region 25000-1800 Å suitable for measurements by readily available spectrophotometers. In order to discriminate against black body radiation from the sample it is advantageous to use spectrophotometers employing phase sensitive detection of electromagnetic radiation, as for example Cary H spectrophotometers.

The spectroscopic method can in principle give information not only about the pressure of the gaseous complexes, but also about their structures and the coordination geometry around M^{y+}.

The method was applied to studies of this type of gas complexation by Øye and Gruen [6]. Usually the salt MX_y to be

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*Short notation for the gaseous molecule $M_mA_{2n}X_{6n+my}$ or mixtures of such gas molecules with different stoichiometry.

studied is enclosed in an evacuated optical cuvette together with the appropriate IIIA halide. On heating, the IIIA halide will evaporate and form complexes with MX_y. The technique is based on first establishing the molar absorptivity of M^{y+} in experiments where a small amount of MX_y is completely evaporated through gas complexation. (Usually the pressure of MX_y is much smaller than M-A-X and can be neglected).

The molar absorptivity of M^{y+} in the gas complex at certain wavelenths, ε_i, is then given according to Beer's law:

$$\varepsilon_i = \frac{A_i VM}{wl} \quad . \tag{2}$$

where A_i = the optical density at wave number i, V = volume, M = molecular weight of MX_y, w = weighed in amount of MX_y and l = optical pathlength. ε_i should be determined as a function of temperature and A_2X_6 pressure, but up till now the data have only permitted one to establish ε_i as function of temperature.

Experiments with excess MX_y (saturated vapour) gives then the "atomic"* vapour pressure P^a of the gas complexes by a combination of Beer's law with the law of ideal gases:

$$P^a = \frac{A_i R\overline{T}}{\varepsilon_i l} \tag{3}$$

Where R is the gas constant and $\overline{T}$ is the average temperature

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$*P^a = \sum_i mi[P(M_{m_i}A_{2n_i}X_{6n_i+m_iy})]$. If the gas complexes, however, contains only one M atom (which usually is the case), then P is equal to the total pressure of the gas complexes present.

(for experimental reasons a small temperature gradient is set up over the cell in order to prevent condensation on the windows). P^a and ε_i must be determined from corresponding conditions, i.e. the same temperature if ε_i is temperature dependent. The pressure of the complexing gas A_2X_6 is usually determined from the weighed in amount correcting for dissociation and gas complexation.

Finally the state of the condensed state must be established, i.e. whether it is a liquid or a solid with defined stoichiometry. The thermodynamics are simplest when the condensed phase is a solid compound. The work on gas complexation between $NdCl_3$ and Al_2Cl_6[6] gives further details on the method.

c) Static pressure technique

The static pressures of heterogeneous or homogeneous mixtures containing gas complexes may be measured by a variety of techniques. Typical methods make use of spiral, membrane or liquid manometers or of quasi-static techniques such as boiling point and dew point methods. Vapour density measurements will also give similar information. A review of many methods is given by Clopper et al. [14]. In general, these have, however, found little use in the study of M-A-X gas complexes probably because the vapour pressure of M-A-X usually is much smaller than the pressure of A_2X_6 or AX_3.

Information about gas complexation between alkali- and aluminium chlorides have, however, been obtained. Fischer [1] reports on formation of $NaAlCl_4$(g) by vapour pressure measurements, but details are not given. Galitskii [15] made use of the transpiration method combined with determination of the total vapour pressure for NaCl-$AlCl_3$ melts in order to determine the thermodynamics of formation of $NaAlCl_4$(g). In order to obtain the necessary information he also made use of the vapour above the melt condensed out in two different steps by the transpiration procedure.

Linga et al. [16] used a theoretically modified boiling point method for determination of total pressure of AlkCl-$AlCl_3$ melts (Alk = Li, Na, K). By making full use of the data and introducing a model for the melt, information on gas complexation was obtained.

d) Mass spectrometry

Mass spectrometry has been widely used for the study of gas complexation. The review by Novikov and Gavryuchenkov [7] gives many examples. Another useful variation of the method is the work by Sidorov and Shol'ts [17] where the liquid activities and the gas complexation reaction are determined by mass spectroscopy and Knudsen effusion experiments using the so-called isothermal evaporation method.

Of particular interest in connection with $AlCl_3$-containing complexes is the recent work by Binnewies [18] which uses a double oven technique. $AlCl_3$ is evaporated at a low temperature of $\approx$ 100°C, and swept over the MCl_y salt to be studied at for instance 350°C. The chemically transported gas complex is then focussed on the ion source of a mass spectrometer through an effusion hole in the crucible. This method has been applied to a variety of divalent chlorides[18,19,20].

The sources of the different ions are established and making the simplifying assumption that the pressure of a certain parent molecule will be proportional to ion intensities of the daughters, equilibrium constants in reasonable agreement with previous investigations are obtained. The temperature dependence of the equilibrium constant is calculated by assuming an entropy of reaction.

e) Structural methods

In addition to stoichiometry and thermodynamic information it is highly desirable to obtain stuructural information on the gas complexes. Information has been obtained through the absorption spectrocopic technique discussed above. Some spectra give very clear-cut information about coordination, but in other instances the spectra are not detailed enough for an unambiguous interpretation. The short-comings in some instances may be illustrated by the study of $CoAl_2Cl_8$(g) and $CoGa_2Cl_8$(g) which give closely similar spectra. The system has been investigated by four different groups but a concensus with respect to the interpretation of the results has not yet been obtained [21-24].

Electron diffraction techniques have not yet been applied to the present gas complexes. Recently some resonance Raman spectra were obtained by Emmenegger et al. [25] and by Papatheodorou and Capote [26]. A square planar coordination was proposed for $PdAl_2Cl_8$ in agreement with absorption spectroscopic measurements. The study of Cu-Al-Cl complexes reveals, however, that utmost care most be used in the interpretation. The three-coordination of Cu^{2+} in $CuAl_2Cl_8$ suggested by Emmenegger et al. [25] appears to be due to $CuAlCl_5$ [26] as the laser beam creates a spectroscopic temperature which is higher than the thermodynamic one.

3. THERMODYNAMICS OF GAS COMPLEXATION

In principle gas complexation is most directly studied by investigating the gaseous equilibrium

$$mMX_Y(g) + nA_2X_6(g) = M_mA_{2n}X_{6n+my}(g) \qquad (4)$$

without any condensed phase being present. By measuring three variables: The total gas pressure, the composition and the vapour density, the stoichiometry of the gas molecules and the thermodynamics of equilibrium (4) can in principle be unambigously determined. In spite of the straightforward thermodynamics, this is not a commonly used approach for the determination of chloroaluminate gas complexes. One principal disadvantage of the method is that it requires all pressures to be of the same order of magnitude. Nonetheless, the approach has been carried out by Novikov and Kotova who studied the $HgAlCl_5$ gas complex [27].

A direct measurement of the relative pressures of the three components has been obtained by mass spectrometry [18-20]. Although the method is informative and rapid, it involves certain approximations (see above) which may lead to only moderate accuracy. Gas complexes with more than two Al atoms per complex molecule are not easily amenable to measurements since low pressures are a necessary condition in the mass spectrometer.

Most studies involve the presence of MX_Y as a condensed phase. The simplest case is when MX_Y is present as a pure solid (or a pure solid compound with A_2X_6). Then the activity of MX_Y is constant and only two variables need to be known, i.e. P_{M-A-X} and $P_{A_2X_6}$. The thermodynamic treatment when $MX_Y(s)$ is present will be illustrated.

For simplicity only one type of gaseous species is assumed present. Undissociated A_2X_6 is considered to be the complexing agent.

$$mMX_Y(s) + nA_2X_6(g) = M_mA_{2n}X_{6n+my}(g) \tag{5}$$

(The treatment is easily extended to more than one gaseous species, see [6], as n will then usually become a non-half integer and vary with temperature).

Using the absorption spectroscopic method as an example (see above) the "atomic" gas pressure ${}_mP_{M_mA_{2n}X_{6n+my}}$ is determined from a characteristic absorption peak. $P_{A_2X_6}$ can then be determined from the weighed in amount of AX_3 correcting for dissociation and complex formation [6].

By performing two different experiments and varying the temperature one has the following equation:

$$\frac{\frac{P^{a}_{M-A-X}}{m}}{P'^{n}_{A_2X_6}} = \frac{\frac{P^{a}_{M-A-X}}{m}}{P''^{n}_{A_2X_6}} = K_5 = \exp - \frac{\Delta H^{o}_{5}}{RT} + \frac{\Delta S^{o}_{5}}{R} \tag{6}$$

The two experiments provide in principle enough data to determine n (stoichiometry with respect to Al) and ΔH_5^{o} and ΔS_5^{o}. The reliability of the analysis is of course improved by doing more than 2 experiments and performing a least squares fit of the data. The thermodynamic analysis will predict correctly the amount of M in the gas phase but m (stoichiometry of M in the gas complex) cannot be determined and is generally included in K. Mass spectroscopic measurements have not yet succeeded in characterizing gas complexes with $M \neq 1$ [18-20].

In the transpiration method $P_{M-A-X} + P_{A_2X_6} = P_{tot}$ and the total amount of M, A and X are determined. If the gas volume or gas density are also measured, the exact stoichiometry (m and n) and the equilibrium thermodynamic functions can be specified. Usually, however, the gas volume is not known [4].

One has then:

$$\text{Ratio of M/A} = \frac{n_M}{n_A} = \frac{mP_{M-A-X}}{2P_{A_2X_6} + 2nP_{M-A-X}} \qquad (7)$$

$$P_{M-A-X} + P_{A_2X_6} = P_{tot} \qquad (8)$$

These two equations can be solved with respect to P_{M-A-X} and $P_{A_2X_6}$ as functions of n_M/n_A, P_{tot}, and m.

By insertion into the equation for the equilibrium reaction (5), results parallel to the spectroscopic method are obtained by varying the total pressure and temperature. Again the correct amount of M in the gas phase can be predicted, but the value of m has to be assumed since the activity of AX_y is not varied.

More care must be applied when equilibria with a liquid phase with varying composition is present, so that a varying activity of the component in the liquid phase enters the equilibrium constant

$$mMX_y(l) + nA_2X_6 = M_mA_{2n}X_{6n+my} \qquad (9)$$

$$K_9 = \frac{P_{M-A-X}}{a_{MX_y} P^n_{A_2X_6}} \qquad (10)$$

If the composition and the corresponding activity of the liquid phase is known, such a study will have the extra advantage that the coefficients m can also be ascertained (being usually 1), by varying the activity of MX_y.

Galitskii [15] performed a thermodynamic analysis of transpiration and total vapour pressure data above $NaCl-AlCl_3$ melts using the additional information that the vapour can be condensed out in two separate steps. He obtained plausible results for the reaction

$$NaCl(g) + AlCl_3(g) = NaAlCl_4(g) \tag{11}$$

but it is difficult to follow the published calculations. Furthermore, it remains unclear how the changing composition of the liquid is taken into account.

Linga et al. [16] studied the total vapour pressure above $MCl-AlCl_3$ ($M = Li, Na, K$) melts as function of temperature in the concentration range $0 < X_{AlCl_3} \leq 0.50$. The detailed data allowed a model to be set up. The liquid was assumed to be an asymmetric regular solution of $AlCl_4^-$ and Cl^- and the data was used to determine ΔH^o and ΔS^o for the two reactions

$$MAlCl_4(l) = MCl(l) + AlCl_3(l) \tag{12}$$

$$MAlCl_4(l) = MAlCl_4(g) \tag{13}$$

By combination with data from JANAF [28] the standard enthalpy and entropy for the reaction

$$MCl(g) + AlCl_3(g) = MAlCl_4(g) \tag{14}$$

was obtained in good agreement with Fischer's [1] and Galitskii's [15] results.

The $AlkAlCl_4$ gas complexation is an example of substantial amounts of gas complexes in equilibrium with a liquid phase at elevated temperatures. Gas complexation in equilibrium with liquid phases at low temperatures $\approx 500K$ are often of a very special kind due to the properties of MX_y-AX_3 melts. We will again use $AlCl_3$ as an example but the arguments are also valid for melts containing other aluminium, gallium, indium and ferric halides.

Pure molten $AlCl_3$ consists of doubly bridged Al_2Cl_6 molecules. Successive additions of a metal chloride MCly whose cation has a relatively low ionic strength (which usually is also the condition for giving a stable liquid phase) results in the sequential formation of the ions $Al_3Cl_{10}^-$, $Al_2Cl_7^-$ and $AlCl_4^-$ [29]. When, however, the composition corresponding to the stoichiometry $M(AlCl_4)_y$ is reached, $AlCl_3$ is no longer a Cl^- acceptor and free Cl^- ions are formed upon further addition of mCl_y.

The equilibrium constant

$$2AlCl_4^- = Al_2Cl_6 + 2Cl^- \qquad (15)$$

is usually very small ($K = 2.8\cdot 10^{-16}$ for $NaAlCl_4$ at 175°C [30,31]), implying a drastic drop in the Al_2Cl_6 activity over a very limited concentration range around $X_{Al_2Cl_6} = y/(y+2)$. For instance, for $NaCl$-$AlCl_3$ mixtures, the decrease in $a_{Al_2Cl_6}$ from $X_{Al_2Cl_6} = 0.35$ to $X_{Al_2Cl_6} = 0.315$ is about $10^{-8.5}$. This means that the melt composition will be nearly constant over an equally large variation in

$P_{Al_2Cl_6}$. Expressed more dramatically *A MCl_y-Al_2Cl_6 melt with composition $X_{Al_2Cl_6}$ = y/(y+2) will in a certain range only exhibit negligible concentration changes in spite of a large variation of the Al_2Cl_6 pressure*. The Gibbs-Duhem equation can then be integrated at constant T assuming constant composition: $X_{Al_2Cl_6} = y/(y+2)$.

$$d\ln a_{MCl_y} = - \frac{X_{Al_2Cl_6}}{1-X_{Al_2Cl_6}} d\ln a_{Al_2Cl_6} = - \int \frac{y}{2} d\ln P_{Al_2Cl_6} \qquad (16)$$

and

$$a_{MCl_y} = C \cdot (P_{Al_2Cl_6}/P^o_{Al_2Cl_6})^{-y/2} \qquad (17)$$

where $P^o_{Al_2Cl_6}$ is the vapour pressure of Al_2Cl_6 above pure $AlCl_3$ and C is a constant to be determined by the choice of the standard state.

If we again make the simplifying assumption that only one type of gas complex is present:

$$MCl_y(l) + nAl_2Cl_6(g) = MAl_{2n}Cl_{6n+y}(g) \qquad (18)$$

the equilibrium constant for this reaction will be

$$K_{18} = \frac{P_{M-Al-Cl}}{a_{MCl_y} \cdot P^n_{Al_2Cl_6}} = \frac{P_{M-Al-Cl}}{C \cdot P^{o\,y/2}_{Al_2Cl_6} \cdot P^{n-y/2}_{Al_2Cl_6}} \qquad (19)$$

If for instance the gas complex is MAl_3Cl_{9+y} then

$P_{M-Al-Cl}/P^{0.5}_{Al_2Cl_6}$ will be constant at constant temperature, i.e. the pressure of the gas complex varies with the square root of the Al_2Cl_6 pressure.

Sørlie and Øye [31,32] made use of this property of chloroaluminate melts in the study of gas complexes in equilibrium with $EuCl_2$-$AlCl_3$ and $TiCl_2$-$AlCl_3$ melts. The analysis was most detailed in the case of the $EuCl_2$-$AlCl_3$ system. More than one gas complex was present and the equation

$$P_{tot}(\text{gas complex}) = C \cdot P^{o\,y/2}_{Al_2Cl_6} \sum_i k_i P^{n_i''-y/2}_{Al_2Cl_6} \qquad (20)$$

had to be used instead of Eqn. (19).
Data from experiments in which $EuCl_2$ or $TiCl_2$ solid phases were present enabled one to evaluate the integration constant C. Such data were used to calculate K_{21} for the equilibrium

$$MCl_2(s) + nAl_2Cl_6(g) \;=\; MAl_{2n}Cl_{6n+2}(g) \qquad (21)$$

4. PRESENTATION OF DATA FOR ALUMINIUM CHLORIDE GAS COMPLEXES

An overview illustration of gas complexation is provided by Table 1 and Figs. 1 and 2 which give a survey of known $AlCl_3$ gas complexation reactions for chlorides in the condensed state. Table 1 lists ΔH^o_{22} and ΔS^o_{22} for the reaction:

$$MCl_y(s) + nAl_2Cl_6(g) \;=\; MAl_{2n}Cl_{6n+y}(g) \qquad (22)$$

In some instances, AlkCl and $EuCl_2$, for example, the reaction is more complex than indicated by equation (22) because the condensed phase is a liquid of unknown composition. For comparison ΔH^o and ΔS^o of vaporization of the pure solid is also given in Table 1 as well as P_{MX_y} at 600 K. The coordination around the complexed ion M^{y+} is given if known from spectroscopic studies.

The standard enthalpies and entropies are listed at the average temperatures of the gas complexation studies. For conversion of data to other temperatures Schäfer [11] proposed ΔC_p^o between $-6\ JK^{-1}$ and $14\ JK^{-1}$ be applied dependent on the gas complex formed. However, we have chosen not to apply this correction term in constructing Figs. 1 and 2 due to the limited temperature span of the measurements and the uncertainty in ΔH^o, ΔS^o as well as ΔC_p^o.

Figs. 1 and 2 give log $P_{M-Al-Cl}$ in the presence of $Al_2Cl_6(g)$ and $AlCl_3(g)$ at 1 and 10 atm total pressure respectively. The dissociation of Al_2Cl_6 to $AlCl_3$ is taken into consideration.

In some instances ($EuCl_2$, $TiCl_2$) the partial pressure of the complexes refer to equilibria involving not only $MCl_y(s)$ (Eqn. 22)) but also above liquid phase of unknown composition in which case dotted lines are shown. Data have been calculated directly from values given in publication [32,33] and not from derived data given in Table 1.

From Fig. 1 it can be seen that the partial pressures of the complexes display two general types of behavior. The larger group shows a maximum in partial pressure between 700 to 900 K. In a few cases, the partial pressures rise monotonically with temperature. The difference between the two groups appears to be simply a consequence of the stoichiometry of the gas complexes. When two or more Al-atoms are present in the gas complexes as in MAl_2Cl_8, MAl_3Cl_{11}, MAl_4Cl_{14}, MAl_2Cl_9, MAl_3Cl_{12}, MAl_4Cl_{15} and MAl_2Cl_{10} then the dissociation reaction

$$Al_2Cl_6(g) = 2AlCl_3(g) \qquad K = 1 \text{ for } T = 883 \text{ K} \qquad (23)$$

results in a diminishing complex pressure above a certain temperature. This is not the case if only one Al-atom is present in the gas complex as in $MAlCl_4(g)$ and $MAlCl_6(g)$.

Another intriguing observation is that the partial pressures of the different complexes show a lower degree of variability when the total pressure is 10 atm than at 1 atm. This behavior may be rationalized on the basis of bond properties of the gas complexes, to be discussed more fully below. The volatilities of the compounds MX_y of course differ by many orders of magnitude in the absence of gas complexing agents but in their presence, the differences are greatly diminished. The effect becomes more pronounced with increasing Al_2Cl_6 pressure for example.

Fig. 3 and 4 illustrate the gas complexation reactions in equilibrium with AlkCl-$AlCl_3$ melts. Fig. 3, which is taken from Ref. [16] gives the pressure of $LiAlCl_4$, $AlCl_3$ and Al_2Cl_6 in equilibrium with LiCl-$AlCl_3$ melts at 819 K. It is seen that $LiAlCl_4$ is the major constituent of the gas. In Fig. 4 [48] the vapour and melt composition at the boiling point (P_{tot} = 1 atm) is given as a function of temperature for AlKCl-$AlCl_3$ mixtures. For the Li system, $LiAlCl_4$ becomes the major species at about 1000 K, continuing to increase and then decreasing slightly with increasing temperature. For the

NaCl and KCl system, higher temperatures are needed in order to make $AlkAlCl_4$ the major species.

Only the data for gas complexation with $AlCl_3$ are given here. The review papers [7-11] mentioned earlier may be referred to for further information on these and other systems. Since those papers were written there has also been information on $MAlCl_5$ [18-20], $MInCl_5$ and MIn_2Cl_8 gas complexes [49,50,51] and complexes involving Fe_2Cl_6, Al_2Br_6 and Ga_2Cl_6 [37] as ligands.

5. STRUCTURE OF M-Al-Cl GAS COMPLEXES

As seen from Table 1, some information has been obtained concerning the coordination of the metal ion M^{y+}. The ligand field spectra which give the clearest information are those of $TiAl_3Cl(g)$ [33] and $VAl_3Cl_{11}(g)$ [35], both showing nearly perfect octahedral coordination, and of $PtAlCl_8$ [39] and $PdAlCl_8$ [38], both interpreted as close to square planar coordination. The other ligand field spectra do not point to a highly symmetric coordination (O_h, T_d, D_{4h}).

An unusual feature of many of these gas complexes are their high molecular weight ($EuAl_4Cl_{14}$ and $NdAl_4Cl_{15}$) and the variety of stoichiometries. It is probable that Al attempts to retain its stable 4 coordination and the molecules $MAlCl_4$, $MAlCl_6$, MAl_2Cl_8, MAl_3Cl_{12} can be understood in terms of coordination of $AlCl_4^-$ groups to M^{y+}. However, $MAlCl_5$ requires a $MCl(AlCl_4)$ coordination, $EuAl_4Cl_{14}$ coordination of $Al_2Cl_7^-$ groups, while $EuAl_3Cl_{12}$ and $NdAl_4Cl_{15}$ involve a mixture of $AlCl_4^-$ and $Al_2Cl_7^-$ groups. The complex UAl_2Cl_{10} most probably is described by the structure $UCl_2(AlCl_4)_2$ [40]. There are several examples indicating that the less symmetric species are more abundant in the temperature and pressure range studied: $TiAl_3Cl_{11} > TiAl_2Cl_8$, $VAl_3Cl_{11} > VAl_2Cl_8$, $EuAl_3Cl_{11} > EuAl_4Cl_{14}$.

In addition to the Lewis acidity and Cl^- acceptor property of Al_2Cl_6, the driving force for the complexation reaction appears to be the retention, of a high coordination number leading to a multiplicity of ionic bonds around the metal ion M^{y+} in the gas phase. Quite the contrary seems to be the case for evaporation of MCl_y(5) in an inert atmosphere

$$MCl_y(s) \;=\; MCl_y(g) \qquad (24)$$

since the MCl_y gas molecule usually has a lower coordination number around for M^{y+} and has a more covalent bond character than the ionic $MCl_y(s)$ crystal where coordination numbers of 6 or 9 are commonly found. This may also explain the much smaller differences in the volatilities in a series of MCl_y solids in Al_2Cl_6 atmospheres (Fig. 1) than in inert atmospheres (Table 1).

When comparing coordination and stoichiometry, one should be aware that both the coordination number and number of Al- atoms in the complex is expected to decrease with increasing temperature. Valid comparisons should hence be carried out only at comparable temperatures. However, this is not always possible due to the different stability ranges of the gaseous complexes and widely varying vapour pressures of the different MCl_y solid compounds. Nonetheless, most studies have been carried out in the region around 650 K and it is interesting that octahedral site stabilizations energies [52] can give some guidance with respect to coordination numbers. Thus, V^{2+}, Cr^{2+}, Ni^{2+}, Cr^{3+} [53], with high octahedral site stabilization energies all have octahedral or near octahedral coordination. On the other hand, Ti^{3+}, V^{3+} and probably Co^{2+} with low octahedral site stabilization energies aretetrahedral or nearly tetrahedrally coordinated. There is one noteable exception, Ti^{2+}, which with a very low octahedral site stabilization energy gives a spectrum characteristic of a nearly perfect octahedron in the complex $TiAl_3Cl_{11}(g)$. Probably at least a coordination number 6 is needed in order to bind a ligand as large as $Al_3Cl_{11}^{2-}$, but it is still surprising that the ligand is not $Al_2Cl_8^{2-}$.

In conclusion, the structures of the gaseous complexes are probably best described in terms of ionically bound $AlCl_4^-$ and $Al_2Cl_7^-$ groups. The (assumed) presence of $Al_2Cl_7^-$ groups is particularly interesting since they may provide an extra degree of stability due to facorable charge distribution in the metal-ligand bonds.

6. STABILITY OF THE CONDENSED PHASE IN EQUILIBRIUM WITH A HIGHLY VOLATILE CHLORIDE

If one considers the system MX_y-A_2X_6 (or AX_3) where A_2X_6 or AX_3 is a highly volatile halide which forms a gaseous complex with MX_y, the condensed phase may be $MX_y(s)$, $MA_{2n}X_{6n+y}(s)$ or MX_y-A_2X_6) (1). Excluding the presence of a solid complex compound and considering the reaction

$$(MX_y-A_2X_6)\ (l) = MX_y(s) + A_2X_6(g) \qquad (25)$$

leads to the enthalpy of Equilibrium (25) given by

$$\Delta H^{o}_{25} = -\Delta H^{o}_{mix}(l) - \Delta H^{o}_{fus}(MX_y) + \Delta H^{o}_{vap}(A_2X_6) \qquad (26)$$

where:

$\Delta H^{o}_{mix}(l)$: Enthalpy of mixing of liquid MX_y and liquid A_2X_6.

Due to the strong interaction between A_2X_6 and MX_y which manifests itself through the formation of gaseous complexes, $\Delta H^{o}_{mix}(l)$ is expected to be negative and because $\Delta H^{o}_{vap}(A_2X_6) > \Delta H^{o}_{fus}(MX_y)$, the reaction enthalpy $\Delta H^{o}_{25} > 0$. Eqns. (25,26) show that a solid phase is stabilized with decreasing pressure of A_2X_6 and increasing temperature provided the temperature is below T_{fus} for MX_y. Examples of this phenomenon are found in the transfromation from a liquid mixture to a pure solid for $NdCl_3$ at around 600 K and 6 atm total pressure [6], and for $EuCl_2$ [32] at around 740 K and 0.05 atm pressure. The presence of a liquid phase rather than the pure solid has also been observed for $CdCl_2$ (673 K) [4], $CaCl_2$ (873-773 K), $BaCl_2$ (873-773 K) and $PbCl_2$ (773-673 K) [54].

The mixing process or the formation of a solid complex is an acceptor-donor reaction where A_2X_6 acts as a X^- acceptor while MX_y acts as a X^- donor. Hence $\Delta H_{mix}(l)$ will be more negative the lower the charge and the greater the size of M^{y+}. Low charge and large size will then make ΔH^{o}_{25} more positive and result in a stabilization of the liquid phase with respect to the solid. This has the consequence that for salts such as the alkali halides, the gas complexes will, at moderate or high pressures, always be in equilibrium with a liquid phase (see for instance [16].

Melt mixtures of the donor-acceptor system MX_y-A_2X_6 may be classified as acidic or basic depending on whether the melt mixture contains more or less A_2X_6 than would correspond to the composition $M(AX_4)_y$. As previously noted very large activity changes often with consequent drastic changes in the melting temperatures take place around this composition. The basic melts containing excess X^- are ionic and have high melting points particularly if the melting point of MX_y is high. Acidic melts are partly covalent and are frequently liquid at temperatures of 100-200°C.

Acidic melts, are generally stable under their own vapour pressures. In the low temperature range (100-300°C) some systems do, however, show a liquid immiscibility gap in the range $0.80 < X_{AlCl_3} < 1.00$ (see for instance phase diagrams by Kendall et al.) [55].

For mixtures with alkali halides and other monovalent halides, a liquid phase can usually also be established in basic melts at high temperatures without generating excessive pressures of A_2X_6 or AX_3, and pure solid MX_y is usually not stable in equilibrium with A_2X_6 gas. The vapour pressure along the liquidus line, however, has a maximum when changing the composition from $AlkAlCl_4$ to more basic melts. This is due to the increase in the liquidus temperature which is not fully compensated by the lowering of the $AlCl_3$ activity. At about $X_{AlCl_3} = 0.15$ the total vapour pressure along the $LiCl-AlCl_3$ liquidus has a maximum of 0.0076 atm while for the $KCl-AlCl_3$ liquidus the maximum is at 0.00085 atm [16]. This effect is still more pronounced for some mixtures of divalent chlorides with $AlCl_3$. Attempts to make basic mixtures of $MnCl_2$ and $MgCl_2$ with $AlCl_3$ result in bursting of the quartz ampoules in which they were sealed due to excessive pressure [56]. Moderate pressures (0.5-5 atm) and temperature ($t \simeq 300°C$) result in the presence of a liquid with composition close to $M(AX_4)_y$ or solid MX_y.

Many of the complex solid compounds have a low stability and only complex compounds with large monovalent cations are stable above 250°C. The melting points are: $CsAlCl_4$: 378°C, $RbAlCl_4$: 336°C, $TlAlCl_4$: 308°C, NH_4AlCl_4: 303°C, $InAlCl_4$: 274°C, $KAlCl_4$: 250°C. (Levin et al. [57]. Chloride complexes of the form $M(Al_2Cl_7)_y$ have only been found to be stable for large cations such as $Te_4(Al_2Cl_7)_2$ (Couch et al. [58]. Some complexes between $AlCl_3$ and divalent chlorides have also been characterized, i.e. $Co(AlCl_4)_2$ (Ibers [59] and $Ti(AlCl_4)_2$ (Brynestad et al. [60].

In conclusion it should be noted that the gas phase above a mixture between MX_y and a highly volatile AX_3 compound will tend to have a gas composition with AX_3 in excess relative to the composition $M(AX_4)_y$. This is so even for very basic $AlkCl-AlCl_3$ melts. For instance the vapour phase above $NaCl-AlCl_3$ with 10 mol% $AlCl_3$ will contain $AlCl_3$ and $AlkAlCl_4$ in the ratio 0.28 at 1100 K. The implication of this is that there always will be $AlCl_3$ in the gas phase available for gas complexation with for instance minor constituents in the melt.

7. APPLICATION AND FUTURE RESEARCH

Hastie has discussed certain aspects of the application of gas complexation in ore trasformation, extractive metallurgy, metal refining, chemical synthesis, industrial fume emission and metal halide lamps (9). Other potentially important fields of application are in heterogeneous catalysis, nuclear fuel refining and high power gas lasers based on rare-earth gas complexes [61].

The unfolding phenomena of gas complexation are in a sense providing "wings to metals", by enabling reactions to be carried out at much lower temperatures than otherwise possible. Often, the enhanced metal halide partial pressures due to gas complexation are a prerequisite for a given process. An additional advantage is the "reversibility" encountered when lowering the temperature in that the components can again be separated into their constituents. This property makes it possible for instance to achieve gas chromatografic separations of metal halides [62,63]. In other cases, gas complexation can result in industrial fumes or high-temperature corrosion and ways must be found to prevent such reactions. It is, however, important that the phenomena always be properly recognized and that gas complexation reactions are included in process equilibrium models when present.

Fundamental research has already come a long way in achieving an understanding of the basic chemistry of gas complexation. The thermodynamic results derived from absorption spectroscopic studies, are largely self consistent and agreement among different laboratories is satisfactory [21,22,23,37]. Notable exceptions exist as with the data for $CaCl_2$ [4], where additional work seems warranted. Due to the high enthalpy of vaporization one would expect the majority complex to contain at least three Al-atoms to offset the unfavourable energetics. Perhaps a liquid phase was present during the studies on $CaCl_2$ so that the apparent stoichiometry is lower than that reported as in the case of $EuCl_2$ [32]. Only moderate agreement between mass spectrometric and absorption spectroscopic [18,19,20] studies has been achieved so far indicating that further work is required here. It is of particular interest to know the extent to which low molecular weight species such as the divalent chloride complex $MACl_5$ are present. Such species are especially important with $InCl_3$ [50], but have also been identified by mass spectrometry. The presence of such species may dominate the vaporization processes above 1000 K. According to Binnewies [20] $P_{MAlCl_5} \approx P_{MAl_2Cl_8}$ at about 950 K for a total pressure of 1 atm. It would be of interest to have this idea confirmed by thermodynamic studies in a higher pressure range than can be used in mass spectrometers.

In spite of information about coordination of the M^{y+} ion from ligand field spectra and some recent Raman studies, there still is too little data about the structure and bond properties of this very interesting class of compounds. It appears to be experimentally difficult to obtain Raman vibration spectra of the gaseous complexes and the observation of resonance Raman spectra would be highly desirable [26]. Indeed the application of a variety of spectroscopic techniques to studies of the structures of these intriguing gaseous molecules would appear to be a fertile field of research for molecular spectroscopy.

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Table 1. Thermodynamic characterization of the gas complexes $MAl_{2n}Cl_{6n+y}$.

	Temp. K	$MCl_y(s)+nAl_2Cl_6(g)=MAl_{2n}Cl_{6n+y}(g)$ $\Delta H^o(kJ)$, $\Delta S^o(JK^{-1})$				Coordination around M^{y+}	$Log_{10}P_{MCl_y}$ (atm) 600K	$MCl_y(s)=MCl_y(g)$ $\Delta H^o(kJ),\Delta S^o(JK^{-1})$	Ref.
		$MAlCl_4$							
LiCl	850	[37,58]*							16,28
NaCl	973	[65,82]							15,28
KCl	1030	[35,69]							16,28
CuCl	640	57,62							34,28
			MAl_2Cl_8	MAl_3Cl_{11}	MAl_4Cl_{14}				
$MgCl_2$	800		61,63	25					4,28
$CaCl_2$	900		43,28	50,34					4,28
$SrCl_2$	573		57,46						20,41
$TiCl_2$	600			39,25		O_h			33,28
VCl_2	730			19,26		O_h			35,42
$CrCl_2$	600		38,46			O_h(?)			36,43
$MnCl_2$	750		53,51	39,32					4,43
$FeCl_2$	673		46,46						19,28
$CoCl_2$	700		42,41			Dist.T_d, (?)			21,28,26
$NiCl_2$	750		51,37			Dist.O_h			4,43,38
$CuCl_2$	550		37,51			Dist.T_d,Sq.pl.(?)			37,44,
$PdCl_2$	700		30,40			Sq.pl.			38
$EuCl_2$	650			[70,71]	[36,19]				32,45
$PtCl_2$	570		33,27			Sq.pl.			39

		$MAlCl_6$	MAl_2Cl_9	MAl_3Cl_{12}	MAl_4Cl_{15}		
$TiCl_3$	770	77,89				Dist.T_d	33,28
VCl_3	700	101,102	55,29			Dist.T_d	35,42
$NdCl_3$	700			45,10	7,-52		6,46

			MAl_2Cl_{10}	
UCl_4	700		66,64	40,47

---

x) [] Stable condensed phase is a liquid.

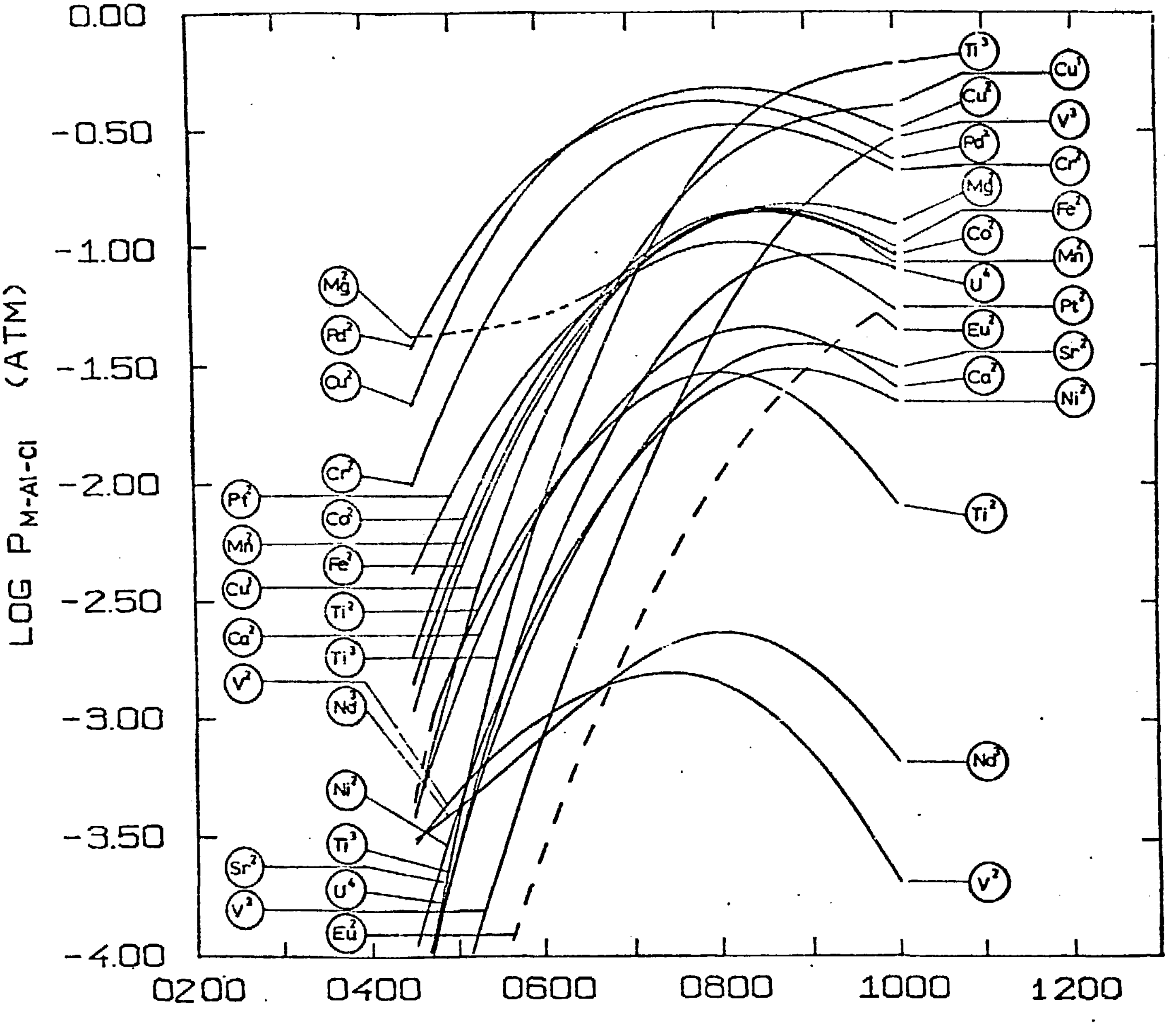
FIGURE LEGENDS

Fig. 1. M-AlCl gas complexes in equilibrium with $MCl_y(s)$, $Al_2Cl_6(g)$ and $AlCl_3(g)$. Total pressure 1 atm. Data from Table 1.

Fig. 2. M-Al-Cl gas complexes in equilibrium with $MCl_y(s)$, $Al_2Cl_6(g)$ and $AlCl_3(g)$. Total pressure 10 atm. Data from Table 1.

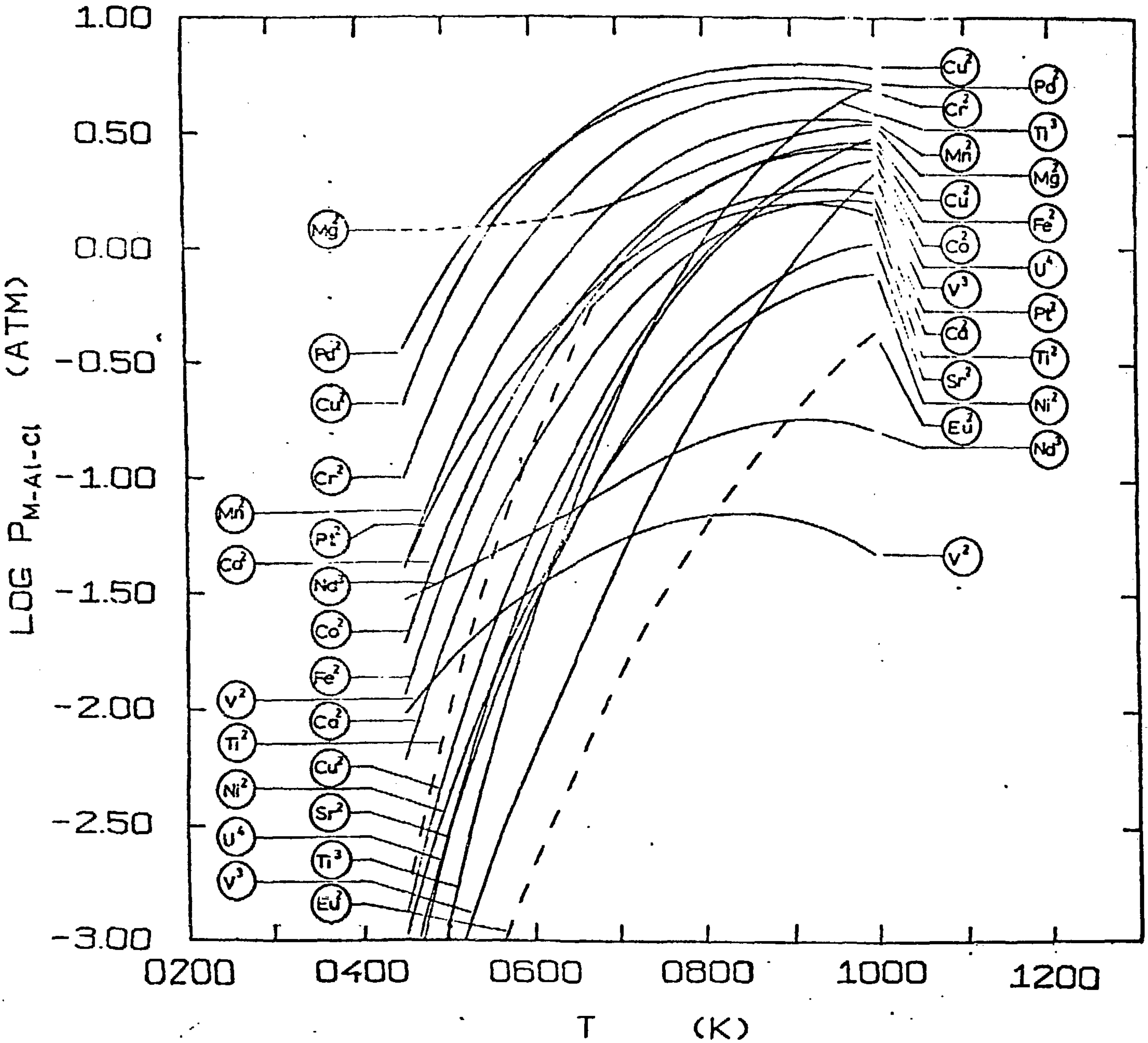
Fig. 3. Total pressure, P_{LiAlCl_4}, P_{AlCl_3}, $P_{Al_2Cl_y}$ above LiCl-$AlCl_3$ melts at 819 K.

Fig. 4. Pressure of $AlkAlCl_4$, $AlCl_3$, Al_2Cl_6 and AlkCl above AlkCl-$AlCl_3$ melts at their boiling point (P_{tot} = 1 atm). Corresponding temperature and composition are given.



LOG $P_{M-Al-Cl}$ (ATM)
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-4.00
0200
0400
0600
0800
1000
1200
T (K)
Mg²
Pd²
Cu²
Cr²
Pt²
Co²
Mn²
Fe²
Cu¹
Ti²
Ca²
Ti³
V²
Nd³
Ni²
Ti³
Sr²
U⁴
V³
Eu²
Ti³
Cu¹
Cu²
V³
Pd²
Cr²
Mg²
Fe²
Co²
Mn²
U⁴
Pt²
Eu²
Sr²
Ca²
Ni²
Ti²
Nd³
V²

Fig.1.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Cu1
Cr2
Mn2
Pt2
Co2
Nd3
Co2
Fe2
V2
Ca2
Ti2
Cu2
Ni2
Sr2
U4
Ti3
V3
Eu2
Cu1
Pd2
Cr2
Ti3
Mn2
Mg2
Cu2
Fe2
Co2
U4
V3
Pt2
Ca2
Ti2
Sr2
Ni2
Eu2
Nd3
V2

Fig. 2.

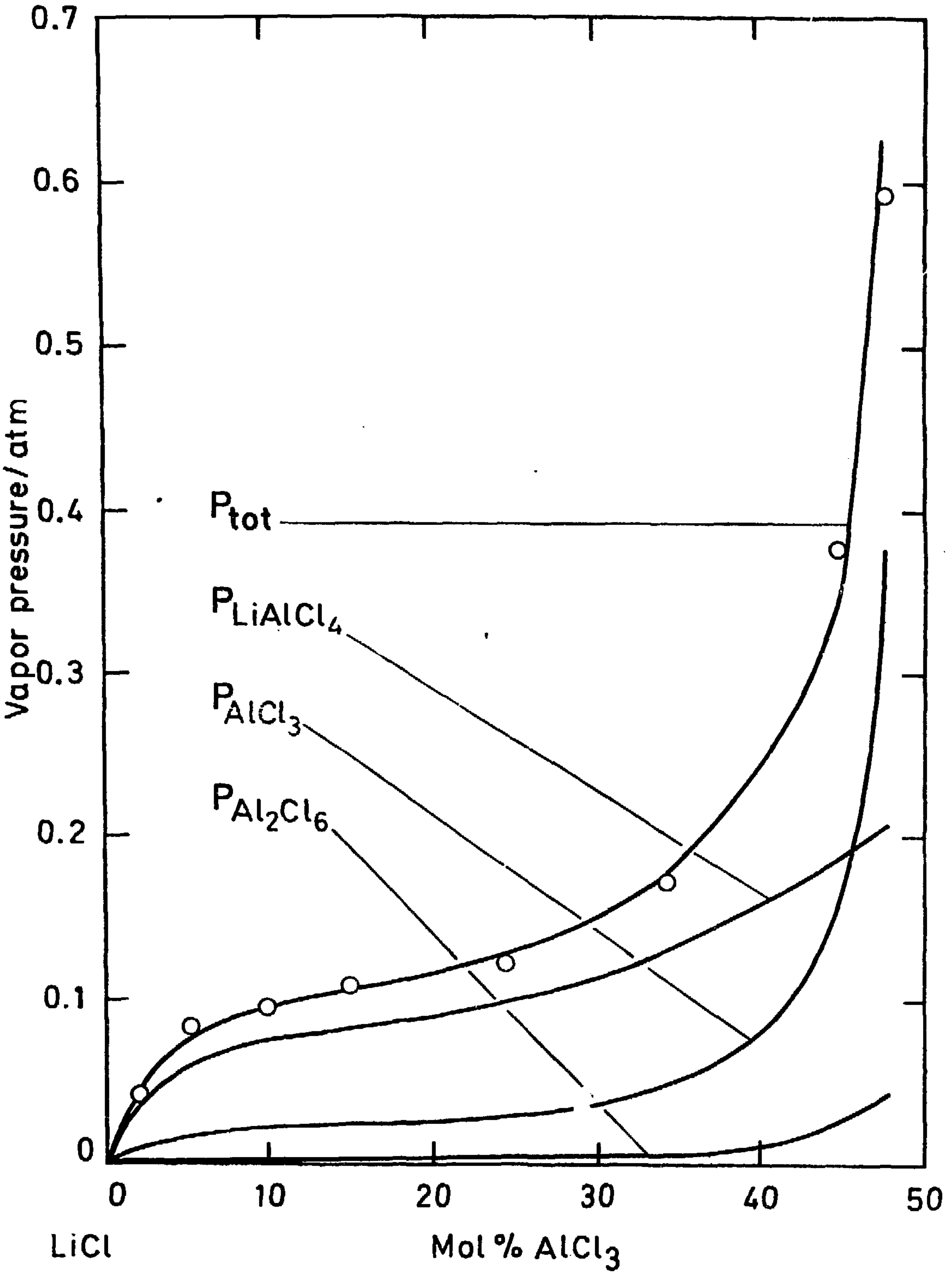
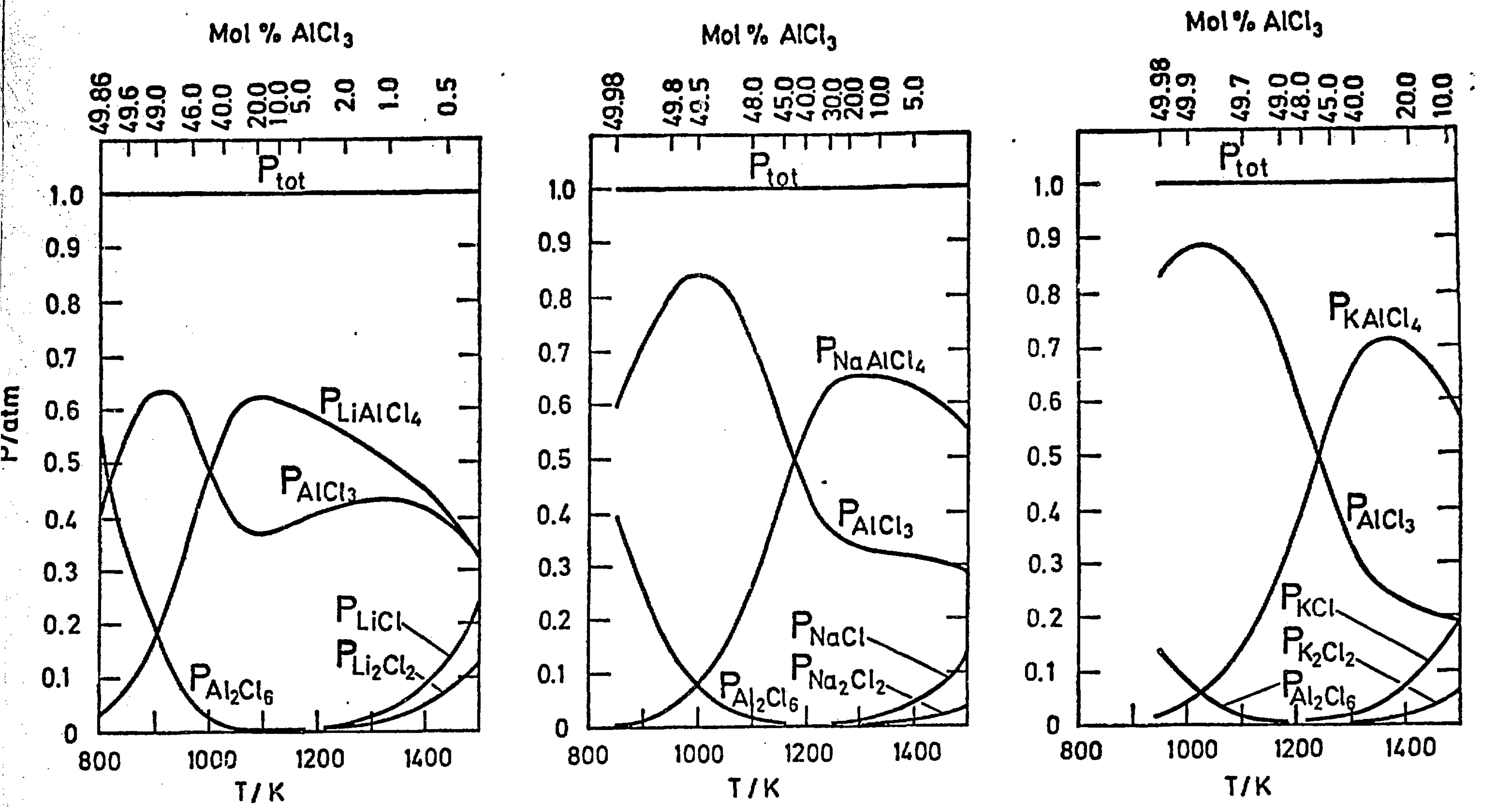

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Vapor pressure/atm
P_{tot}
P_{LiAlCl_4}
P_{AlCl_3}
$P_{Al_2Cl_6}$
0
10
20
30
40
50
LiCl
Mol % $AlCl_3$

Fig. 3



LiCl - Al Cl$_3$

NaCl - AlCl$_3$

KCl - AlCl$_3$

Fig. 4