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# GASEOUS CHLORIDE COMPLEXES CONTAINING HALOGEN BRIDGES

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## I. Introduction

Several authors have already reviewed gaseous halide complexes from different points of view. Particular mention must be made of the following: Novikov and Gavryuchenkov (*78*), *Complex halides in vapors at high temperatures* (1967); Büchler and Berkowitz-Mattuck (*20*), *Gaseous ternary compounds of the alkali metals* (1967); Hastie (*50*), Section in *High Temperature Vapors* (1975); Schäfer (*110*), *Gasförmige*

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*Chloridkomplexe mit Halogenbrücken; Homöokomplexe und Heterokomplexe* (1976); see also (*106–108, 111–113*); Emmenegger (*37*), *Stability of gaseous complexes between two- and three-valent metal halides* (1977); Øye and Gruen (*83*), *Metal halide-group III halide vapor complexes with emphasis on aluminum chloride* (1979); Papatheodorou (*91*), *Spectroscopy, structure and bonding of high-temperature metal halide vapor complexes* (1980).

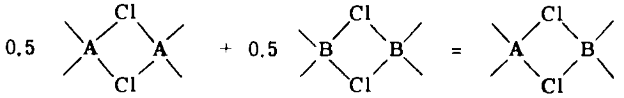
This chapter deals particularly with publications that have appeared in recent years, especially on the chloride complexes that have been investigated most frequently and above all on systematic thermodynamics in relation to coordination relationships. This allows a critical assessment of data and useful estimates for systems that have not as yet been investigated. In addition, an account is given of practical experience in the use of such complexes.

## II. General Review

By determining molecular weights by Dumas' method, Sainte-Claire Deville and Troost (*103*) found as early as 1857 that the gaseous chlorides of aluminum and of trivalent iron were present as dimers. Almost 100 yr later mass-spectrometric investigations by Ionov (*55*) showed the vapors of the alkali halides to contain a more or less large proportion of the dimers. In addition, a very small proportion is present as still larger aggregates (*38, 156*). We now know that most chlorides form gaseous dimers in addition to monomers, though often to only a small degree (*110, 117*).

The simplest types of gaseous complexes are mixed dimers [Eq. (1)], many of which have been detected qualitatively (*13*).

$$0.5\ A_2Cl_{2n}(g) + 0.5\ B_2Cl_{2m}(g) = ABCl_{(n+m)}(g)$$



(1)

This reaction, first formulated by Novikov (*78*), takes place without change in the coordination numbers (C.N.) of A and B. It is therefore to be expected that $\Delta H$ for such reactions should lie close to 0 kcal. For alkali-free complexes this does in fact prove to be the case, $\Delta H_1{}^0 = 0 \pm 3$ kcal (*110*). The reaction entropy is also close to 0 cal/K; $\Delta S_1{}^0 = 0 \pm 2$ cal/K. For alkali-containing complexes, on the other hand, $\Delta H_1{}^0$ is significantly negative, but it is yet always capable of being estimated with a useful degree of accuracy (Section IV).

Because dimerization enthalpies are known for some 50 chlorides (*110*), it follows from a consideration of the possible combinations of them that stabilities can be predicted for the expected 1225 complexes of this type (Eq. 1). In addition, there are numerous other types of complexes the stability of which is also predictable on the basis of coordination relationships (Section V). It must be borne in mind that gaseous halide complexes may be significant in all equilibrium systems containing two or more gaseous chlorides (halides).

Most investigations have been concerned with chloride systems, and discussion of these therefore predominates here. In addition, however, extensive mass-spectrometric studies have been made on the formation of complexes by alkali fluorides (*148*). Other coordinatively unsaturated fluorides are as a rule of low volatility and, as a result, little suited for complex formation (or as yet not investigated). Also, little work has been done with bromides and iodides (Section V,B,5).

Good complex-forming species are those that are relatively quite volatile and with saturated vapors that contain appreciable concentrations of dimer. This leads to three groups of complex-forming compounds: alkali chlorides (Section IV), trichlorides ($AlCl_3$, $GaCl_3$, $InCl_3$, $FeCl_3$), (Section V), and uranium(V) chloride (Section VI). Other complexes will not be dealt with here, but see Binnewies and Schäfer (*13, 15*).

## III. Methods for the Study of Thermodynamic Properties

Equilibria that are established in the reaction of, for example $Al_2Cl_6$ (g) with a solid or, in exceptional cases, a liquid component, (e.g., MCl, $MCl_2$, or $MCl_3$) are studied by the following methods: entrainment methods (see, e.g., *32, 165*); spectrophotometry (see, e.g., *82, 86*); mass spectrometry with double cells (see, e.g., *10, 123*); total-pressure measurements, in certain cases without a solid phase (see, e.g., *79*); labeling with radioactive isotopes and measurement of the activity in the gaseous phase (*94*); distillation at a predetermined pressure and analysis of the condensate (*80, 158*); quenching methods (see, e.g., *165*); and chemical transport in a temperature gradient (*136, 140*). The last two methods are particularly suitable for obtaining supplementary information.

A method that always permits the detection of several complexes in the presence of one another and therefore permits the measurement of a specific complex in frequently occurring mixtures is mass spectrometry (with double cells); see, for example, $Pd_2Al_2Cl_{10}$ (*40*), $CoAl_3Cl_{11}$ (*124*). In favorable cases [$CuCl_2/GaCl_3$ (*35*)] spectrophotometry also allows the direct determination of two complexes in the presence of one another. As a rule, however, all of the methods apart from mass spectrometry give only the overall effect, which may then be divided among the various complexes by calculation. Clearly, this is meaningful only if the accuracy of measurement is high and there is a wide variation in the conditions of measurement. If the second phase is liquid, it is without exception necessary to have information or to make assumptions on the activity of the components in the melt.

## IV. Complexes Formed by Alkali Halides

### A. THERMODYNAMIC CONSIDERATIONS

Numerous combinations $ACl/MCl_n$ (A = alkali) have now been investigated. Frequently, however, only qualitative or relatively inexact results are obtained for complex formation from the monomers (e.g., $\Delta H$ with error limits of ±5 kcal or more). We therefore restrict ourselves to a critical selection of the published material.

Complex formation is represented as in Eq. (1) with the combination of the dimers [dimerization enthalpy according to (*110*)]. Equation (2) may then be written for alkali-containing complexes as

$$0.5A_2Cl_2(g) + 0.5M_2Cl_{2n}(g) = AMCl_{(n+1)}(g) \tag{2}$$

$$\Delta H^0(AMCl_{n+1}) = 0.5\Delta H^0(A_2Cl_2) + 0.5\Delta H(M_2Cl_{2n}) + Y$$

The quantity $Y$ equals zero for alkali-free compounds [Eq. (1)], but it is an important (negative) quantity for those containing alkali. If Eq. (2) is considered in terms of the Pauling derivation of electronegativities, $Y$ will include the difference in electronegativities of A and M. This effect is, however, reduced by the bridging Cl atoms. It is therefore understandable that the influence of $Y$ operates to a significant extent only for complexes containing alkalis (Table I).

In the series LiCl–CsCl/$MCl_x$ it will be recognized that $Y$ for a particular $MCl_x$ (M = Sc, Al, Ga) varies parallel with the difference in electronegativity (*122, 143*). It is unknown at present if it is possible to have a single systematic treatment of the $Y$ values for all $MCl_x$ species because of the uncertainty in the values of $Y$ and also of the electronegativities. For complexes formed by two alkali chlorides, reference may

TABLE I

FORMATION OF GASEOUS COMPLEXES FROM THE DIMERS ACCORDING TO EQ. (2)[a]

| | A | | | | |
|---|---|---|---|---|---|
| | Li | Na | K | Rb | Cs |
| $AMgCl_3$ | | 5.7 (*143*) | | | |
| $AScCl_4$ | 7.8 (*141*) | 9.9 (*166*) | 11.2 (*167*) | 10.8 (*168*) | 11.4 (*142*) |
| $AAlCl_4$ | 11.6 (*69*) | 12.2 (*69*) | 18.3 (*69*) | | |
| $AFeCl_4$ | | 8.8 (*102*) | | | |
| $AGaCl_4$ | 9.7 (*122*) | | 16.6 (*122*) | | $\geqq$ 18.4 (*122*) |

[a] Values for $-Y$ are given in kilocalories.

be made to Schäfer (*110*), who also has given $\Delta G^0$ values for the formation of $ALnCl_4$ complexes.

The larger $A_2MCl_{n+2}$ and $A_2M_2Cl_{2n+2}$ complexes must also be discussed in addition to $AMCl_{n+1}$ (A = alkali). As far as is known at present, the simplest complexes $AMCl_{n+1}$ predominate, as a rule. It is nevertheless advisable to test this relationship from case to case.

In addition to $AMCl_{n+1}$, the following are examples of some of the complexes detected qualitatively: $A_2AgCl_3$, $AAg_2Cl_3$ (*160*); $NaCu_2Cl_3$ (*44*); $Na_2Zn_2Cl_6$ (*16*); $A_2GaCl_5$, $A_2Ga_2Cl_8$ (*122*); and $Na_2ScCl_5$ and $Na_2Sc_2Cl_8$ (*166*). Analogous complexes are known for fluorides [e.g., $Na_2BeF_4$, $Na_2Be_2F_6$, and $Na_2Al_2F_8$ (*150*)]. Measured values of $\Delta H^0$ are available for the dimerization of some chloride complexes:

$$2NaMgCl_3(g) = Na_2Mg_2Cl_6(g) \qquad (3)$$
$$\Delta H^0(298) = -44.8 \text{ kcal } (\mathit{143})$$

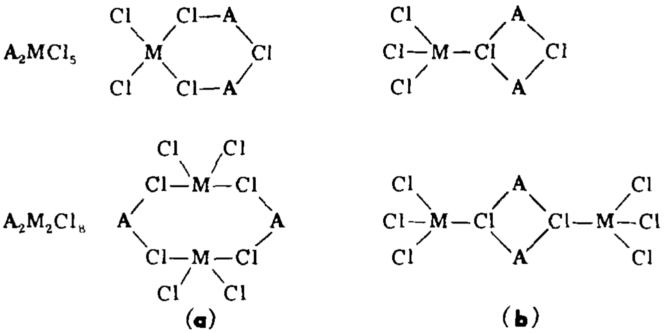
$$2LiScCl_4(g) \quad Li_2Sc_2Cl_8(g) \qquad (4)$$
$$\Delta H^0(298) = -39.1 \text{ kcal } (\mathit{141});\ \Delta S^0(298) = -33.9 \text{ cal/K}$$

$$2KGaCl_4(g) = K_2Ga_2Cl_8(g) \qquad (5)$$
$$\Delta H^0(298) = -34.4 \text{ kcal } (\mathit{122})$$

## B. STRUCTURES

Structural determinations by electron diffraction are possible so far only for the simplest complexes present in relatively high concentration.

Considering the $AMCl_4$ molecule, A may be situated at an apex, an edge, or a face of the $MCl_4$ tetrahedron. As a rule, A, corresponding with Eq. (1), is found at the tetrahedral edge ($C_{2v}$ symmetry). Bonding of A to the relatively rigid $MCl_4$ tetrahedron is, however, only loose, so that A may possibly also occupy to a small extent other positions (with fluctuation), of $KAlCl_4$ (*49, 153*). In the extreme case of $CsAlCl_4$, Cs is even found on a face of the $AlCl_4$ tetrahedron ($C_{3v}$ symmetry) (*96*). It is possible that the special stability (the large value for $-Y$) of $CsGaCl_4$ depends on this fact (Table I). Various structures may also be envisaged for larger molecules where M is always surrounded tetrahedrally by Cl.



Structure **a**, with the larger ring, has been proposed for fluorides by Sholts and Siderov (*148*). Our mass-spectrometric observations on the fragmentation of $K_2Ga_2Cl_8$, which produces the $K_2Cl^+$ fragment, however, indicate structure **b** (*122*). This may be seen in relation to the special stability of alkali chloride dimers.

## V. Trichlorides $LCl_3$ [L = Al, Ga, In, Fe(III), Sc] as Complex-Forming Species

Aluminum chloride is a specially suitable compound for complex formation. The first such investigation was by W. Fischer, who in 1949 detected the existence of $NaAlCl_4$ by the entrainment method (*39*). Dewing's work in 1970 on the complexes of dichlorides with $AlCl_3$ and $FeCl_3$ (*32*) gave an important further impulse to the subject.

### A. $MCl/LCl_3$

Complexes containing alkali (M = alkali) have been dealt with already in Section IV. There are qualitative observations on the following: $AlCl_3$ complexes with CuCl (*14, 119*), AgCl (*119*), and InCl (*101*);

$GaCl_3$ complexes with GaCl (*22, 118*); $InCl_3$ complexes with CuCl (*14*), InCl (*118*), InCl, and TlCl (*22*); and $FeCl_3$ complexes with AgCl (*57*). Quantitative mass spectroscopy of the complicated $CuCl/AlCl_3$ (*137*) system lead to the conclusion that $Cu_3AlCl_6$ and $Cu_2Al_2Cl_8$, and not $CuAlCl_4$ (*66*), are the actual gaseous complexes.

$$3CuCl(s) + 0.5\ Al_2Cl_6(g) = Cu_3AlCl_6(g) \tag{6}$$

$$\Delta H^0(590) = 19.0\ \text{kcal};\ \Delta S^0(590) = 20.3\ \text{cal/K}$$

$$2CuCl(s) + Al_2Cl_6(g) = Cu_2Al_2Cl_8(g) \tag{7}$$

$$\Delta H^0(590) = 5.9\ \text{kcal};\ \Delta S^0(590) = 5.3\ \text{cal/K}$$

With $Cu_4Cl_4(g)$ these data may be combined to give

$$Cu_4Cl_4(g) + Cu_2Al_2Cl_8(g) = 2Cu_3AlCl_6(g) \tag{8}$$

$$\Delta H^0 = -2.5\ \text{kcal};\ \Delta S^0 = 2.0\ \text{cal/K}$$

As expected, these values lie close to zero. It might be supposed that the complexes would have the same cubic structure as that postulated for $Cu_4Cl_4$ (*137*). Because, however, this would lead to an unusual coordination of Al[C.N.(Al) = 5], a ring structure with C.N.(Al) = 4 is probably more likely. Recently a ring structure for $Cu_4Cl_4$ has also been shown to be likely (*74*).

One may suppose that all $CuCl/LCl_3$ and $AgCl/LCl_3$ complexes would have structures like those found for $CuCl/AlCl_3$. On the other hand, we assume that $LCl_3$ forms "normal" complexes with GaCl, InCl and TlCl and that $\Delta H$ for their formation from the dimers is close to zero (Eq. 1). A small amount of $Tl_2InCl_5$ has been observed mass spectroscopically in addition to $TlInCl_4$ (*14*).

## B. $MCl_2/LCl_3$

The complexes formed from dichlorides and aluminum trichloride are by far the most fully studied and are therefore given prominence here. Complexes formed with $GaCl_3$, $InCl_3$, $FeCl_3$, and $ScCl_3$ will, however, also be dealt with.

The following types of compounds have been observed so far with L = Al:

| | | | |
|---|---|---|---|
| $MAlCl_5$ | $MAl_2Cl_8$ | $MAl_3Cl_{11}$ | $MAl_4Cl_{14}$ |
| | $M_2Al_2Cl_{10}$ | | |
| | $M_3Al_2Cl_{12}$ | | |

In the medium-temperature range (~400–600°C) the type encountered most frequently over solid $MCl_2$ is $MAl_2Cl_8$. With increasing temperature $MAlCl_5$ and $MCl_2(g)$ become increasingly significant. Complexes richer in $AlCl_3$ occur at lower temperatures (and higher $Al_2Cl_6$ pressure) in addition to $MAl_2Cl_8$, and also in special cases. It is shown, however, in Section B,1, that the particular formula type predominating depends also on the relative stability of the coexisting solid phase $MCl_2(s)$. Complexes of the type $M_2Al_2Cl_{10}$ are observed mass spectroscopically with M = Pd (*40*) or Be (*100*) as is $M_3Al_2Cl_{12}$ with M = Be (*100*). Here the close relationship to the structures of the solid dichlorides is already apparent (see Sections B,1 and 3).

### 1. *Complex Type and the Coordination of M*

It is clear from Eqs. (9) and (10) that a greater stability of $MCl_2$ leads to formation of complexes richer in $AlCl_3$.

$$MCl_2(s) + MAl_2Cl_8(g) = 2MAlCl_5(g) \tag{9}$$

$$MCl_2(s) + 2MAl_3Cl_{11}(g) = 3MAl_2Cl_8(g) \tag{10}$$

TABLE II

COMPLEX TYPE AND COORDINATION OF M IN $MCl_2(s)$ AND IN THE COMPLEX[a]

| | Gaseous complex present | | | | |
|---|---|---|---|---|---|
| | $MAlCl_5$ | $MAl_2Cl_8$ | $MAl_3Cl_{11}$ | $MAl_4Cl_{14}$ (+ $MAl_3Cl_{11}$) | $Al_2Cl_6$ |
| | Hg | Be to Cd (Table III) | Ti, V | Eu | Mo |
| C.N. in $MCl_2(s)$ | 2(+2+2) | 4, 4(+2), or 6 | 6 + M − M[b] | 7(+2) | 4 + M − M[c] |
| C.N. of M in the complex | 3 | 4 or 6 | 6 | 6 | — |

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[a] C.N., Coordination number. The Cl ligands in parentheses have only a small influence because of their greater distance from M. It can be seen that $HgAlCl_6$ is relatively more stable because of the greater coordination number compared to that of $HgCl_2(s)$. With $EuAl_4Cl_{14}$ or $EuAl_3Cl_{11}$, for example, the reverse relationship holds.

[b] Magnetic measurements indicate the presence of M—M bonds and thus greater stability.

[c] $MoCl_2$ has the structure $[Mo_6Cl_8]Cl_2Cl_{4/2}$ with relatively strong M—M bonds and therefore forms no $AlCl_3$ complexes; the $AlCl_3$-rich compound $Al_2Cl_6$ is present in addition to $MoCl_2$.

The coordination relationships serve as a measure of the stability of $MCl_2(s)$ (*126*) rather than the sublimation enthalpies, which are strongly influenced by the bond distances and angles in $MCl_2(g)$.

### 2. *Complexes of the Type $MLCl_5$*

*a. Qualitative Observations of $MLCl_5$.* $AlCl_3$ complexes with M(II) = Fe (*11*); Mn, Co, Ni, Mg, Sn, Pb (*12*); Pd (*40*); and Hg (*79*). $GaCl_3$ complexes with M(II) = Ge (*114*). $InCl_3$ complexes with M(II) = Be (?), Sn, and Zn (*13*). $FeCl_3$ complexes with M(II) = Be (?) (*13*). $ScCl_3$ complexes with M(II) = Ca, Sr, and Ba (*169*).

*b. Thermodynamic Investigations.* $CuAlCl_5$ is observed in small concentrations at relatively low temperatures in addition to $CuAl_2Cl_8$ (*165*). $HgAlCl_5$ is found mass spectroscopically to be the only complex. Equation (11) is valid for combination of the dimers (*126*); [for the dimerization enthalpy see Schäfer (*110*)].

$$0.5Hg_2Cl_4(g) + 0.5Al_2Cl_6(g) = HgAlCl_5(g) \tag{11}$$

$$\Delta H^0(298) = 1.2 \text{ kcal};\ \Delta S^0(298) = -2 \text{ cal/K}$$

Values of $\Delta H^0$ of 0.4, 1.0, and 0.4 kcal were found mass spectroscopically for Eq. (12) with M = Mn, Co, or Ni (*12*), taking an estimated $\Delta S^0$ value of 0 cal/K.

$$0.5M_2Cl_4(g) + 0.5Al_2Cl_6(g) = MAlCl_5(g) \tag{12}$$

When M = Cr, $\Delta H^0$ = 7 kcal, which may indicate the presence of a Cr—Cr bond in $Cr_2Cl_4$. Analysis of systems containing $MLCl_5$ and $ML_2Cl_8$ leads to Eqs. (14)–(18).

The literature gives mostly thermodynamic values for

$$MCl_2(s) + LCl_3(g) = MLCl_5(g) \tag{13}$$

These, with $\Delta H^0(MCl_2, \text{subl. } T)$ (*7*), $\Delta C_p(g) = 3$ cal/K, and the dimerization enthalpies (*110*) then yield the $\Delta H^0$ values shown in Eqs. (14)–(18), with an uncertainty of about ±3 kcal.

$$0.5Cu_2Cl_4(g) + 0.5Ga_2Cl_6(g) = CuGaCl_5(g) \tag{14}$$

$$\Delta H^0(298) = +0.3 \text{ kcal } (35)$$

$$0.5Cu_2Cl_4(g) + 0.5In_2Cl_6(g) = CuInCl_5(g) \tag{15}$$

$$\Delta H^0(298) = -1.2 \text{ kcal } (36)$$

$$0.5\mathrm{Co_2Cl_4(g)} + 0.5\mathrm{In_2Cl_6(g)} = \mathrm{CoInCl_5(g)} \qquad (16)$$

$$\Delta H^0(298) = +1.3\ \mathrm{kcal}\ (\mathit{34})\ -2.1\ \mathrm{kcal}\ (\mathit{62})$$

$$0.5\mathrm{Ni_2Cl_4(g)} + 0.5\mathrm{In_2Cl_6(g)} = \mathrm{NiInCl_5(g)} \qquad (17)$$

$$\Delta H^0(298) = -4.9\ \mathrm{kcal}\ (\mathit{33})$$

The value of $\Delta H^0$ for Eq. (18) with M = Mg, Ca, or Mn is known only approximately (*36*).

$$0.5\mathrm{M_2Cl_4(g)} + 0.5\mathrm{In_2Cl_6(g)} = \mathrm{MInCl_5(g)} \qquad (18)$$

$$\Delta H^0(298) = (-2.5)\ \mathrm{kcal}$$

Measurements of the total pressure (*23*) or preliminary mass spectroscopic measurements (*14*) lead to

$$0.5\mathrm{Zn_2Cl_4(g)} + 0.5\mathrm{In_2Cl_6(g)} = \mathrm{ZnInCl_5(g)} \qquad (19)$$

$$\Delta H^0(298) = +3.7\ \mathrm{kcal}\ (\mathit{23}),\ +2.8\ \mathrm{kcal}\ (\mathit{14})$$

Equations (20)–(21) also result from mass spectrometric measurements.

$$0.5\mathrm{Sn_2Cl_4(g)} + 0.5\mathrm{In_2Cl_6(g)} = \mathrm{SnInCl_5(g)} \qquad (20)$$

$$\Delta H^0(298) = +0.9\ \mathrm{kcal}\ (\mathit{14})$$

$$0.5\mathrm{Mg_2Cl_4(g)} + 0.5\mathrm{Sc_2Cl_6(g)} = \mathrm{MgScCl_5(g)} \qquad (21)$$

$$\Delta H^0(298) = -0.7\ \mathrm{kcal};\ \Delta S^0(298) = +2.0\ \mathrm{cal/K}\ (\mathit{169})$$

Combination of trimers to form complexes also fits into this scheme:

$$\tfrac{2}{3}\mathrm{Mg_3Cl_6(g)} + \tfrac{1}{3}\mathrm{Sc_3Cl_9(g)} = \mathrm{Mg_2ScCl_7(g)} \qquad (22)$$

$$\Delta H^0(298) = -0.1\ \mathrm{kcal}\ (\mathit{169})$$

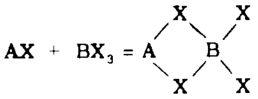
$$\tfrac{1}{3}\mathrm{Mg_3Cl_6(g)} + \tfrac{2}{3}\mathrm{Sc_3Cl_9(g)} = \mathrm{MgSc_2Cl_8(g)} \qquad (23)$$

$$\Delta H^0(298) = -2.5\ \mathrm{kcal}\ (\mathit{169})$$

Over all it seems reasonable to maintain that one is justified in formulating the reaction equations in such a way that the coordination numbers of the atoms remain unchanged. In this case $\Delta H^0$ is zero (kcal) within the limits of error of the measurements. For $\mathrm{CoInCl_5}$ and $\mathrm{LCl_3}$ (L = Al, Ga, In) this constancy of C.N. also corresponds with indications based on the spectra (*91*). The entropy change of such reactions is also close to zero. The value of $\Delta S^0$ would be weakly positive if symmetry numbers alone were decisive for $\Delta S^0$, but this is not yet apparent from the experiments.

*c. Estimation of* ΔH *Values According to Hastie* (*50*). For the sake of completeness the following methods may be mentioned.

*i. Additivity of bonding increments.* On the basis of bonding enthalpies $D$ in the monomers AX and $BX_3$ (X = halogen) and in their dimers $A_2X_2$ and $B_2X_6$, $D$(bridge) $\cong$ 0.6 ($\pm$0.04) $\cdot$ $D$(terminal). From this it follows that



(24)

$$\Delta H \cong [D(\mathrm{A{-}X}) + 3D(\mathrm{B{-}X})] - [2 \cdot 0.6D(\mathrm{A{-}X}) + 2 \cdot 0.6D(\mathrm{B{-}X}) + 2D(\mathrm{B{-}X})]$$

$$\cong -0.2[D(\mathrm{A{-}X}) + D(\mathrm{B{-}X})]$$

Because of the large contribution of $D$(A—X) and $D$(B—X), the result depends largely on the magnitude and reliability of these values and of the numerical factor.

*ii. Ionic model.* If we take

$$A_2X_2 + B_2X_6 = 2ABX_4 \qquad (25)$$

as an example, the balance of the cation–cation repulsion potentials $\Delta U$ may be used as a measure of the relative values for $\Delta H$.

$$\Delta U = [6/(r_A + r_B)] - (\tfrac{1}{2}r_A + \tfrac{9}{2}r_B)$$

Graphical representation of the experimental values of $\Delta H$ as a function of $\Delta U$ enables rough estimates of unknown values of $\Delta H$ to be made. These methods (*i, ii*) do not of course lead to the minimum accuracy of ± ≤3 kcal, which is necessary in these systems for thermodynamic purposes.

### 3. *Complexes of the Type* $ML_2Cl_8$

*a. Qualitative Observations with* $Ml_2Cl_8$. $AlCl_3$ complexes with M(II) = Be (*100, 146*); Mg, Cr, Mn, Co (*12*); Ca, Ba, Pb (*119*); Cr (*65, 129*); Cr, Co, Pd (*10*); Fe (*11*); Fe, Co, Ni, Cu, Pd, Pt (*119*); Mn, Fe, Co, Ni, Cu, Pd (*134*); Zn, Cd, Pb (*32*); Ti (*18*); Pd (*40*); and Sm (*93*). $GaCl_3$ complexes with M(II) = Co, Ni (*119*); Ca, Cr, Co, Cu, and Pd (*140*).

$InCl_3$ complexes with M(II) = Be (*13*). $FeCl_3$ complexes with M(II) = Be (*13*); Fe, Cu (*119*); and Fe (*11*).

*b. Thermodynamic Investigations with $ML_2Cl_8$.* $AlCl_3$ complexes with M(II) = Mg, Ca, Mn, Co, Ni (*32*); Co (*31, 88, 163*); Ni (*67*); Pd (*75, 86*); Pt (*85*); Cr (*2, 132*); Cu (*37, 159, 165*); Co, Ni, Cu (*136*); Be, Fe, Zn, Cd, Pt (*125*); and Fe (*91*). $GaCl_3$ complexes with M(II) = Co (*4, 37*) and Cu (*35, 159*). $InCl_3$ complexes with M(II) = Co (*34, 62*); Mg, Ca, Mn (*36*); Ni (*33*); and Be (*14*). $FeCl_3$ complexes with M(II) = Mn, Co, Ni, Cd (*32*); Mg, Ca, Sr, and Ba (*37*). $ScCl_3$ complexes with M(II) = Mg (*169*).

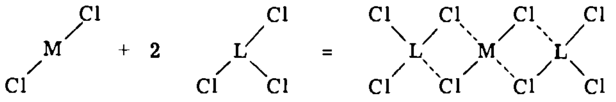
*c. Bonding Relationships and Thermodynamic Models.* In 1970 Dewing (*32*) wrote with reference to the relatively small differences in $\Delta H^0$ from equilibrium measurements on the reactions

$$MCl_{2(s)} + 2AlCl_{3(g)} = MAl_2Cl_{8(g)} \qquad (26)$$

$$M = Mg, Ca, Mn, Co, Ni$$

> The stabilities of the complexes are obviously quite unrelated to the vapor pressures of the dichlorides themselves. This is best interpreted by implying that the bonding of the divalent ion in the complexes is very similar to that in the solid, so that the energy of forming the complexes from the solid is essentially constant and does not depend on the energy of separating the solid into individual gaseous molecules [p. 2174].

Like Hastie (Section V,B,2,*c*), Emmenegger (*37*) based his estimates on bond energies. For the combination of gas molecules he formulated the reactions as


(α)


(β)


(γ)

In Eq. ($\alpha$) 2M—Cl bridges and 2L—Cl bridges are formed. The same is true for Eqs. ($\beta$) and ($\gamma$). From this it follows that

$$\Delta H^0_{(\alpha)} = \Delta H^0_{(\beta)} + \Delta H^0_{(\gamma)}$$

Starting from solid $MCl_2$, reaction with $L_2Cl_6$ leads to

$$MCl_{2(s)} + L_2Cl_{6(g)} = ML_2Cl_{8(g)} \tag{27}$$

$$\Delta H^0_{(27)} = \Delta H^0_{(\beta)} + \Delta H^0\,(MCl_2,\ \text{subl.})$$

The $\Delta H^0$ values calculated by Emmenegger in this way (*37*) deviate by about 10 or more kcal from the experimental values, which indicates that such estimates are uncertain by several orders of magnitude for the complex concentrations. This relates clearly to the fact that the scheme does not take into consideration the change in the coordination of M. For the same reason the use of the same $\Delta H^0$ for Eqs. (28) and (29) (*36*) is only a very rough approximation.

$$MCl_2(g) + LCl_3(g) = MLCl_5(g) \tag{28}$$

$$MLCL_5(g) + LCl_3(g) = ML_2Cl_8(g) \tag{29}$$

A somewhat better but still unsatisfactory estimate is obtained by assuming that $\Delta H^0_{(27)}$ corresponds roughly with the enthalpy of melting of the dichloride (or the tri- or tetrachloride) (*110*).

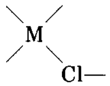
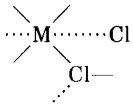
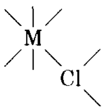
Very much better estimates for $\Delta H^0_{(27)}$ become possible if one starts from the coordination of M and Cl in the solid dichloride (Table III) (*125*). This contains the mean $\Delta H^0$ values obtained by various authors (see *125*).

This systematic treatment of relative stabilities of the complexes [refer to Eq. (27)] may be understood on the basis that M in the complexes is coordinated by Cl (the same coordination number and a similar arrangement), as in solid $MCl_2$. The different values for various $MCl_2$ structures (Table III) are then attributable to different coordination of Cl in $MCl_2(s)$ and $MAl_2Cl_8(g)$. $\Delta H^0_{(27)}$ then becomes smaller the less firmly Cl is bound in the solid dichloride.

In the special case with C.N.(M) = 4 and C.N.(Cl) = 2, the coordination numbers in the solid dichloride are the same as in the gaseous complex. The small $\Delta H^0$ values that still remain (7 kcal) may be attributed principly to the long-range order in the dichloride. Therefore, the $\Delta H^0$ becomes close to zero if the long-range order is removed (or reduced) while the coordination numbers of M and Cl (or Br) remain unchanged [$\Delta H^0$ for $MX_2(s) = \frac{1}{6}M_6X_{12}(g)$ according to Schäfer (*109*)]:

TABLE III

$\Delta H^0(298)$ AND $\Delta S^0(298)$ FOR THE REACTION $\mathrm{MCl_2(s) + Al_2Cl_6(g) = MAl_2Cl_8(g)}$ AND THE COORDINATION IN THE SOLID DICHLORIDE

| $\mathrm{MCl_2}$ | Coordination in $\mathrm{MCl}_{2(f)}$ | $\Delta H^0$ (kcal) | $\Delta S^0$ (cal/K) | Mean value $\Delta H^0$ (kcal) | Mean value $\Delta S^0$ (cal/K) |
|---|---|---|---|---|---|
| $\mathrm{BeCl_2}$ | $\mathrm{MCl_{4/2}}$ | (6.0) | — | 7 ± 1 | 8.5 ± 1 |
| $\mathrm{ZnCl_2}$ |  | 6.8 | 8.3 | | |
| $\mathrm{PdCl_2}$ | | 7.0 | 9.4 | | |
| $\mathrm{PtCl_2}$ | | 7.9 | 7.8 | | |
| $\mathrm{CrCl_2}$ | $\mathrm{MCl_{4(+2)/2(+1)}}$<br> | 9.0 | 10.7 | 9 ± 0.5 | 11.5 ± 1 |
| $\mathrm{CuCl_2}$ | | 9.1 | 12.4 | | |
| $\mathrm{MgCl_2}$ | | 14.7? | 15.7? | 12 ± 2 | 11 ± 3 |
| $\mathrm{CaCl_2}$ | $\mathrm{MCl_{6/3}}$ | 10.4 | 7.7 | | |
| $\mathrm{MnCl_2}$ |  | 12.8 | 12.9 | | |
| $\mathrm{FeCl_2}$ | | 12.5 | 13.2 | | |
| $\mathrm{CoCl_2}$ | | 11.0 | 11.5 | | |
| $\mathrm{NiCl_2}$ | | 12.3 | 9.6 | | |
| $\mathrm{CdCl_2}$ | | 10.9 | 8.8 | | |

$$\tfrac{1}{6}\mathrm{Pd_6Cl_{12}(g) + Al_2Cl_6(g) = PdAl_2Cl_8(g)} \tag{30}$$

$$\Delta H^0(298) = -2 \ \text{kcal}$$

$$\tfrac{1}{6}\mathrm{Pd_6Br_{12}(g) + Al_2Br_6(g) = PdAl_2Br_8(g)} \tag{31}$$

$$\Delta H^0(298) = -1.2 \ \text{kcal}$$

$$\tfrac{1}{6}\mathrm{Pt_6Cl_{12}(g) + Al_2Cl_6(g) = PtAl_2Cl_8(g)} \tag{32}$$

$$\Delta H^0(298) = -1.1 \ \text{kcal}$$

Formation and reaction enthalpies are different. Consequently, in general it is not possible to establish a correlation with the structure of only one of the reaction partners. It can, however, be done—as in the present case—if in the reaction the structure (C.N.) of only one of the partners changes significantly. In contrast to this, the influence of the structure on sublimation enthalpies of the dichlorides is not so apparent.

*d. Structures.* Table III leads to the conclusion that M in the gaseous complexes is coordinated in the same way through Cl as in the solid dichlorides, although distortion of the coordination polyhedra is not excluded. This consideration is also borne out by the absorption spectra of the complexes (*91*). Until recently the interpretation of the spectrum of $CoAl_2Cl_8$ was uncertain [C.N. = 4 or 6 (?)], but measurements on the spectra of mixed halogen complexes of the type $CoAl_2Cl_nI_{8-n}$ (*68*) have now settled the question in favor of a distorted octahedral array round the cobalt atom.

It is noteworthy that compounds of the type $MAl_2Cl_8$ may also be obtained in a crystalline form at temperatures greater than 200°C. Roentgenographic structure determinations showed that $CuAl_2Cl_8$ (*121*) and $PdAl_2Cl_8$ (*68*) crystallize in a molecular lattice with C.N.(Cu) = 4 (+2) and C.N.(Pd) = 4 the coordination of M corresponding with that in the solid dichloride. $CoAl_2Cl_8$, which is isotypic with the compounds where M = V, Cr, Mn, Fe, Cd (*8*), Ni (*19*), or Ti (*18*), forms a coordination lattice in which Co is surrounded by a distorted octahedral and Al by a tetrahedral arrangement of Cl (*54*). Here then the rearrangement of the molecules from the gaseous to the crystal structure involves no deep-seated changes (*68*).

### 4. *Transition from L = Al to Ga, In, Fe, or Sc in $ML_2Cl_8$*

Starting from the most fully investigated $AlCl_3$ complexes, we may write

$$MAl_2Cl_8(g) + L_2Cl_6(g) = ML_2Cl_8(g) + Al_2Cl_6(g) \qquad (33)$$

We must assume here that the coordinations of M and L (or Al) do not change. Therefore, $\Delta H^0_{(33)}$ is expected to be zero. This also implies that $\Delta H^0_{(34)}$ should be independent of whether L = Al or Ga, In, Fe, or Sc:

$$MCl_2(s) + L_2Cl_6(g) = ML_2Cl_8(g) \qquad \Delta H^0_{(34)} \qquad (34)$$

With M = Co, $\Delta H^0$ values shown in Eqs. (35)–(38) were measured.

$$CoCl_2(s) + Al_2Cl_6(g) = CoAl_2Cl_8(g) \qquad (35)$$

$\Delta H^0(298) = 11.0$ kcal; $\Delta S^0(298) = 11.5$ cal/K (*31, 32, 88, 163*)

$$CoCl_2(s) + Ga_2Cl_6(g) = CoGa_2Cl_8(g) \qquad (36)$$

$\Delta H^0(298) \approx 10.9$ kcal; $\Delta S^0(298) = 9.6$ cal/K (*4*)

$$CoCl_2(s) + In_2Cl_6(g) = CoIn_2Cl_8(g) \tag{37}$$

$\Delta H^0(298) = 13.5$ kcal; $\Delta S^0(298) = 11.9$ cal/K (*33*); 11.9 kcal; 10.2 cal/K (*62*); 11.6 kcal; 10.0 cal/K (*35*)

$$CoCl_2(s) + Fe_2Cl_6(g) = CoFe_2Cl_8(g) \tag{38}$$

$\Delta H^0(298) = 17.7$ kcal; $\Delta S^0(298) = 16.4$ cal/K (*32*)

Bearing in mind the evident scatter in the measurements for Eq. (37), the measured values with L = Al, Ga, and In agree closely. The measured values for $CoCl_2/Fe_2Cl_6$ [Eq. (38)], which deviate from those for the related reactions, come from preliminary results; the discrepancy is due to the formation of mixed crystals (solid $CoCl_2$ with $FeCl_2$) arising from the decomposition of $FeCl_3$ (*116*). For further information on this problem see Schäfer (*116*).

For a given value of $P(Ga_2Cl_6, 293\text{ K}) = 0.5$ atm, the dissociation $Ga_2Cl_6 = 2GaCl_3$ results in the value for $P(MGa_2Cl_8)$ passing through a maximum between 600 and 700 K:

$$\begin{gathered} MCl_2(s) + Ga_2Cl_6(g) = MGa_2Cl_8(g) \\ \text{endothermic} \end{gathered} \tag{39}$$

$$\begin{gathered} MCl_2(s) + 2GaCl_3(g) = MGa_2Cl_8(g) \\ \text{exothermic} \end{gathered} \tag{40}$$

With a further temperature increase, $MGaCl_5(g)$ [and $MCl_2(g)$] are formed endothermically:

$$\begin{gathered} MCl_2(s) + GaCl_3(g) = MGaCl_5(g) \\ \text{endothermic} \end{gathered} \tag{41}$$

The temperature dependence of the solubility λ is a measure of the chemical transport of $MCl_2$ (*105*):

$$\lambda = \frac{\Sigma P(M)}{\Sigma P(Ga)} = \frac{P(MGa_2Cl_8 + MGaCl_5 + MCl_2)}{P(2Ga_2Cl_6 + GaCl_3 + 2MGa_2Cl_8 + MGaCl_5)}$$

The value of λ first rises with $T$ [Eq. (39)] and then falls again [Eq. (40)], finally rising again [Eq. (41)]. Transport to the hotter zone [Eq. (40)] has been experimentally confirmed with M = Ca, Cr, Co, Cu and Pd (*140*). If Eq. (41) is superimposed on Eq. (40), formation of the maximum for λ is hindered. Comparison of the calculated $\lambda/T$ curves with the results of transport experiments permits a check of the thermodynamic values, introduced with λ (*140*). For smaller $Al_2Cl_6/AlCl_3$

pressures the corresponding $MAl_2Cl_8$ maxima have been observed mass spectroscopically with M = Mg, Cr, Mn, and Co (*12*).

### 5. *Comparison of Chlorides with Bromides and Iodides*

If one starts with the assumption that the coordination of M and Al in $MAl_2X_8$ is the same with X = Cl, Br, or I, and if this also is valid for $MX_2$, almost equal values for $\Delta H^0$ and $\Delta S^0$ are expected for

$$MCl_2(s) + Al_2Cl_6(g) = MAl_2Cl_8(g) \tag{42}$$

$$MBr_2(s) + Al_2Br_6(g) = MAl_2Br_8(g) \tag{43}$$

$$MI_2(s) + Al_2I_6(g) = MAl_2I_8(g) \tag{44}$$

This is the case with M = Co (Table IV) (*75*). For M = Pd, on the other hand, the value of $\Delta H^0$ increases in the order Cl < Br < I, which is clearly caused by the structures of the solid halides. The $\alpha$-$PdCl_2$ structure consists of infinite, planar $PdCl_{4/2}$ chains with the Pd atom square-planar coordinated. The $PdBr_2$ structure is similarly made up of $PdBr_{4/2}$ chains, but these are corrugated with differing Pd—Br distances of 2.34 and 2.57 Å (*17*). In the structure of the stable $\beta$-form of $PdI_2$ (*162*) Pd has C.N. = 4(+1+1) [Pd—I = 2.61 Å (4×) and 3.29 or 3.49 Å]. The more distant I atoms increase coordination to octahedral. This increased coordination renders the removal of $PdI_2$ from the lattice in the process of forming the complex more difficult.

In the analogous $MCl_2$ systems (Table III), change in the coordination of M in the solid dichloride from C.N. = 4 to 4(+2) raises the $\Delta H^0$ value by about 2 kcal. The behavior of the palladium halides fits almost qualitatively into this picture, although the effect of coordination

TABLE IV

THERMODYNAMIC DATA FOR THE REACTIONS $MX_2(s) + Al_2X_6(g) = MAl_2X_8(g)$[a]

| M | X | $\Delta H^0(298)$ (kcal) | $\Delta S^0(298)$ (cal/K) | References |
|---|---|---|---|---|
| Co | Cl | 11.0 | 11.5 | (*31, 32, 88, 163*) |
| Co | Br | 10.3 | 10.2 | (*92*) |
| Co | I | 10.8 | 12.4 | (*155*) |
| Pd | Cl | 6.7 | 8.9 | (*25, 75*) |
| Pd | Br | 8.3 | 8.4 | (*25, 75*) |
| Pd | I | (13) | (10) | (*75*) |

[a] M = Co, Pd; X = Cl, Br, I (*75*).

on $\Delta H^0$ is apparently greater for iodides than for chlorides. Further investigation of this problem is desirable.

### 6. *$MAl_3Cl_{11}$ Complexes*

Three complexes are known in the $CoCl_2/Al_2Cl_6$ system, with $CoAl_2Cl_8$ predominating under the usual conditions:

$$CoCl_2(s) + 0.5Al_2Cl_6(g) = CoAlCl_5(g) \tag{45}$$

$\Delta H^0(298) = 34.9$ kcal; $\Delta S^0(298) = 29.2$ cal/K [values combined from (*7*, *12*, *117*)]

$$CoCl_2(s) + Al_2Cl_6(g) = CoAl_2Cl_8(g) \tag{46}$$

$\Delta H^0(298) = 11.0$ kcal; $\Delta S^0(298) = 11.5$ cal/K (values from Table III)

$$CoCl_2(s) + 1.5Al_2Cl_6(g) = CoAl_3Cl_{11}(g) \tag{47}$$

$\Delta H^0(298) = 2.9$ kcal; $\Delta S^0(298) = -4.8$ cal/K [values from Schäfer and Flörke (*124*)]

When M(II) = Ti or V, only the formula of type $MAl_3Cl_{11}$ is found (*5*, *152*), which is understandable on the basis of Table II.

$$TiCl_2(s) + 1.5Al_2Cl_6(g) = TiAl_3Cl_{11}(g) \tag{48}$$

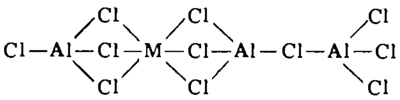
$\Delta H^0(600) = 9.2$ kcal; $\Delta S^0(600) = 5.95$ cal/K

$$VCl_2(s) + 1.5Al_2Cl_6(g) = VAl_3Cl_{11}(g) \tag{49}$$

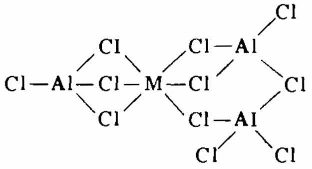
$\Delta H^0(730) = 4.5$ kcal; $\Delta S^0(730) = -6.1$ cal/K

The values for the formation of $VAl_3Cl_{11}$ show it to be somewhat less stable than $CoAl_3Cl_{11}$, which may be explained by the presence of V—V bonds in $VCl_2$ (see Section V,B,1). The values for $TiAl_3Cl_{11}$ formation (Eq. 48), particularly the entropy, do, however, leave some questions open.

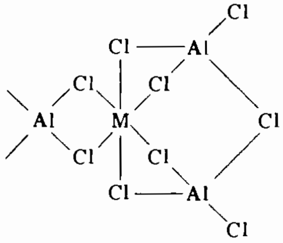
Structures $\alpha$, $\beta$, $\gamma$, and $\delta$ must be considered, $\delta$ with C.N.(M) = 4 being unlikely in view of the $MCl_2$ structures with C.N.(M) = 6. In fact the absorption spectrum of $VAl_3Cl_{11}$ indicates that there is octahedral coordination of V(II) (*91*). Further $AlCl_3$-rich complexes are considered in Section V,D.



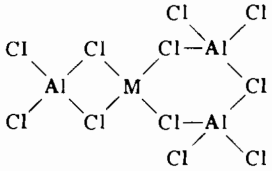
($\alpha$)



(β)



(γ)



(δ)

## C. $MCl_3/LCl_3$ ($MLCl_6$, $ML_2Cl_9$, $ML_3Cl_{12}$)

### *1. Qualitative Observations*

$AlCl_3$ complexes with M(III) = Cr (*3, 63, 64, 132*); Fe (*42, 77, 145*); Sc, Y, La (*119*); Ln (*157, 172*); Nd (*47*); Tb (*27, 94*); Ho, Er, Tb (*51*); Ho (*53*); Er (*9, 26, 27, 89, 91*); U (*99*); and Actinides (*173*). $GaCl_3$ complexes with M(III) = Er (*9, 89, 91*). $InCl_3$ complexes with M(III) = Er (*9, 89, 91*). $FeCl_3$ complexes with M(III) = Y (*119*) and Au (*48*).

### *2. Thermodynamic Investigations*

$AlCl_3$ complexes with M(III) = Ti (*130, 152*); V (*5, 128*); Ti, V, Sc, Nd (*127*); Fe (*147*); Nd (*82*); Sm (*93*); Gd (*29*); Ho (*94*); Ga (*1*); In (*22*); and Bi (*60*). $GaCl_3$ complexes with M(III) = Nd (*41*) and In (*21*). $InCl_3$ complexes with M(III) = Ga (*21*). $FeCl_3$ complexes with M(III) = Gd (*29*). The following complexes have been described in these systems: $MLCl_6$, $ML_2Cl_9$, $ML_3Cl_{12}$, and $ML_4Cl_{15}$. At higher temperatures complexes poorer in $LCl_3$ predominate. Quantitative results are collected in Table V. For $ML_4Cl_{15}$, see also Section V,D.

TABLE V

COMPLEXES FROM $MCl_3(s)$ AND $nL_2Cl_6(g)$ ($n = 0.5, 1.0, 1.5$)

| Type | Complex[a] | $T$ (K) | $\Delta H^0(T)$ (kcal) | $\Delta S^0(T)$ (cal/K) | References |
|---|---|---|---|---|---|
| $\alpha$ | $TiAlCl_6$ | 298 | 19.6 | 24.1 | (*127, 152*) |
| | | 298 | 22.7 ± 0.5 | 21.3 ± 3 | (*127*) |
| | $VAlCl_6$ | 298 | 25.8 | 27.8 | (*5, 127*) |
| | | 298 | 25.6 ± 0.5 | 23.0 ± 3 | (*127*) |
| | $FeAlCl_6$ | 298 | 17.3 | 30.2 | (*147, 156*) |
| | $ScAlCl_6$ | 298 | 39.6 ± 3 | 33.4 ± 3 | (*127*) |
| | $NdAlCl_6$ | 298 | 37.5 ± 3 | 26.3 ± 3 | (*127*) |
| | $NdGaCl_6$ | 298 | 34.9 | 28.2 | (*41, 127*) |
| $\beta$ | $AlAl_2Cl_9$ | 298 | 8.8 | 10.3 | (*123, 156*) |
| | $TiAl_2Cl_9$ | 770 | (−10.3) | (−22.8) | (*152*) |
| | $VAl_2Cl_9$ | 695 | 13.1 | 6.9 | (*5*) |
| $\gamma$ | $NdAl_3Cl_{12}$ | 815 | 10.6 | +2.3 | (*82*) |
| | $SmAl_3Cl_{12}$ | 700 | 6.7 | −1.0 | (*93*) |
| | $GdAl_3Cl_{12}$ | 750 | 8.1 | +2.4 | (*29*) |
| | $GdFe_3Cl_{12}$ | 800 | (~12.7)[b] | (2.4)[b] | (*29*) |

[a] M is equivalent to the first element in the formula.

[b] Preliminary values; estimated $\Delta S^0$ (*29*).

*a. Complexes of Type α (Table V).* No systematic order is discernable in the $\Delta H^0$ values for the formation of the gaseous $MLCl_6$ complexes from solid $MCl_3$ and gaseous $L_2Cl_6$ (Table V). If, however, the process is associated with the combination of the dimers, it would be expected that $\Delta H^0$ would approximate zero (Table VI).

*b. Complexes of Type β (Table V).* The molecule $Al_3Cl_9$, which has been detected mass spectroscopically, is included in the series of $MAl_2Cl_9$ complexes (Table V). It is natural to postulate a ring structure with C.N. = 4 for all the metal atoms in the $MAl_2Cl_9$ complexes, and this is also in agreement with the spectra of $VAl_3Cl_9$ (and $VAlCl_6$) (*5, 91*). The general reaction will accordingly take place without change in the coordination numbers. Approximately equal thermodynamic values are to be expected for all of the M atoms, and $\Delta H^0$ should be weakly negative because of the flexibility of the ring. With M = Al, $\Delta H_{50}{}^0(298) = -5.05$ kcal and $\Delta S_{50}{}^0(298) = -20.4$ cal/K (*123*). Results for the dimerization of $VCl_3$ are lacking for the corresponding evalua-

TABLE VI

COMBINATION OF DIMERS TO FORM COMPLEXES[a]

| | MLCl$_6$ | | | | | |
|---|---|---|---|---|---|---|
| | ScAlCl$_6$ | TiAlCl$_6$ | FeAlCl$_6$ | GaAlCl$_6$ | InAlCl$_6$ | GaInCl$_6$ |
| $\Delta H^0$ (kcal) | +1.4 | −0.6 | 0<br>(±0.5) | −0.65 | −1.85<br>(±1.5) | −0.7 |
| References | *(127)* | *(6, 7, 127)* | *(147)* | *(1)* | *(22)* | *(21)* |

[a] $0.5M_2Cl_6(g) + 0.5L_2Cl_6(g) = MLCl_6(g)$; $\Delta H^0(298)$.

tion in the case of VAl$_2$Cl$_9$. The data for TiAl$_2$Cl$_9$ clearly do not agree (see later discussion).

$$0.5M_2Cl_6(g) + Al_2Cl_6(g) = MAl_2Cl_9(g) \tag{50}$$

Analogous considerations apply with tetrahedral coordination for all of the metals M, which should lead to data in approximate agreement:

$$MAlCl_6(g) + 0.5Al_2Cl_6(g) = MAl_2Cl_9(g) \tag{51}$$

M = Al: $\Delta H^0(298) = -\ 5.05$ kcal; $\Delta S^0(298) = -20.4$ cal/K *(123)*

M = V: $\Delta H^0(695) = -11.1$ kcal; $\Delta S^0(695) = -17.5$ cal/K *(5)*

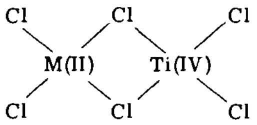
M = Ti: $\Delta H^0(770) = -31.50$ kcal; $\Delta S^0(770) = -41.3$ cal/K *(152)*

There is some measure of agreement in the values obtained for M = Al and V, but the values for M = Ti, which are subject to a small correction in the estimation of the main component TiAlCl$_6$ *(152)*, deviate markedly. Chemical transport experiments also fail to confirm them *(130)*.

*c. Complexes of Type $\gamma$ (Table V).* Solid lanthanide chlorides LnCl$_3$ (with Ln = Nd, Sm, or Gd) all have the same UCl$_3$ structure with C.N. = 9. If Ln in the gaseous complexes is situated between the faces of 3AlCl$_4$ tetrahedra, the C.N. will also equal 9. This is feasible with the distances and angles in SmCl$_3$(s) and AlCl$_4^-$ *(93)*. It may be concluded from this that formation of these complexes should occur with approximately similar (and small) values for $\Delta H^0$ and $\Delta S^0$. This is so within the limits of error in the measurements (Table V). In the complexes of the heavier lanthanides a coordination of six for Ln would be expected [corresponding to CrAl$_3$Cl$_{12}$ *(3)*], as in the solid trichlorides.

### 3. *Remarks on the Nature of the Bonding in $MLCl_6$*

If one starts from a model with ionic bonding, it would be expected that molecules $\alpha$ and $\beta$ would have similar stabilities. The repulsion potential of the cations is indeed smaller in $MTiCl_6$ (8) than in $Al_2Cl_6$ (9). Yet, $MTiCl_6$ molecules have not so far been observed [e.g., no transport of $CoCl_2$ with $TiCl_4$ or $SiCl_4$ (*116*)]. From this it must be concluded that bonding is not purely ionic in nature but that donor–acceptor interaction in the sense of Scheme $\gamma$ is of real significance (*116*). Structure $\delta$ with C.N.(Ti) = 5, which is also conceivable for $MTiCl_6$, is unfavorable, which also follows from the very low stability of $Ti_2Cl_8$ (*117*); note also the relationship between the dimerization enthalpy and coordination number (*110*).



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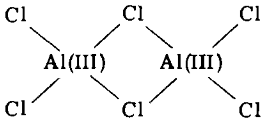

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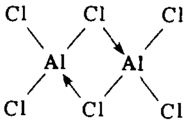
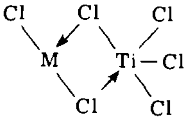


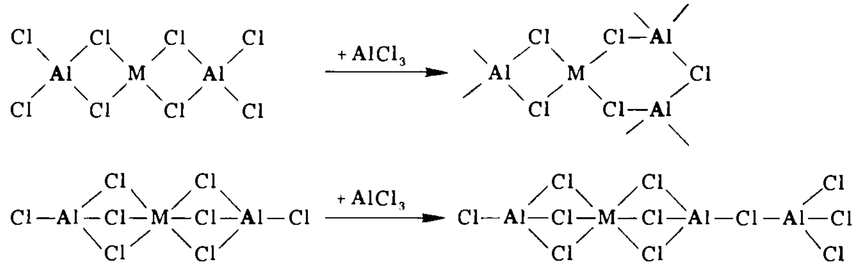
($\gamma$)



($\delta$)

## D. Complexes Richer in $AlCl_3$

The normal $AlCl_3$ complexes that have been described are able to take up additional $AlCl_3$ (*115*) without change in the coordination number of M:



For further structural possibilities see Section V,B,6. One can expect that the energy balance for addition of $AlCl_3$ ($0.5Al_2Cl_6$) will be almost independent of the nature of M. There are direct mass-spectroscopic measurements for such systems only in the case of the equilibria

$$CoAl_2Cl_8(g) + 0.5Al_2Cl_6(g) = CoAl_3Cl_{11}(g) \tag{52}$$

$\Delta H^0(298) = -7.7$ kcal; $\Delta S^0(298) = -15.7$ cal/K (*124*)

$$Al_2Cl_6(g) + 0.5Al_2Cl_6(g) = Al_3Cl_9(g) \tag{53}$$

$\Delta H^0(298) = -5.05$ kcal; $\Delta S^0(298) = -20.4$ cal/K (*123*)

There are also measurements from which the existence of complexes richer in $AlCl_3$ and their thermodynamic data can be deduced by calculation from the overall composition of the equilibrium gas. This method naturally involves an increased uncertainty. Furthermore, the measurements may be falsified by the occurrence of gaseous oxyhalides (*120*). Table VII shows all the results so far available. Values shown in parentheses (Table VII) for M = Mg, Ca, and Mn, which are based on preliminary experiments (*32*), deviate much more markedly from these expected (cf. *115*); further measurements for resolution of this problem are desirable.

## E. $MCl_4/LCl_3$ ($MLCl_7$, $ML_2Cl_{10}$)

### *1. Qualitative Observations*

$AlCl_3$ complexes with M(IV) = U (*45*); Th, U (*119*); and Zr (*161*). $InCl_3$ complexes with M(IV) = U (*13*).

TABLE VII

COMPARISON OF HOMOGENEOUS EQUILIBRIA[a]

| Reaction | | | $\Delta H^0$ (kcal) | $\Delta S^0$ (cal/K) | References |
|---|---|---|---|---|---|
| $CoAl_2Cl_8(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= CoAl_3Cl_{11}(g)$ | −7.7 | −15.7 | (*124*) |
| $CoAl_2Cl_8(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= CoAl_3Cl_{11}(g)$ | −8.1 | −13.1 | (*32*) |
| $MgAl_2Cl_8(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= MgAl_3Cl_{11}(g)$ | (−15.7) | (−22.9) | (*32*) |
| $CaAl_2Cl_8(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= CaAl_3Cl_{11}(g)$ | (+0.3) | (−1.1) | (*32*) |
| $MnAl_2Cl_8(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= MnAl_3Cl_{11}(g)$ | (−4.5) | (−6.7) | (*32*) |
| $EuAl_3Cl_{11}(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= EuAl_4Cl_{14}(g)$ | −8.9 | −14.2 | (*151*) |
| $NdAl_3Cl_{12}(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= NdAl_4Cl_{15}(g)$ | −10.0 | −16.9 | (*82*) |
| $NdGa_3Cl_{11}(g)$ | $+ 0.5Ga_2Cl_6(g)$ | $= NdGa_4Cl_{15}(g)$ | −12.2 | −20.9 | (*41*) |
| $VAlCl_6(g)$ | $+ 0.5Al_2Cl_6(g)$ | $= VAl_2Cl_9(g)$ | −11.9 | −19.2 | (*5*) |

[a] Data corrected to 298K (*115*). Expected for addition of 1 $AlCl_3$ (represented as $Al_2Cl_6$): $\Delta H^0 = -8 \pm 3$ kcal; $\Delta S^0 = -16 \pm 4$ cal/K.

## 2. *Thermodynamic Investigations*

$AlCl_3$ complexes are known with M(IV) = U (*46*) and Zr (*127*). The following values have been measured.

$$ZrCl_4(s) + 0.5Al_2Cl_6(g) = ZrAlCl_7(g) \qquad (54)$$

$$\Delta H^0(298) = 17.8 \text{ kcal}; \ \Delta S^0(298) = 26.6 \text{ cal/K} \ (127)$$

This leads (*127*) to

$$0.5Zr_2Cl_8(g) + 0.5Al_2Cl_6(g) = ZrAlCl_7(g) \qquad (55)$$

$$\Delta H^0(298) = -0.9 \text{ kcal}; \ \Delta S^0(298) = 0 \text{ cal/K} \ (127)$$

These data support the view that the $ZrAlCl_7$ molecule contains a double Cl bridge, which is clearly the case for $Zr_2Cl_8$ also (C.N. = 5). It is not possible, however, a priori to exclude a triple Cl bridge (C.N. = 6) for $ZrAlCl_7$.

$$ZrCl_4(s) + Al_2Cl_6(g) = ZrAl_2Cl_{10}(g) \qquad (56)$$

$$\Delta H^0(298) \cong 10.8 \text{ kcal}; \ \Delta S^0(298) \cong 11 \text{ cal/K} \ (127)$$

$$UCl_4(s) + Al_2Cl_6(g) = UAl_2Cl_{10}(g) \qquad (57)$$

$$\Delta H^0(700) = 15.8 \text{ kcal}; \ \Delta S^0(700) = 15.3 \text{ cal/K} \ (46)$$

The different values for Eqs. (56) and (57) must be related to the different structures of $ZrCl_4(s)$ and $UCl_4(s)$ (C.N. = 6 or 8). In $ZrAl_2Cl_{10}$ and $UAl_2Cl_{10}$, Zr and U are probably octahedrally coordinated by Cl.

## F. $MCl_5/LCl_3$ ($MAlCl_8$)

### *1. Qualitative Observations*

$AlCl_3$ complexes with M(V) = U (*90*). $InCl_3$ complexes with M(V) = U (*13, 14*).

### *2. Thermodynamic Investigations*

Measurements have been made for $AlCl_3$ complexes with M(V) = U (*46*) and Ta (*127*)

$$UCl_4(s) + 0.5Cl_2 + 0.5Al_2Cl_6(g) = UAlCl_8(g) \tag{58}$$

From the values measured for Eq. (58) it was possible with data for $UCl_5(s) = UCl_4(s) + 0.5Cl_2$ (from *6*) to obtain $\Delta H^0$ and $\Delta S^0$ values for

$$UCl_5(s) + 0.5Al_2Cl_6(g) = UAlCl_8(g) \tag{59}$$

$$\Delta H^0 = 19.1 \text{ kcal};\ \Delta S^0 = 26.8 \text{ cal/K}\ (\mathit{127})$$

These values are in close agreement with those for the corresponding reaction [Eq. (60)] with $TaCl_5$, which can be ascribed to similar $M_2Cl_{10}$ molecular lattices for the two pentachlorides (*127*).

$$TaCl_5(s) + 0.5Al_2Cl_6(g) = TaAlCl_8(g) \tag{60}$$

$$\Delta H^0(298) = 17.9 \text{ kcal};\ \Delta S^0(298) = 28.4 \text{ cal/K}$$

It is found, as expected, that

$$0.5Ta_2Cl_{10}(g) + 0.5Al_2Cl_6(g) = TaAlCl_8(g) \tag{61}$$

$$\Delta H^0 = +1.1 \text{ kcal};\ \Delta S^0 = 0 \text{ cal/K}\ (\mathit{127})$$

Uranium and tantalum atoms in the complexes are probably octahedrally coordinated by chlorine. Aluminum always has C.N. = 4.

## VI. Complex Formation by $UCl_5/U_2Cl_{10}$

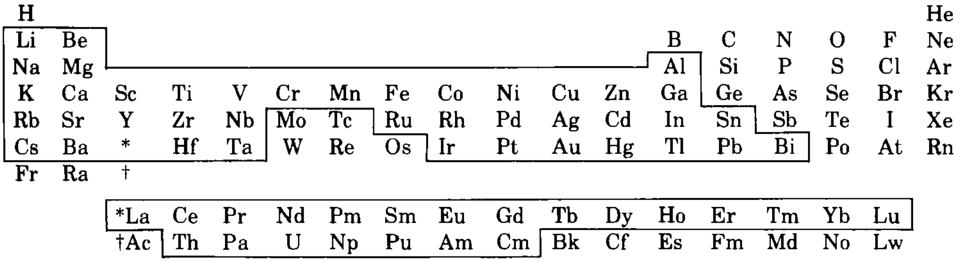
Gruen and McBeth (*46*) concluded from measurements on the reaction $UCl_4(s) + Cl_2$ that the dimer $U_2Cl_{10}(g)$ is formed. The existence of $U_2Cl_{10}$ (as well as $UCl_5$) may also be detected mass spectroscopically at 423 K (*116*). Accordingly, $U_2Cl_{10}/UCl_5$ should be suitable for forming complexes. In the corresponding experiments thermal decomposition of $U_2Cl_{10}$ to $UCl_4$ must be suppressed by addition of $Cl_2$. In fact, it was observed (*164*) that a small uranium content in chloride samples leads to an increased volatility for chlorides of Eu, Nd, Tb, and Am. Some experiments (*116*) showed that $CaCl_2$ and $CoCl_2$ were transported chemically with $UCl_5/U_2Cl_{10}$ (773 → 673 K). $Au_2Cl_6$ could similarly be suitable for forming complexes.

## VII. Practical Applications of Halide Complexes

Table VIII shows the elements the chlorides (bromides and iodides) of which form readily volatile complexes with the trichlorides (tribromides and triiodides) $AlX_3$, $GaX_3$, $InCl_3$, and $FeX_3$. It is essential throughout that the M content in the gas phase can be increased by powers of 10 over the saturation pressure of $MX_n$ and that the complexes be labile, $MX_n$ being rapidly available as required. In this section whenever $AlX_3$ (or $LX_3$) is referred to it is always as the gaseous equilibrium mixture $AlX_3 + Al_2X_6$ (or $LX_3 + L_2X_6$). Useful applications will now be summarized.

TABLE VIII

ELEMENTS OF WHICH THE CHLORIDES (BROMIDES, IODIDES) FORM VOLATILE COMPLEXES WITH THE TRICHLORIDES (BROMIDES, IODIDES) $AlX_3$, $GaX_3$, $InCl_3$ AND $FeX_3$



| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | * | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | † | | | | | | | | | | | | | | | |
| | | *La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | †Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lw | |

### A. HALIDES

Preparation of halide crystals, for example, those of $CuCl_2$ (*179*), may be accomplished by chemical transport (*104*) with $AlCl_3$ in a temperature gradient is an example of preparation of oxide-free halides by transport with $AlCl_3$. Oxygen remains in the residue as AlOCl or, at higher temperatures, as $Al_2O_3$ (*134*).

Halide syntheses may be accomplished by reaction of oxides with $AlCl_3$ and removal of the halides by means of the $MCl/AlCl_3$ complexes (*91, 93*). Decomposition of Cu- and Fe-containing ores with $Cl_2$ results in appreciable votalization of Cu (as $CuFe_2Cl_8$) (*154*). If surface layers are formed during the reaction, which hinder its progress, attack is greatly accelerated if the solid reaction product (the surface layer) is removed to other parts of the reaction space by means of the gaseous complex (*134*):

$$Co + Br_2 + AlBr_3 \rightarrow CoBr_2 \text{ (134)}$$

$$Ni + Br_2 + AlBr_3 \rightarrow NiBr_2 \text{ (134)}$$

$$Pt + Br_2 + AlBr_3 \rightarrow PtBr_3 \text{ (144) [similarly, } PtCl_2 \text{ (144)]}$$

$$Cr + CrCl_3 + HCl + AlCl_3 \rightarrow CrCl_2 \text{ (65, 129) [similarly, } CrBr_2, CrI_2]$$

$$UCl_4 + Al + AlCl_3 \rightarrow UCl_3 \text{ (91)}$$

$$Ti + TiCl_3 + AlCl_3 \rightarrow Ti_7Cl_{16} \text{ (130, 131) [similarly, } Ti_7Br_{16} \text{ (130, 131)]}$$

$$PdI_2 + AlI_3 \rightarrow Pd_5AlI_2 \text{ (76)}$$

If surface films serve to protect from corrosion, removal of the surface film may result in considerably increased attack, for example, Monel + $Cl_2$ + $AlCl_3$ (*91*).

Difficultly volatile halides may be intercalated in graphite with $AlCl_3$ as carrier (transport agent) (*157*), $UCl_5$ and $UCl_4$ may be separated by transport with $AlCl_3 + Cl_2$ (*91*). Lanthanides (or actinides) may be separated by gas chromatography by volatilization of the chlorides in a He/$AlCl_3$ stream (*172, 173*). $CoCl_2$, $NiCl_2$, or $FeCl_2$ may be dehalogenated by transport in an $AlBr_3$ or $AlI_3$ atmosphere (*134*).

### B. METAL TRANSPORT

The following reactions involving gaseous halide complexes are of interest and represent a development of van Arkel's classical work on the transport of metals with iodine (*104*) ($T_1$ is the lower temperature,

$T_2$ the higher, and the arrow gives the direction of transport in the temperature gradient):

$Cu + HCl + AlCl_3$: Cu transport (400 → 600°C) (*138*)

$Ag + HCl + AlCl_3$: Ag transport (450 → 700°C) (*138*)

$Au + I_2 + AlI_3$: Au transport (300 → 350°C) (*138*)

$Ru + Cl_2 + AlCl_3$: Ru transport (450 → 650°C) (*138*)

$Rh + Cl_2 + AlCl_3$: Rh transport (600 → 800°C) (*138*)

$Pd + Cl_2 + FeCl_3$ ($AlCl_3$): Pd transport (400 → 900°C) (*138*)

$Pd + I_2 + AlCl_3$: Pd transport (375 → 600°C) (*134*)

$Ir + Cl_2 + AlCl_3$: Ir transport (600 → 800°C) (*138*)

$Pt + Cl_2 + AlCl_3$ ($FeCl_3$): Pt transport (600 → 800°C) (*138*)

$Co + GaX_3$ ($X = Cl, I$): Co transport ($T_1 \rightarrow T_2$) (*133*)

$Ni + I_2 + InI_3$: Ni transport ($T_1 \rightarrow T_2$) (*135*)

$Pd + I_2 + AlI_3$: $Pd_2Al$ (375 → 600°C) (*134, 138*)

In the decomposition of copper oxide-containing ores with carbon, NaCl, $SiO_2$, and a little water, HCl and $Na_2SiO_3$ are the primary products, and then $Cu_3Cl_{3(g)}$, $NaCu_2Cl_{3(g)}$, and $Na_2CuCl_{3(g)}$. These copper-containing molecules come into contact with carbon and are there reduced by $H_2$ to metal (*44*); this is the copper-segregation process (*50*). Formation of the relatively stable alkali metal complexes can be particularly useful if coupled with a subsequent reaction—here, reduction by hydrogen.

### C. OXIDE TRANSPORT

Aluminum trichloride cannot be used as a transport agent for oxides because of the great stability of $Al_2O_3$. With some limitations, however, $GaCl_3$ is suitable for this purpose. Transport leads, for example, to deposition of $Fe_2O_3$ in the hot zone:

$Fe_2O_3 + HCl + GaCl_3$: $Fe_2O_3$ transport (327 → 427°C) (*139*)

Because of the similar ionic radii of $Fe^{3+}$ and $Ga^{3+}$, a few percent of Ga atoms also go over into the solid phase.

## D. CHALCOGENIDES

For the transport of the spinel $CdCr_2(S_{1-x}Se_x)_4$ with $I_2 + AlCl_3$, see Pickardt *et al.*, (*97*); for that of $Mn_xHg_{1-x}Se$ and $Mn_xCd_{1-x}Se$ with $Cl_2 + AlCl_3$, see Pajaczkowska (*84*). Transport of chromium sulfides and selenides with $AlCl_3$ (*72, 73*) may require the additional presence of HCl (from the hydrolysis of $AlCl_3$). This is true for the synthesis of $Cu_xHg_{1-x}Cr_2Se_4$ from the elements in the presence of $AlCl_3$ (*81*) and for transport of $CrTe_3$ with $AlCl_3$ (*59*). Synthesis of $HgCr_2Se_4$, for example, from the elements is successful when $HgCl_2$ is added as a source of $Cl_2$ together with $AlCl_3$ to form the complex (*43, 119*).

## E. DISCHARGE LAMPS

Discharge lamps in which, for example, Na atoms are to be excited in the plasma column, are charged with NaI. The Na content in the gas phase (quartz wall ~800°C) is increased by complex formation of NaI with $AlCl_3$ (*28, 71*). Other fillers for lamps where complex formation takes place are $CeI_3 + SmI_2 + CsI + NaI$ (*171*) and $ScI_3 + NaI$ (*58*). See also (*52, 170*).

## F. LASERS

$AlCl_3$ complexes of suitable lanthanide chlorides have been tested in high-energy lasers (*27, 51–53, 56, 61*).

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## REFERENCES

*1.* I. L. Agafonov, L. G. Nikolaeva, and N. Kh. Agliulov, *Russ. J. Phys. Chem.* (*Engl. Transl.*) **48,** 623 (1974).

*2.* M. Aits and H. Schäfer, *Z. Anorg. Allg. Chem.* **408,** 37 (1974).

*3.* M. Aits and H. Schäfer, *J. Less-Common Met.* **57,** 219 (1978).

*4.* A. Anundskås, A. E. Mahgoub, and H. A. Øye, *Acta Chem. Scand. Ser. A* **30,** 193 (1976).

*5.* A. Anundskås and H. A. Øye, *J. Inorg. Nucl. Chem.* **37,** 1609 (1975).

6. I. Barin and O. Knacke, *Thermochem. Prop. Inorg. Subst., 1973* (1973).
7. I. Barin, O. Knacke, and O. Kubaschewski, *Thermochem. Prop. Inorg. Subst., 1977 Suppl.,* (1977).
8. R. F. Belt and H. Scott, *Inorg. Chem.* **3,** 1785 (1964).
9. R. W. Berg and G. N. Papatheodorou, *Inorg. Chim. Acta* **45,** L211 (1980).
10. M. Binnewies, *Z. Anorg. Allg. Chem.* **435,** 156 (1977).
11. M. Binnewies, *Z. Anorg. Allg. Chem.* **437,** 19 (1977).
12. M. Binnewies, *Z. Anorg. Allg. Chem.* **437,** 25 (1977).
13. M. Binnewies and H. Schäfer, *Z. Anorg. Allg. Chem.* **395,** 77 (1973).
14. M. Binnewies and H. Schäfer, *Z. Anorg. Allg. Chem.* **407,** 327 (1974).
15. M. Binnewies and H. Schäfer, *Z. Anorg. Allg. Chem.* **410,** 149 (1974).
16. H. Bloom, B. V. O'Grady, R. G. Anthony, and V. C. Reinsborough, *Aust. J. Chem.* **23,** 843 (1970).
17. K. Brodersen, G. Thiele, and H. Gaedcke, *Z. Anorg. Allg. Chem.* **348,** 162 (1966).
18. J. Brynestad, S. von Winbush, H. L. Yakel, and G. P. Smith, *Inorg. Nucl. Chem. Lett.* **6,** 889 (1970).
19. J. Brynestad, H. L. Yakel, and G. P. Smith, *Inorg. Chem.* **9,** 686 (1970).
20. A. Büchler and J. B. Berkowitz-Mattuck, *Adv. High Temp. Chem.* **1,** (1967).
21. I. T. Buraya, O. G. Polyachenok, and G. I. Novikov, *Zh. Fiz. Khim.* **48,** 1609 (1974); *Russ. J. Phys. Chem.* (*Engl. Transl.*) **48,** 952 (1974).
22. I. T. Buraya, O. G. Polyachenok, and G. I. Novikov, *Vestn. Akad. Nauk SSR, Ser. Khim. Nauk.* p. 53 (1975); *Chem. Abstr.* **84,** 80563 (1976).
23. I. T. Buraya, O. G. Polyachenok, O. N. Komshilova, and G. I. Novikov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **19,** 1797 (1976).
24. M. A. Capote, G. H. Kucera, and G. N. Papatheodorou, *Proc.—Electrochem. Soc.* **78-1** (1978).
25. M. A. Capote and G. N. Papatheodorou, *Inorg. Chem.* **17,** 3414 (1978).
26. W. T. Carnall, J. P. Hessler, H. R. Hoekstra, and C. W. Williams, *J. Chem. Phys.* **68,** 4304 (1978).
27. W. T. Carnall, J. P. Hessler, C. W. Williams, and H. R. Hoekstra, *J. Mol. Struct.* **46,** 269 (1978).
28. A. G. Chalmers, D. O. Wharmby, and F. L. Whittacker, *Light. Res. Technol.* **7,** 11 (1975).
29. M. Cosandey and F. P. Emmenegger, *J. Electrochem. Soc.* **126,** 1601 (1979).
30. S. J. Cyvin, B. N. Cyvin, and A. Snelson, *J. Phys. Chem.* **75,** 2609 (1971).
31. A. Dell'Anna and F. P. Emmenegger, *Helv. Chim. Acta* **58,** 1145 (1975).
32. E. W. Dewing, *Metall. Trans.* **1,** 2169 (1970).
33. F. Dienstbach and F. P. Emmenegger, *Inorg. Chem.* **16,** 2957 (1977).
34. F. Dienstbach and F. P. Emmenegger, *Helv. Chim. Acta* **60,** 166 (1977).
35. F. Dienstbach and F. P. Emmenegger, *Z. Anorg. Allg. Chem.* **436,** 127 (1977).
36. F. Dienstbach and F. P. Emmenegger, *J. Inorg. Nucl. Chem.* **40,** 1299 (1978).
37. F. P. Emmenegger, *Inorg. Chem.* **16,** 343 (1977).
38. D. H. Feather and A. W. Searcy, *High Temp. Sci.* **3,** 155 (1971).
39. W. Fischer, *Angew. Chem.* **61,** 336 (1949).
40. U. Flörke and H. Schäfer, *Z. Anorg. Allg. Chem.* **459,** 140 (1979).
41. T. Foosnaes (Mentor H. A. Øye), Dissertation, University of Trondheim (1979).
42. R. M. Fowler and S. S. Melford, *Inorg. Chem.* **15,** 473 (1976).
43. P. Gibart, *J. Cryst. Growth* **43,** 21 (1978).
44. P. Gross and M. C. Stuart, *Metall. Chem., Proc. Symp., 1971,* p. 499 (1972).
45. D. M. Gruen and R. L. McBeth, *Inorg. Nucl. Chem. Lett.* **4,** 299 (1968).

*46.* D. M. Gruen and R. L. McBeth, *Inorg. Chem.* **8,** 2625 (1969).

*47.* D. M. Gruen and H. A. Øye, *Inorg. Nucl. Chem. Lett.* **3,** 453 (1967).

*48.* J. P. Hager and R. B. Hill, *Metall. Trans.* **1,** 2723 (1970).

*49.* M. Hargittai and I. Hargittai, "The Molecular Geometries of Coordination Compounds in the Vapour Phase." Akad. Kiadó, Budapest, 1977.

*50.* J. W. Hastie, "High Temperature Vapors." Academic Press, New York, 1975.

*51.* J. P. Hessler, F. Wagner, C. W. Williams, and W. T. Carnall, Vortrag Amsterdam, 1976.

*52.* D. L. Hildenbrand and D. D. Cubicciotti, *Proc.—Electrochem. Soc.* **78-1** (1978).

*53.* H. R. Hoekstra, J. P. Hessler, C. W. Williams, and W. T. Carnall, *152nd Meet. Electrochem. Soc., 1977.*

*54.* J. A. Ibers, *Acta Crystallogr.* **15,** 967 (1962).

*55.* N. I. Ionov, *Dokl. Akad. Nauk SSSR* **59,** 467 (1948).

*56.* R. R. Jacobs, W. F. Krupke, J. P. Hessler, and C. W. Carnall, *Opt. Commun.* **21,** 395 (1977).

*57.* S. E. James and J. P. Hager, *Metall. Trans.* **9B,** 501 (1978).

*58.* W. M. Keeffe, *IES Trans.* p. 260 (1975).

*59.* K. O. Klepp and H. Ipser, *Monatsh. Chem.* **110,** 499 (1979).

*60.* E. S. Kotova, A. L. Kuzmenko, and G. I. Novikov, *Russ. J. Phys. Chem. (Engl. Transl.)* **46,** 1690 (1972).

*61.* W. F. Krupke, *Electron. Transition Lasers* [*Proc. Summer Colloq.*], *2nd, 1975* p. 148 (1976).

*62.* G. H. Kucera and G. N. Papatheodorou, *J. Phys. Chem.* **83,** 3213 (1979).

*63.* K. Lascelles and H. Schäfer, *Angew. Chem.* **83,** 112 (1971); *Angew. Chem., Int. Ed. Engl.* **10,** 1728 (1971).

*64.* K. Lascelles and H. Schäfer, *Z. Anorg. Allg. Chem.* **382,** 249 (1971).

*65.* K. Lascelles, R. A. J. Shelton, and H. Schäfer, *J. Less-Common Metals* **29,** 109 (1972).

*66.* W. C. Laughlin and N. W. Gregory, *J. Phys. Chem.* **80,** 127 (1976).

*67.* W. Lenhard and H. Schäfer, *Z. Anorg. Allg. Chem.* **482,** 167 (1981).

*68.* W. Lenhard, H. Schäfer, H. U. Hürter, and B. Krebs, *Z. Anorg. Allg. Chem.* **482,** 19 (1981).

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

*70.* C. S. Liu and R. J. Zollweg, *J. Chem. Phys.* **60,** 2384 (1974).

*71.* R. Lorenz, *Light. Res. Technol.* **8,** 136 (1976).

*72.* H. D. Lutz and Cs. v. Lovász, *Angew. Chem.* **80,** 562 (1968).

*73.* H. D. Lutz, Cs. v. Lovász, K. H. Bertram, M. Sréckovié, and U. Brinker, *Monatsh. Chem.* **101,** 519 (1970).

*74.* T. P. Martin and H. Schaber, private communication. (1979).

*75.* H. B. Merker and H. Schäfer, *Z. Anorg. Allg. Chem.* **480,** 76 (1981).

*76.* H. B. Merker, H. Schäfer, and B. Krebs, *Z. Anorg. Allg. Chem.* **462,** 49 (1980).

*77.* T. N. Naumova, L. S. Zhevnina, R. V. Poponova, M. S. Chupakhin, and B. D. Stepin, *Russ. J. Inorg. Chem. (Engl. Transl.)* **24,** 13 (1979).

*78.* G. I. Novikov and F. G. Gavryuchenkov, *Russ. Chem. Rev. (Engl. Transl.)* **36,** 156 (1967).

*79.* G. I. Novikov and E. S. Kotova, *Zh. Fiz. Khim.* **47,** 483 (1973).

*80.* G. I. Novikov and O. G. Polyachenok, *Russ. J. Inorg. Chem. (Engl. Transl.)* **6,** 996 (1961)

*81.* I. Okańska-Kozlowska, M. Jelonek, and Z. Drzazga, *Z. Anorg. Allg. Chem.* **436,** 265 (1977).

82. H. A. Øye and D. M. Gruen, *J. Am. Chem. Soc.* **91,** 2229 (1969).
83. H. A. Øye and D. M. Gruen, *NBS Spec. Publ.* (*U.S.*) **561** (1979).
84. A. Pajaczkowska, *Mater. Res. Bull.* **15,** 1509 (1980).
85. G. N. Papatheodorou, *Inorg. Chem.* **12,** 1899 (1973).
86. G. N. Papatheodorou, *J. Phys. Chem.* **77,** 472 (1973).
87. G. N. Papatheodorou, *Inorg. Nucl. Chem. Lett.* **10,** 115 (1974).
88. G. N. Papatheodorou, *Z. Anorg. Allg. Chem.* **411,** 153 (1975).
89. G. N. Papatheodorou and R. W. Berg, *Chem. Phys. Lett.* **75,** 483 (1980).
90. G. N. Papatheodorou and D. A. Buttry, *Inorg. Nucl. Chem. Lett.* **15,** 51 (1979).
91. G. N. Papatheodorou, *Curr. Top. Mater. Sci.* (submitted) (1980).
92. G. N. Papatheodorou and G. H. Kucera, *Inorg. Chem.* **16,** 1006 (1977).
93. G. N. Papatheodorou and G. H. Kucera, *Inorg. Chem.* **18,** 385 (1979).
94. E. J. Peterson, J. A. Caird, J. P. Hessler, H. R. Hoekstra, and C. W. Williams, *J. Phys. Chem.* **83,** 2458 (1979).
95. E. J. Peterson, J. A. Caird, W. T. Carnall, J. P. Hessler, H. R. Hoekstra, and C. W. Williams, *Argonne Rep.* **1979,** *conf.* 790641. *Chem. Abstr.* **92,** 117350 (1980).
96. K. P. Petrov, V. A. Kulikov, V. V. Ugarov, and N. G. Rambidi, *Zh. Strukt. Khim.* **21,** 71 (1980); *Chem. Abstr.* **93,** 159515 (1980).
97. J. Pickardt, E. Riedel, and B. Reuter, *Z. Anorg. Allg. Chem.* **373,** 15 (1970).
98. O. G. Polyachenok and O. N. Komshilova, *Teplofiz. Vys. Temp.* **10,** 195 (1972); *Chem. Abstr.* **76,** 132322 (1972).
99. S. Poturay-Gutniak, *Nukleonika* **13,** 1157 (1968).
100. H. Rabeneck and H. Schäfer, *Z. Anorg. Allg. Chem.* **395,** 69 (1973).
101. P. L. Radloff and G. N. Papatheodorou, *J. Chem. Phys.* **72,** 992 (1980).
102. R. R. Richards and N. W. Gregory, *J. Phys. Chem.* **68,** 3089 (1964).
103. H. Sainte-Claire Deville and L. Troost, *C. R. Hebd. Seances Acad. Sci.* **45,** 821 (1857).
104. H. Schäfer, "Chemische Transportreaktionen." Weinheim, 1962; "Chemical Transport Reactions." Academic Press, New York, 1964.
105. H. Schäfer, *Z. Anorg. Allg. Chem.* **400,** 242 (1973).
106. H. Schäfer, *Proc. Conf. Chem. Vap. Deposition, Int. Conf., 5th, 1975* p. 3 (1975).
107. H. Schäfer, *J. Cryst. Growth* **31,** 31 (1975).
108. H. Schäfer, *Z. Anorg. Allg. Chem.* **414,** 151 (1975).
109. H. Schäfer, *Z. Anorg. Allg. Chem.* **415,** 217 (1975).
110. H. Schäfer, *Angew. Chem.* **88,** 775 (1976); *Angew. Chem., Int. Ed. Engl.* **15,** 713 (1976).
111. H. Schäfer, *Pure Appl. Chem.* **49,** 871 (1977).
112. H. Schäfer, *Z. Chem.* **19,** 362 (1979).
113. H. Schäfer, *NBS Spec. Publ.* (*U.S.*) **561** (1979).
114. H. Schäfer, *Z. Anorg. Allg. Chem.* **461,** 29 (1980).
115. H. Schäfer, *Z. Anorg. Allg. Chem.* **479,** 99 (1981).
116. H. Schäfer, *Z. Anorg. Allg. Chem.* **479,** 105 (1981).
117. H. Schäfer and M. Binnewies, *Z. Anorg. Allg. Chem.* **410,** 251 (1974).
118. H. Schäfer and M. Binnewies, *Rev. Chim. Miner.* **13,** 24 (1976).
119. H. Schäfer, M. Binnewies, W. Domke, and J. Karbinski, *Z. Anorg. Allg. Chem.* **403,** 116 (1974).
120. H. Schäfer, M. Binnewies, and U. Flörke, *Z. Anorg. Allg. Chem.* **427,** 31 (1981).
121. H. Schäfer, M. Binnewies, R. Laumanns, and H. Wächter, *Z. Anorg. Allg. Chem.* **461,** 31 (1980).

*122*. H. Schäfer and D. Boos, *Z. Anorg. Allg. Chem.* **477,** 35 (1981).

*123*. H. Schäfer and U. Flörke, *Z. Anorg. Allg. Chem.* **462,** 173 (1980).

*124*. H. Schäfer and U. Flörke, *Z. Anorg. Allg. Chem.* **469,** 172 (1980).

*125*. H. Schäfer and U. Flörke, *Z. Anorg. Allg. Chem.* **478,** 57 (1981).

*126*. H. Schäfer and U. Flörke, *Z. Anorg. Allg. Chem.* **479,** 84 (1981).

*127*. H. Schäfer and U. Flörke, *Z. Anorg. Allg. Chem.* **479,** 89 (1981).

*128*. H. Schäfer, U. Flörke, and M. Trenkel, *Z. Anorg. Allg. Chem.* **478,** 191 (1981).

*129*. H. Schäfer and R. Laumanns, *Z. Anorg. Allg. Chem.* **436,** 47 (1977).

*130*. H. Schäfer and R. Laumanns, *Z. Anorg. Allg. Chem.* **474,** 135 (1981).

*131*. H. Schäfer, R. Laumanns, B. Krebs, and G. Henkel, *Angew. Chem.* **91,** 343 (1979); *Angew. Chem. Int. Ed. Engl.* **18,** 325 (1979).

*132*. H. Schäfer and W. Lenhard, *Z. Anorg. Allg. Chem.* **482,** 163 (1981).

*133*. H. Schäfer and J. Nowitzki, *Z. Anorg. Allg. Chem.* **435,** 49 (1977).

*134*. H. Schäfer and J. Nowitzki, *J. Less-Common Metals* **61,** 47 (1978).

*135*. H. Schäfer and J. Nowitzki, *Z. Anorg. Allg. Chem.* **439,** 80 (1978).

*136*. H. Schäfer and J. Nowitzki, *Z. Anorg. Allg. Chem.* **457,** 13 (1979).

*137*. H. Schäfer and H. Rabeneck, *Z. Anorg. Allg. Chem.* **443,** 28 (1978).

*138*. H. Schäfer and M. Trenkel, *Z. Anorg. Allg. Chem.* **414,** 137 (1975).

*139*. H. Schäfer and M. Trenkel, *Z. Anorg. Allg. Chem.* **426,** 113 (1976).

*140*. H. Schäfer and M. Trenkel, *Z. Anorg. Allg. Chem.* **437,** 10 (1977).

*141*. H. Schäfer and K. Wagner, *Z. Anorg. Allg. Chem.* **450,** 88 (1979).

*142*. H. Schäfer and K. Wagner, *Z. Anorg. Allg. Chem.* **451,** 61 (1979).

*143*. H. Schäfer and K. Wagner, *Z. Anorg. Allg. Chem.* **452,** 89 (1979).

*144*. H. Schäfer, U. Wiese, C. Brendel, and J. Nowitzki, *J. Less-Common Metals* **76,** 63 (1980).

*145*. K. N. Semenenko, T. N. Naumova, L. N. Gorokhow, G. A. Semenova, and A. W. Novoselova, *Dokl. Akad. Nauk UdSSR* **154,** 169 (1964).

*146*. K. N. Semenenko, T. N. Naumova, L. N. Gorokhow, and A. W. Novoselova, *Dokl. Akad. Nauk UdSSR* **154,** 648 (1964).

*147*. C. F. Shieh and N. W. Gregory, *J. Phys. Chem.* **79,** 828 (1975).

*148*. V. B. Sholts and L. N. Sidorov, *Vestn. Mosk. Univ., Ser. 2: Khim.* **1972,** 371 (1972), and further publications of the Sidorov team.

*149*. E. Sibbing and H. Schäfer, *Z. Anorg. Allg. Chem.* **410,** 67 (1974).

*150*. L. N. Sidorov, *Mod. Prob. Phys. Chem.* **6,** 295 (1972) (in Russian).

*151*. M. Sørlie and H. A. Øye, *J. Inorg. Nucl. Chem.* **40,** 493 (1978).

*152*. M. Sørlie and H. A. Øye, *Inorg. Chem.* **17,** 2473 (1978).

*153*. V. P. Spiridonov, E. V. Erokhin, and B. I. Lutoshkin, *Vestn. Mosk, Univer., Ser. 2: Khim.* **26,** 296 (1971).

*154*. B. W. Spreckelmeyer, *Ger. Offen.* **2,216,807** (1972).

*155*. B. Stelthove and H. Schäfer, *Z. Anorg. Allg. Chem.* **451,** 25 (1979).

*156*. D. R. Stull and H. Prophet, "Janaf Thermochemical Tables, 2nd ed. NSRDS-NBS 37, Washington, D.C., 1971.

*157*. E. Stumpp and G. Nietfeld, *Z. Anorg. Allg. Chem.* **456,** 261 (1979).

*158*. Mien-tsêng Su and G. I. Novikov, *Russ. J. Inorg. Chem. (Engl. Transl.)* **11,** 270 (1966).

*159*. S. Sutakshuto (Mentor H. A. Øye), Dissertation, University of Trondheim (1976).

*160*. R. C. Svedberg (1966), cited in Büchler and Berkowitz-Mattuck (*20*).

*161*. D. R. Taylor and E. M. Larsen, *J. Inorg. Nucl. Chem.* **41,** 481 (1979).

*162*. G. Thiele, K. Brodersen, E. Kruse, and B. Holle, *Chem. Ber.* **101,** 2771 (1968).

*163*. P. J. Thistlethwaite and S. Ciach, *Inorg. Chem.* **14,** 1430 (1975).

*164*. S. S. Travnikov, A. V. Davydov, and B. F. Myasoedov, *Radiokhimiya* **21,** 579 (1979); *Chem. Abstr.* **91,** 150382 (1979).

*165*. H. Wächter and H. Schäfer, *Z. Anorg. Allg. Chem.* **471,** 38 (1980).

*166*. K. Wagner and H. Schäfer, *Z. Anorg. Allg. Chem.* **450,** 107 (1979).

*167*. K. Wagner and H. Schäfer, *Z. Anorg. Allg. Chem.* **450,** 115 (1979).

*168*. K. Wagner and H. Schäfer, *Z. Anorg. Allg. Chem.* **451,** 57 (1979).

*169*. K. Wagner and H. Schäfer, *Z. Anorg. Allg. Chem.* **452,** 83 (1979).

*170*. I. L. Wilson and L. P. Rehder, *152nd Meet. Electrochem. Soc. 1977,* p. 989 (1977).

*171*. R. J. Zollweg, C. S. Liu, C. Hirayama, and J. W. McNall, IES *Conf., 1974,* 249 (1974); *J. IES* p. 249 (1975).

*172*. T. S. Zvarova, *Radiochem. Radioanal. Lett.* **11,** 113 (1972).

*173*. T. S. Zvarova and I. Zvára, *J. Chromatogr.* **49,** 290 (1976).