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COMPLEX HALIDES IN VAPOURS AT HIGH TEMPERATURES

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I. INTRODUCTION

The extremely rapid development of high temperature chemistry makes necessary the systematic study of the properties of substances in the vapour state. The antiquated ideas about vapour as a medium barren of processes and compounds are now undergoing considerable changes. It is becoming more and more evident that in the variety of forms and peculiarities of their interaction a vapour is often comparable with condensed phases.

Problems of vaporisation and the chemistry and structure of complex molecules in vapour-phase media at high temperatures have repeatedly formed the subject of discussions in monographs and articles. In this connection mention must be made of the works of Margrave [1,2], Searcy [3], Kireev [4], Glemser [5], Novikov [6], Drowart and Goldfinger [7], and some others. They give many examples of polymerisation and complex formation by oxides and halides in vapour form, producing compounds of the hydrate type, salts of oxo-acids, oxide halides, and complex halides. In all the examples considered reference is made only to compounds which exist in the form of neutral molecules, but it may be assumed that in ionised vapour the variety of species will be even greater, since compounds non-existent in the form of neutral molecules can be made stable by addition or loss of electrons and the formation of ionic molecules. Unfortunately, the quantitative physicochemical characteristics of complex vapour-phase molecules — not only ionised but also neutral — are known in very few instances.

The vapour-phase double or complex halides, mainly of the type $MM'X_n$, where M is an alkali metal, M' a metal of another group, and X a halogen are better studied in this respect than other compounds. The review given below will be restricted to these forms alone and will not be concerned with compounds of the type $BeAlCl_5$,[8] In_xCl_y,[9] $SiBCl_5$,[10] etc., which have been studied less extensively.

The practical importance of investigations in the region defined above is obvious, since under industrial conditions many metals are obtained either by electrolysis of molten salt mixtures (including salts of the alkali metals), or by metallothermic reduction of halides.

The study of complexes in vapour form is of great theoretical interest above all for the further development of the chemistry of coordination compounds.

II. COMPLEX HALIDES IN VAPOUR FORM

The simplest representatives of complex compounds of the type $MM'X_n$ in the vapour state are the mixed dimers of alkali metal halides.

As already mentioned, the alkali metal halides exist in vapours in the form of a collection of monomeric, dimeric, and some more complex molecules. However, the relation between the monomer and various polymeric forms is such that for most purposes only dimerisation need be considered and the more complex forms are essential only for lithium halides [11-13].

The stability of the vapour forms of the dimers of the alkali metal halides falls from Li to Cs, as is shown by the data [14] given in Table 1.

In the interaction of dimeric molecules of the various alkali metal halides the constituent parts can be interchanged as a result of which mixed dimers are obtained. Thus data have been given for the reaction [15]:

(1) $(Li_2F_2) + (Na_2F_2) = 2(NaLiF_2)$ $\Delta H^\circ_{1000} = 0.$

The results of a mass spectrometric investigation [16] of equilibria in the disproportionation by stepwise replacement are known:

(2) $(CsRbF_2) = {}^1/_2(Rb_2F_2) + {}^1/_2(Cs_2F_2)$ ΔH°_{904} 1.3 kcal mole^{-1},
(3) $(RbKF_2) = {}^1/_2(K_2F_2) + {}^1/_2(Rb_2F_2)$ ΔH°_{980} 1.4 kcal mole^{-1},
(4) $(KNaF_2) = {}^1/_2(Na_2F_2) + {}^1/_2(K_2F_2)$ ΔH°_{925} 1.5 kcal mole^{-1},
(5) $(NaLiF_2) = {}^1/_2(Li_2F_2) + {}^1/_2(Na_2F_2)$ ΔH°_{1173} 2.3 kcal mole^{-1},
(6) $(RbLiF_2) = {}^1/_2(Li_2F_2) + {}^1/_2(Rb_2F_2)$ ΔH°_{985} 3.0 kcal mole^{-1}.

In the mass spectrometric analysis of the composition of the vapour over LiCl–MCl mixtures [17] (M = Na, K, Rb, Cs) the ions $LiCl^+$, Li_2Cl^+, M^+, MCl^+, M_2Cl^+, and $LiMCl^+$ were observed in the molecular beam. The ion $LiMCl^+$ could be a fragment of molecules of mixed dimers. Analogous results were obtained by Novikov and coworkers [18], but in addition the ion Cs_2LiCl^+ was observed, which the authors took to be a fragment of a molecule of the mixed trimer Cs_2LiCl_3. Thermodynamic characteristics have also been given [18-21] for the disproportionation of the following mixed dimers:

		ΔH°_T, kcal mole^{-1}	t, °C
(7)	$(RbNaCl_2) = {}^1/_2(Rb_2Cl_2) + {}^1/_2(Na_2Cl_2)$	5.8	800
(8)	$(RbKCl_2) = {}^1/_2(Rb_2Cl_2) + {}^1/_2(K_2Cl_2)$	0	800
(9)	$(CsLiCl_2) = {}^1/_2(Cs_2Cl_2) + {}^1/_2(Li_2Cl_2)$	7.0	650—900
(10)	$(CsNaCl_2) = {}^1/_2(Cs_2Cl_2) + {}^1/_2(Na_2Cl_2)$	5.2	650—900
(11)	$(CsKCl_2) = {}^1/_2(Cs_2Cl_2) + {}^1/_2(K_2Cl_2)$	2.7	650—900

TABLE 1. Thermodynamic characteristics of the process $(M_2X_2) = 2(MX)$.

		Li	Na	K	Rb	Cs
Fluorides	ΔH°_{1000}, kcal mole^{-1}	61.5	56.9	49.6	43.9	39.2
	ΔS°_{1000}, e.u.	34.0	31.6	32.4	29.4	30 5
Chlorides	ΔH°_{1000}, kcal mole^{-1}	52.1	48.5	44.5	41.7	39.0
	ΔS°_{1000}, e.u.	32.1	29.0	28.4	28.1	28.0

It should be noted that the substitutions (2)–(11) are exothermic and the thermal effect is the greater the further apart the alkali metals, that is, the greater the difference in properties of their compounds. With increase in this difference the molecule of the mixed dimer becomes less and less symmetrical; the halogen atoms become more and more displaced towards one of the alkali metal atoms, which thus acquires the function of complex formation. To compare the mixed and true dimers as regards stability in the vapour state we will examine the thermodynamic scheme:

Scheme 1

$(M_2X_2) = 2(MX)$	ΔH_1°	$\Delta S_1^\circ \simeq 30$ e.u.
$(M'_2X_2) = 2(M'X)$	ΔH_2°	$\Delta S_2^\circ \simeq 30$ e.u.
$(MM'X_2) = {}^1/_2(M_2X_2) + {}^1/_2(M'_2X_2)$	ΔH_3°	$\Delta S_3^\circ \simeq 0$
$(MM'X_2) = (MX) + (M'X)$	ΔH_4°	ΔS_4°

It is easy to see that:

$$\Delta H_4^\circ = {}^1/_2(\Delta H_1^\circ + \Delta H_2^\circ) + \Delta H_3^\circ$$
$$\Delta S_4^\circ = {}^1/_2(\Delta S_1^\circ + \Delta S_2^\circ) \quad 30 \text{ e.u.} \qquad (B)$$

Hence the change in entropy during the dissociation of simple and mixed dimers is approximately the same, but the enthalpy of dissociation of the mixed dimer (ΔH_4) is greater than the arithmetic mean of the enthalpies of dissociation of the simple dimers by the quantity ΔH_3. Consequently in stability the mixed dimer will approximate to the more stable of the simple dimers, that is, the dimer which has the strongest M–Cl bond.

Since the stability of the dimers falls from Li to Cs (that is, with increase in the ionic radius), in the mixed dimer the ion with the smaller radius will function as the complex-forming atom.

We shall now consider the vapour-phase double compounds formed by the alkali metal chlorides with the dichlorides of some other metals.

The formation of a vapour-phase complex species was first proposed by the investigators of the BeF_2–NaF binary system[22], since this was the most rational explanation for unusual observations on the pressure and composition of the vapour. From the location of the maximum on the curve for the partial pressure of NaF calculated by the Duhem–Margules equation (without allowance for the pressure of the double species) the composition of the complex was found to be $NaBeF_3$. Berkowitz and Chypka[23] observed the analogous compound of beryllium and lithium fluorides (more correctly the ion $LiBeF_2^+$) in a mass spectrometric investigation of the composition of the vapour in the BeF_2–LiF system. For the process:

(12) $$(LiBeF_3) = (LiF) + (BeF_2)$$

they obtained the value ΔH_{900}° = 53 kcal mole^{-1}.

Many papers only qualitatively justify the assumption of a double compound in the vapour, although the experimental results sometimes allow the composition of the vapour to be calculated.

Among such studies is an investigation of the $BeCl_2$–NaCl and $BeCl_2$–KCl systems[24], the study of the BeF_2–NaF system[22] mentioned above, the work of Barton and Bloom[25] (who studied the formation of double compounds by lead and cadmium chlorides), an article with data on the KCl–$MgCl_2$ system[26], and work on the pressure and composition of the vapour in the $CaCl_2$–KCl and KCl–$SrCl_2$ systems[27]. The formation of $KCoCl_3$, $KNiCl_3$, K_2CdCl_4, and $KZnCl_3$ in the vapour has been proposed[28,29].

Novikov and Kuz'menko[30,31], using published data[22,24,26,27], calculated the thermodynamic characteristics of the dissociation processes of some double chlorides, namely:

		T, °C	ΔH_T°, kcal mole^{-1}	ΔS_T°, e.u.
(13)	$(NaBeF_3) = (NaF) + (BeF_2)$	900	52±2	21±3
(14)	$(NaBeCl_3) = (NaCl) + (BeCl_2)$	720	54±5	23±2
(15)	$(KBeCl_3) = (KCl) + (BeCl_2)$	720	48±5	24±2
(16)	$(KMgCl_3) = (KCl) + (MgCl_2)$	1080	58±5	31±2
(17)	$(KCaCl_3) = (KCl) + (CaCl_2)$	1100	63±3	30±2
(18)	$(KSrCl_3) = (KCl) + (SrCl_2)$	1100	67±17	32±13

The decrease in stability of the double compound $KM'Cl_3$ in the sequence Sr–Be was attributed by the authors[31] to the mutual repulsion of the ligands, the force of which rises in the order Sr–Be.

The change in the stability of the double chlorides along the alkali metal series can be seen in the example of the compounds $MFeCl_3$, the thermodynamic characteristics of the dissociation of which have been given[23,28]:

		ΔH_T°, kcal mole^{-1};
(19)	$(LiFeCl_3) = (LiCl) + (FeCl_2)$	43.0
(20)	$(KFeCl_3) = (KCl) + (FeCl_2)$	34.7
(21)	$(CsFeCl_3) = (CsCl) + (FeCl_2)$	24.7

Obviously, the stability of the double compounds falls from Li to Cs, that is, in the same sequence as the stability of the dimeric alkali metal chlorides.

We shall now consider the thermodynamic characteristics of the vapour-phase complexes in the MCl–$M'Cl_3$ and MF–$M'F_3$ systems.

As in the above examples, the formation of vapour-phase double compounds by the elements of Periodic Groups I and II, the information concerning the compounds of type $MM'X_4$ relate mainly to the fluorides and chlorides.

A large number of investigations have disclosed the formation of volatile double compounds in MCl–$AlCl_3$ and MF–AlF_3 systems.

The existence of the compound $NaAlF_4$ has been shown by X-ray analysis[32] of the condensate obtained on vaporisation of a melt with equimolecular amounts of NaF and AlF_3. An investigation of the condensate obtained by passing an inert gas over AlF_3–NaF melt led Howard[33] to conclude that the volatile compound $NaAlF_4$ existed.

The existence of $NaAlF_4$ in the vapour was confirmed by investigations of the pressure and composition of the vapour in the AlF_3–NaF system made by Vetyukov and coworkers[34] and also Ginsberg and Böhme[35].

Porter and Zeller[36], in studying the AlF_3–LiF system mass spectrometrically, observed two double compounds in the vapour: $LiAlF_4$ and $Li_2Al_2F_8$ (or Li_2AlF_5). These authors calculated the thermodynamic characteristics of the equilibrium:

(22) $(LiAlF_4) = (LiF) + (AlF_3)$ $\Delta H_{1000}^\circ = 73$ kcal mole^{-1}; $\Delta S_{1000}^\circ = 37$ e.u.

As regards the analogous systems of aluminium and alkali metal chlorides, mention must be made of the studies of Naryshkin[37], Plotnikov and coworkers[38], Morozov and coworkers[39,40], and Grothe[41].

An approximate value of the ΔH°_{T} for the equilibrium

(23) $(NaAlCl_4) = (NaCl) + (AlCl_3)$

is ~ 50 kcal mole^{-1}, given by Dewing [42]; this equilibrium was studied in detail by Galitskii [43] with the aid of a combination of tensimetry and analysis of the condensates. He obtained the thermodynamic characteristics:

$$\Delta H^{\circ}_{970} = 49.2 \pm 2 \text{ kcal mole}^{-1}; \Delta S^{\circ}_{970} = 28.9 \pm 2 \text{ e.u.}$$

In the same work [43] data are given for the equilibria:

(24) $(NaFeCl_4) = (NaCl) + (FeCl_3)$ $\Delta H^{\circ}_{970} = 51.6 \pm 2,5$ kcal mole^{-1}; $\Delta S^{\circ}_{970} = 28.9$ e.u.

(25) $(Na_3CrCl_6) = 3(NaCl) + (CrCl_3)$ $\Delta H^{\circ}_{1180} = 139.0 \pm 10$ kcal mole^{-1}; $\Delta S^{\circ}_{1180} = 74.0 \pm 7$ e.u.

(26) $(K_3CrCl_6) = 3(KCl) + (CrCl_3)$ $\Delta H^{\circ}_{1180} = 132.0 \pm 10$ kcal mole^{-1}; $\Delta S^{\circ}_{1180} = 76.0 \pm 7$ e.u.

These results are quite interesting although in the last two examples the correctness of the formula selected for the double compound seems doubtful.

Richards and Gregory [44] investigated the $FeCl_3$–NaCl system by a flow method, passing the vapour of $FeCl_3$ over solid NaCl. For the equilibrium:

(27) $[NaCl] + (FeCl_3) = (NaFeCl_4)$

they obtained the following thermodynamic characteristics:

$$\Delta H^{\circ}_{723} = 3.7 \pm 1 \text{ kcal mole}^{-1}; \Delta S^{\circ}_{723} = 6.5 \pm 1.5 \text{ e.u.}$$

When the equilibrium is recalculated for NaCl vapour, we obtain:

$$\Delta H^{\circ}_{723} = 51.3 \pm 1 \text{ kcal mole}^{-1}; \Delta S^{\circ}_{723} = 29.5 \pm 1.5 \text{ e.u.},$$

that is, values very close to those obtained by Galitskii [43].

Cook and Dann [45], after analysing vapour pressure data for MCl–$FeCl_3$ systems, concluded that vaporisation of the compounds $NaFeCl_4$ and $KFeCl_4$ was possible.

As can be concluded from the above examples, the vapour-phase double compounds of aluminium and iron have the formula $MM'X_4$ in the great majority of instances.

French investigators, in studying the AlF_3–NaF system by the flow and boiling point methods [46], suggested the existence of a heavy vapour-phase molecule, $Na_5Al_3F_{14}$, but this is very improbable. In preferring the form $MM'X_4$ for the vapour phase double compounds of alkali metal chlorides with the trichlorides of other elements we are convinced by the tensimetric and mass-spectrometric investigations of the MCl–$LnCl_3$ systems, where Ln is a rare-earth element (r.e.e.). In the mass-spectrometric analysis of the composition of the vapour over mixtures of the chlorides KCl–$ErCl_3$, [47] NaCl–$LnCl_3$ (Ln = Nd, Er, Y) [48], LiCl–$NdCl_3$, [48] and CsCl–$NdCl_3$ and CsCl–$ErCl_3$, [49] in addition to the ions corresponding to the simple chlorides, the ion $MLnCl_3^+$ has been recorded; this is a fragment of the double chloride molecule $MLnCl_4$.

The thermodynamic characteristics of the dissociation of the complex:

(28) $(MLnCl_4) = (MCl) + (LnCl_3)$

were calculated, starting from the values of

$$K_{equil} = \frac{P_{MCl} P_{LnCl_3}}{P_{MLnCl_4}}$$

for various temperatures. The necessary partial pressures of the components of the vapour were found strictly by the method proposed by Novikov and Gavryuchenkov [50] for the systems $ErCl_3$–KCl, [50] $LaCl_3$–NaCl, [51] NaCl–$NdCl_3$, [48] CsCl–$NdCl_3$ and CsCl–$ErCl_3$, [49] and with some assumptions for the $ErCl_3$–NaCl [52] and KCl–$LnCl_3$ systems [53] (Ln = La, Ce, Pr, and Nd). To calculate the composition of the vapour in these systems we used data on the saturated vapour pressure obtained by tbe boiling point method [54], and information on the gross composition of the vapour obtained by analysis of the condensates.

Table 2 gives the values of the thermodynamic characteristics of the dissociation of $MLnCl_4$, taken from the works cited above [48-53]. It suggests that the stabilities of the r.e.e. chloro-complexes are similar. Along the alkali metal series Na–K–Cs their stability changes in the same sequence as for the dimers of the alkali metal halides. As shown above, there is the same change in stability for the double halides of type $MM'X_3$.

The data are still insufficient to decide reliably how the stability of the $MM'X_4$ double chlorides changes with the nature of the complex-forming element, but since $NaLaCl_4$ is more stable than the corresponding aluminium double chloride by almost 20 kcal mole^{-1} and the double chlorides of boron decompose at ~ 300° without passing into the vapour [55], it can be taken that in the sequence B–Al–La the stability of the double chlorides will increase.

Let us now consider the formation of vapour-phase double compounds of the elements of Periodic Group IV.

The halides of elements in the quadrivalent state have less tendency to form stable double compounds in vapour form than those of elements in a bivalent or tervalent state.

Thus Flengas and Ingraham [56], who studied the behaviour of K_2TiCl_6 in heating, found that this compound, without passing into the vapour, decomposes according to the scheme:

(29) $[K_2TiCl_6] = 2[KCl] + (TiCl_4)$ $\Delta H^{\circ} = 26.4$ kcal mole^{-1}; $\Delta S^{\circ} = 33.3$ e.u.

Just as in the systems CsCl–$TiCl_4$ and RbCl–$TiCl_4$, [57] NaCl–$ZrCl_4$, [58-60] KCl–$ZrCl_4$, [59] and CsCl–$ZrCl_4$, [61] so also in the analogous systems with $HfCl_4$ [61,62] the double compounds do not pass into the vapour, but decompose to form $ZrCl_4$ or $HfCl_4$ vapour.

$ThCl_4$, which is even less volatile, can form a rather stable vapour-phase double chloride [63] with potassium chloride:

(30) $(KThCl_5) = (KCl) + (ThCl_4)$ $\Delta H^{\circ}_{1280} = 49.3 \pm 3$ kcal mole^{-1}; $\Delta S^{\circ}_{1280} = 28.0 \pm 3$ e.u.

TABLE 2. Values of ΔH°_{T}, kcal mole^{-1}, and ΔS°_{T}, e.u., for the dissociation of compounds in the vapour phase.

Compound		Ln				
		La	Ce	Pr	Nd	Er
$NaLnCl_4$	ΔH°_{1400}	69.8	—	—	61.3	63.0
	ΔS°_{1400}	32.8	—	—	32 6	34.0
$KLnCl_4$	ΔH°_{1350}	61.4	61.0	59.3	59.3	59.5
	ΔS°_{1350}	32.6	32.6	32.6	32.6	32.6
$CsLnCl_4$	ΔH°_{1300}	—	—	—	57.2	58.0
	ΔS°_{1300}	—	—	—	29.8	30.8

The authors[63] based the calculation for this system on the pressure and gross composition of the vapour. The form of the compound is determined by analogy with the form of the double fluoride in the $NaF-ZrF_4$ system. The latter system was investigated in detail by Sidorov[64,65]. As a result of the mass spectrometric study of the composition of the vapour in the $NaF-ZrF_4$ system he found that the compound corresponds to the formula $NaZrF_5$ and the value of ΔH°_T was calculated for the process:

(31) $(NaZrF_5) = (NaF) + (ZrF_4)$ $\Delta H^\circ_{1170} = 64.4$ kcal mole^{-1}.

Sense and coworkers[66,67] give for this process very similar values for the thermodynamic characteristics:

$$\Delta H^\circ_{1300} = 67 \text{ kcal mole}^{-1};\ \Delta S^\circ_{1170} = 29 \text{ e.u.}$$

and also suggest the formation of volatile fluorides in the ZrF_4-MF systems (M = Li, Rb).

Comparison of the data for the $NaCl-ZrCl_4$ [58-60] and $NaF-ZrF_4$ [64-67] systems indicates that double compounds of fluorides are more stable than the analogous compounds of chlorides, and this conclusion can evidently be taken as general.

Reverting to the complex chlorides, it is interesting to compare the stability of the double compounds of Groups I, II, III, and IV. Table 3 gives the values of the thermodynamic characteristics of the dissociation of some vapour-phase double compounds.

The choice of the elements in Table 3 is not fortuitous. From their position in the Periodic Table, K, Sr, La, and Th are diagonal analogues, which permits a comparison of the thermodynamic properties of monotypical compounds of these elements.

On comparing the quantities in Table 3, it is seen that there are extrema in the stability characteristics of the vapour-phase double chlorides of the type $KMCl_n$ as n goes from 2 to 5.

Extrema occur because the stability of the vapour-phase double compounds is influenced by at least two opposing tendencies: on the one hand, increase in the charge of the nucleus of the atom of the complex-forming element in the series K–Sr–La–Th, on the other, an increase in the coordination number, and consequently a rise in the repulsion energy of the ligands (Cl) for one another.

The increase in stability of the compounds $MM'Cl_n$ on going down the groups of the Periodic Table which we noted earlier becomes understandable from this point of view, since the coordination number here remains unchanged, whereas the size of the atom of the complex-forming element increases, and consequently the energy of repulsion of the ligands falls.

It is also interesting to note that double compounds which are stable in the vapour are formed when the chlorides reacting have similar volatility. On the other hand, if one of the chlorides has much greater volatility than the other, then the degree of association and the energy of complex formation in the vapour are much less. This can be illustrated by the examples quoted above for reactions in the systems $KCl-M'Cl_4$ (M' = Ti, Zr, Hf, Th). At the same temperature the saturation vapour pressures of titanium, zirconium, and hafnium chlorides are respectively 10^{12}, 10^7, and 10^8 times the vapour pressure of KCl. As already noted, these chlorides do not form volatile double compounds. On the other hand, $ThCl_4$, which has a saturation vapour pressure almost the same as that of KCl, forms the stable vapour-phase compound $KThCl_5$.

TABLE 3.

Equilibrium	ΔH°_T, kcal mole^{-1}	ΔS°_T, e.u.	Reference
$(KKCl_2) = (KCl) + (KCl)$	44.5	28.4	9
$(KSrCl_3) = (KCl) + (SrCl_2)$	67	32	25
$(KLaCl_4) = (KCl) + (LaCl_3)$	61	33	47
$(KThCl_5) = (KCl) + (ThCl_4)$	49	28	56

In conclusion we shall refer to the problem of the vaporisation of ammonium double halides. The facts given above show that double chlorides of the type $MM'Cl_n$ are rather involatile compounds, but stable in the vapour. On the other hand, double chlorides based on ammonium chloride are thought by many authors to be readily volatile.

Thus, Morozov and Toptygin[68], in studying the $AlCl_3-NH_4Cl$ system by the flow method, supposed that the compound NH_4AlCl_4 volatilises without decomposition and found its boiling point to be 402°. In the same system results obtained[69] by a static method indicate that the composition with 50 mole % has maximal boiling point.

Investigators of the $NH_4Cl-FeCl_3$ system[70] found that the compound $FeCl_3.NH_4Cl$ not only exhibits a congruent melting point, but also boils without decomposition and the boiling point of the melt with 50 mole % composition is maximal, as in the $NH_4Cl-AlCl_3$ system.

Li[71] states that $(NH_4)_2SnCl_6$ sublimes at 412°, whereas the alkali metal hexachlorostannates decompose without entering the vapour.

Note that in all the studies mentioned above there is no direct proof of the existence of double chlorides of the type $NH_4M'Cl_x$ in vapour form.

The conclusion that the ammonium double chlorides vaporise (or sublime) without decomposition is usually based on the fact that the condensate obtained in the vaporisation has the same composition as the initial compound. However, when the double compound is formed by ammonium chloride and a rather volatile chloride ($AlCl_3$, $FeCl_3$, $SnCl_4$, etc.) the composition of the condensate and the original compound will be the same even if the compound dissociates completely in the vapour but then is formed again on condensation, as happens in the vaporisation of NH_4Cl. When the double compound is formed by ammonium chloride and another relatively more involatile chloride, then such behaviour is impossible and the composition of the condensate will not correspond to the composition of the compound, as for example, in the $NH_4Cl-ZnCl_2$ and $NH_4Cl-CdCl_2$ systems[70]. Such behaviour by ammonium salts is easy to explain qualitatively. It is well known that the stabilisation of such forms is connected with the formation of the NH_4^+ ion. On transfer to the vapour the degree of ionicity of the bonds in the molecules drops sharply, which in ammonium compounds should lead to marked weakening of them.

Hence there is still no single opinion concerning the formation of ammonium double chlorides in vapour form.

III. INCREASE IN THE THERMAL STABILITY OF COMPLEX HALIDES ON VAPORISATION

To determine whether strengthening or weakening of bonds in complex chlorides occurs on vaporisation it is obviously necessary to compare their stability in relation

to dissociation into simple chlorides in the condensed and vapour states.

The dissociation of double chlorides in these states of aggregation can be related to one another by the following scheme:

Scheme 2

$[MM'Cl_{n+1}] = [MCl] + [M'Cl_n]$	ΔH_1°;	ΔS_1°
$[MCl] = (MCl)$	ΔH_2°;	ΔS_2°
$[M'Cl_{n+1}] = (M'Cl_n)$	ΔH_3°;	ΔS_3°
$[MM'Cl_{n+1}] = (MM'Cl_n)$	ΔH_4°;	ΔS_4°
$(MM'Cl_{n+1}) = (MCl) + (M'Cl_n)$	ΔH_5°;	ΔS_5°

$$\Delta H_5^\circ - \Delta H_1^\circ = (\Delta H_2^\circ + \Delta H_3^\circ) - \Delta H_4^\circ,$$
$$\Delta S_5^\circ - \Delta S_1^\circ = (\Delta S_2^\circ + \Delta S_3^\circ) - \Delta S_4^\circ.$$

According to Scheme 2, bond strengthening in the compound on passing into the vapour is determined by the difference in the thermodynamic characteristics of the first and last processes and appears as the result of the competition of the volatility of the double chloride (ΔH_4°) and of the dissociation products (ΔH_2° and ΔH_3°).

The quantities ΔS_2°, ΔS_3°, and ΔS_4° vary little for the different halides; therefore the difference ($\Delta S_2^\circ + \Delta S_3^\circ$) - ΔS_4° can be taken as constant at ~ 25 e.u. At 1000–1300°K such a change in entropy will correspond with a change in free energy of 25–30 kcal mole^{-1}, that is,

$$\Delta G_5^\circ - \Delta G_1^\circ = (\Delta H_5^\circ - \Delta H_1^\circ) - (25\text{-}30)T.$$

Consequently, the strengthening of the double compounds will take place if (ΔH_5° - ΔH_1°) ≥ 25–30 kcal mole^{-1}. From the relation

$$\Delta H_5^\circ - \Delta H_1^\circ = (\Delta H_2^\circ + \Delta H_3^\circ) - \Delta H_4^\circ$$

it can be concluded that the quantities ΔH_2, ΔH_3, and ΔH_4 (that is, the volatility characteristics of the simple and double chlorides) determinine the strengthening or weakening of binding in the double compound on passage into the vapour and, consequently, also the possibility of its existence. Let us examine this question by specific examples.

In the first example we will examine the vapour-phase double chlorides of the r.e.e. and potassium.

For the dissociation of these compounds:

(32) $$(KLnCl_4) = (KCl) + (LnCl_3),$$

where Ln = La, Ce, Pr, Nd, and Er, very similar thermodynamic characteristics have been proposed[50-53].

$$\Delta H_{1350}^\circ = 60 \text{ kcal mole}^{-1};\quad \Delta S_{1350}^\circ = 32.6 \text{ e.u.}$$

In the same studies the following characteristics have been proposed for the sublimation of the double chloride:

(33) $[KLnCl_4] = (KLnCl_4)$ $\Delta H_T^\circ = (60\text{—}70)$ kcal mole^{-1}; $\Delta S_T^\circ = 41$ e.u.

Hence in the example under consideration both the double chlorides and their dissociation products are of low volatility. Thus, for $LnCl_3$ (ΔH_S° = 75–65 kcal mole^{-1}, ΔS_S° = = 45–42 e.u.)[72] and for KCl (ΔH_S° = 53.3 kcal mole^{-1}, ΔS_S° = = 33.3 e.u.)[14], the value of ΔH_4° according to Baev's estimate[73] is ~ 4–6 kcal; therefore the difference (ΔH_2° + ΔH_3°) - ΔH_4° will here be greater than the quantity ~ 55 kcal mole^{-1}, which ensures strengthening of the bonds in the complex during vaporisation.

We will consider a second, frequently encountered, example that occurs when the double compound and one of the dissociation products is of low volatility but the other is volatile.

The two chlorides of different volatility KCl and $TiCl_4$ (ΔH_e = 9.6 kcal mole^{-1}) form a compound K_2TiCl_6, which, as is well known[56], decomposes above 300°:

(34) $$[K_2TiCl_6] = 2[KCl] + (TiCl_4)$$ $\Delta H_{920}^\circ = 26{,}4 \pm 1.3$ kcal mole^{-1}; $\Delta S_{920}^\circ = 28{,}5 \pm 2.3$ e.u.

This process proceeds without noticeable appearance of potassium chloride in the condensate† which could serve as an indication of the formation of the double compound in the vapour to even a slight extent. We will compare this reaction with the hypothetical appearance in the vapour of $KTiCl_5$ (by analogy with $NaZrF_5$):[55]

(35) $$[K_2TiCl_6] = [KCl] + (KTiCl_5).$$

Let the experimentally imperceptible equilibrium in the vapour:

$$(KTiCl_5) = (KCl) + (TiCl_4),$$

be characterised by the value ΔS° = 28 e.u., like the analogous process of the dissociation of $KThCl_5$:[63]

$$\Delta H_{610}^\circ = 27 \text{ kcal mole}^{-1}.$$

Let us draw up Scheme 3:

Scheme 3

		ΔH kcal mole^{-1}	ΔS, e.u.
(a)	$[K_2TiCl_6] = 2[KCl] + (TiCl_4)$	$\Delta H_1^\circ = 26.4$	$\Delta S_1^\circ = 33.3$
(b)	$[KCl] = (KCl)$	$\Delta H_2^\circ = 50.2$	$\Delta S_2^\circ = 32{,}6$
(c)	$(KTiCl_5) = (KCl) + (TiCl_4)$	$\Delta H_3^\circ = (\leqslant 32)$	$\Delta S_3^\circ = (28)$
(d)	$[K_2TiCl_6] = [KCl] + (KTiCl_5)$	ΔH_4° (⩾45)	$\Delta S_4^\circ = (38)$

From the experimental data on the vapour pressure of ($TiCl_4$) over $[K_2TiCl_6]$ 1 atm is reached at 798°K. Let us suppose that the condition of near involatility of the double compound at this temperature corresponds to a $KTiCl_5$ pressure ≤ 10^{-4} atm. Starting from this value at ΔS_4° = = 38 e.u. we find for equilibrium (*d*) $\Delta H_4^\circ \geqslant 45$ kcal mole^{-1}, whence for equilibrium (*c*) we obtain $\Delta H_3^\circ \leqslant 32$ kcal mole^{-1}. If on the basis of these quantities we calculate ΔG_T° of stabilisation according to Scheme 2, we obtain ΔG_T° = = 28 - $T \times 28 \times 10^{-3}$ kcal mole^{-1} from whence it follows that in the vapour $KTiCl_5$ has enhanced stability only up to 1000°K, when its volatility is negligible, whereas under these conditions the decomposition of $[K_2TiCl_6]$ with formation of ($TiCl_4$) has already ceased.

† In the analogous NaCl–$ZrCl_4$ system Korschunov and Gregory[60] note a little NaCl in the condensate but explain this by entrainment of dust. According to their results the only process is:

(36) $$[Na_2ZrCl_6] = 2[NaCl] + (ZrCl_4)\quad \Delta S_{610}^\circ = 28 \text{ e.u.}$$

The following example, in which a rather difficultly volatile compound decomposes on heating to give two readily volatile compounds, is encountered comparatively rarely. An example is the equilibrium:

$$(37)\qquad [NH_4Cl] = (NH_3) + (HCl) \qquad \begin{matrix}\Delta H^\circ_{298} = 42.4 \text{ kcal mole}^{-1},\\ \Delta S^\circ_{298} = 68.4 \text{ e.u.}\end{matrix}$$

The values ΔH° = 9.4 kcal mole^{-1} and ΔS° = 3.1 e.u. have been proposed[74-76] for the dissociation of ammonium chloride in the vapour:

$$(38)\qquad (NH_4Cl) = (NH_3) + (HCl).$$

Combining these two equilibria, for the sublimation of ammonium chloride we obtain ΔG° = 33 000 - 37T, from which at T = 620°K the saturated vapour pressure of $NH_4Cl \simeq 0.3$ mm, whereas at this temperature its dissociation pressure reaches 1 atm.

These examples lead to the following conclusions.

1. A double compound can be present in vapour in appreciable quantities if the thermodynamic characteristics of its volatility are close to the analogous quantities for the dissociation products.

2. The lower the volatility of the dissociation products (that is, the greater ΔG°_2 and ΔG°_3 in Scheme 2), the more stable the initial compound in the vapour state (the greater ΔG°_5) and the more it is stabilised on transfer to the vapour (the greater the difference ΔG°_5 - ΔG°_1).

On the other hand, if we write the balance equation compiled according to Scheme 2 in the following form:

$$\Delta G^\circ_5 + \Delta G^\circ_4 = \Delta G^\circ_1 + \Delta G^\circ_2 + \Delta G^\circ_3,$$

then we see that in each specific instance the sum ΔG°_5 + + ΔG°_4, that is, the sum of the characteristics of stability and volatility of the double compound, will be constant. This signifies that the greater the volatility of the double compound (the less ΔG°_4), the greater its stability in the vapour state (the greater ΔG°_5).

IV. CONNECTION BETWEEN COMPLEX FORMATION AND DIMERISATION OF COMPOUNDS IN THE VAPOUR STATE

In considering the vapour states of complex compounds formed by the halides of the alkali metals with those of the elements of Periodic Groups II, III, and IV, it is noted[7,48-52] that their stability alters along the series of alkali metals symbathically with the stability of the dimeric alkali metal chlorides. The same symbathic nature is observed in the change in stability of the complex chlorides and dimeric molecules of chlorides of complex-forming elements.

For example, the heats of dissociation of the $KMgCl_3$ and $KBeCl_3$ molecules[30] are 58.0 and 48.0 kcal mole^{-1}, but those of the dimers[77,78] Mg_2Cl_4 and Be_2Cl_4 are 39.2 and 23.0 kcal mole^{-1} respectively. Hence the molecule of the complex chloride as it were inherits the properties of the dimeric molecules of the initial chlorides. The vapour-phase complex chlorides, like the vapour-phase dimers of the simple chlorides, are usually formed by two molecules, for example, $KMgCl_3$, $NaAlCl_4$, $MLnCl_4$, $KThCl_5$, etc., that is, in form these are substituted dimers, formed not by the same, but by different molecules.

Complex chlorides composed of more than two molecules of simple chlorides are encountered very rarely; just as in the vaporisation of pure chlorides the vapour consists mainly of monomeric and dimeric molecules, but trimers and higher molecular weight polymers are usually observed in much smaller proportions.

The formation of molecules of complex chlorides can be represented as a substitution:

$$(39)\qquad (M_2Cl_{2n}) + (M'_2Cl_{2m}) = 2(MM'Cl_{n+m}).$$

When the reacting dimers have similar properties the heat of substitution is close to zero, for example[16,20]:

$$(40)\qquad (Rb_2Cl_2) + (K_2Cl_2) = 2(RbKCl_2)\quad \Delta H^\circ \simeq 0$$
$$(41)\qquad (Na_2F_2) + (K_2F_2) = 2(NaKF_2)\quad \Delta H^\circ = -2.9 \text{ kcal mole}^{-1}.$$

On going to the double compounds of the alkali metal chlorides with the chlorides of the elements of Periodic Groups II and III the difference in properties of the simple chlorides rises, and there is a corresponding increase in the ΔH° of the substitution. For example[30,43]:

$$(42)\qquad (Na_2Cl_2) + (Al_2Cl_6) = 2(NaAlCl_4)\quad \Delta H^\circ = -27 \text{ kcal mole}^{-1}$$
$$(43)\qquad (Na_2Cl_2) + (Be_2Cl_4) = 2(NaBeCl_3)\quad \Delta H^\circ = -22 \text{ kcal mole}^{-1}.$$

According to Scheme 1 considered above, in its stability to dissociation into simple chlorides a double chloride either approaches the more stable dimer or surpasses it, depending on the heat of substitution. In this connection the concentration of the double chloride in the vapour is either greater than that of each of the dimers or approximately the same as the more stable of the dimers. To illustrate this position we will consider Scheme 4:

Scheme 4

$[MCl_n] = (M_2Cl_{2n})$	ΔH_1	ΔS_1
$[M'Cl_m] = (M'_2Cl_{2m})$	ΔH_2	ΔS_2
$MM'Cl_{n+m}] = [MCl_n] + [MCl_m]$	ΔH_3	ΔS_3
$MM'Cl_{n+m}) = {}^1/_2(M'_2Cl_{2n}) + {}^1/_2(M'_2Cl_{2m})$	ΔH_4	$\Delta S_4 \simeq 0$
$[MM'Cl_{n+m}] = (MM'Cl_{n+m})$	ΔH_5	ΔS_5

$\Delta H_5 = {}^1/_2(\Delta H_1 + \Delta H_2) + (\Delta H_3 - \Delta H_4)$
$\Delta S_5 = {}^1/_2(\Delta S_1 + \Delta S_2) + \Delta S_3$

Usually $\Delta H_4 > \Delta H_3$; therefore the enthalpy of sublimation of the complex chloride (ΔH_5) is less than the arithmetic mean of the heats of sublimation of the dimers ($\frac{1}{2}\Delta H_1 + \frac{1}{2}\Delta H_2$). At the same time the change in the entropy of sublimation of the complex chloride is greater than the arithmetic mean of the entropies of sublimation of the dimers by the quantity ΔS_3, since $\Delta S_4 \simeq 0$ as the entropy of a reaction proceeding without change in the number of moles of gas.

In this connection the sublimation of a complex chloride can be energetically more favourable than the sublimation of dimers and therefore its concentration in the vapour is significant even when the dimerisation of one of the chlorides is experimentally imperceptible.

From this point of view the existence in the vapour of a complex chloride can indicate the possibility of dimerisation of the simple chlorides which form it.

When the thermodynamic characteristics of the dissociation of a complex chloride (ΔH°_1 and ΔS°_1) are known, for

example, for $KM'Cl_{n+1}$, then the energy‡ of dimerisation of a chloride MCl_n can be calculated by the method already proposed[6]. The thermodynamic Scheme 5 is drawn up:

Scheme 5

$(KM'Cl_{n+1}) = (KCl) + (M'Cl_n)$	ΔH_1°	$\Delta S_1^\circ \simeq 30$ e.u.
$(KM'Cl_{n+1}) = {}^1/_2(K_2Cl_2) + {}^1/_2(M_2Cl_{2n})$	ΔH_δ°	$\Delta S_\delta^\circ \simeq 0$
${}^1/_2(K_2Cl_{2n}) = (KCl)$	$\Delta H_2^\circ = 22.3$ kcal mole^{-1}	
	$\Delta S_2^\circ = 14.2$ e.u.	
${}^1/_2(M_2Cl_{2n}) = (MCl_n)$	${}^1/_2\Delta H_{dim}^\circ = \Delta H_1^\circ - \Delta H_\delta^\circ - \Delta H_2^\circ$	
	${}^1/_2\Delta S_{dim}^\circ = \Delta S_1^\circ - \Delta S_2^\circ$	

On the basis of many comparisons in this work[6] values for ΔH_δ° from 14 to 22 kcal mole^{-1} are proposed, depending on the position of the element in the Periodic System. The energies of dimerisation for the chlorides calculated in that work agree satisfactorily with the available experimental data. For the dimerisation of the alkaline earth metal chlorides, processes which have not been studied, the following values for the energies have been evaluated: 45, 50, and 42 kcal × × mole^{-1} for $CaCl_2$, $SrCl_2$, and $BaCl_2$ respectively. Although these values are rather high, and this shows the stability of the dimeric molecules in the vapour, they do not contradict the well-known monomeric nature of calcium, strontium, and barium chlorides in the vapour. The fact is that in the range 1000–1500°K the vapour pressure of the alkaline earth metal chlorides is low (1–20 mmHg) and consequently the degree of association should also be small.

In the general form the expression for the degree of association of the species in the saturated vapour has the form[6]:

$$\alpha = \frac{1}{1 + 0.5\exp\left(-\frac{\Delta S^\circ_{sub} - \Delta S^\circ_{diss.dim}}{R}\right)\exp\left(\frac{\Delta H^\circ_{sub} - \Delta H^\circ_{diss.dim}}{RT}\right)},$$

from which it follows that the value of α is determined by the difference in the thermodynamic characteristics of sublimation (vaporisation) and the dissociation of the dimer and also by the temperature.

This means that the degree of association in the vapour is determined not solely by the characteristics of stability of the dimeric molecules. High values of ΔH° for the dissociation of dimers can go with very low degrees of association in the vapour and contrariwise. Examples of this are $FeCl_3$ and KCl. The former is almost completely dimerised in the vapour at the boiling point ($\alpha = 1$) whereas the latter has the value $\alpha \simeq 0.04$ at the same temperature, although the dimer Fe_2Cl_6 is less stable than K_2Cl_2 ($\Delta H^\circ_{diss.dim} = 31.6$ and 44.5 kcal mole^{-1} respectively)[14,79].

It follows that instances when experiment does not disclose dimeric (or polymeric) molecules cannot always be proof of the instability of the latter, but is evidence only of the insufficient sensitivity of the method. In this respect the following example is instructive. An investigation of the vapour-phase chlorides of the rare-earth elements by electron diffraction[77] showed that they are monomers but in a mass spectrometric analysis of the vapour of the same chlorides[81] ions of the $Ln_2Cl_5^+$ type are observed, that is, fragments of a dimeric molecule.

‡ Strictly "enthalpy of dimerisation" (Ed. of Translation).

Judging by the thermodynamic characteristics of the dissociation:

$$(Ln_2Cl_6) = 2(LnCl_3) \quad \begin{matrix}\Delta H^\circ_{1000} \simeq 40 \text{ kcal mole}^{-1} \\ \Delta S^\circ_{1000} \simeq 30 \text{ e.u.}\end{matrix}$$

the dimeric molecules are completely stable, but since at 1000°K the vapour pressure of the r.e.e. chlorides is very low ($\sim 10^{-3}$ mmHg) the vapour contains only 0.1–1% of dimeric molecules and therefore it is impossible to detect them by electron diffraction.

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As the above material shows, the contemporary state of the problem of vapour-phase complex halides is to a significant degree on the level of the accumulation of facts. Attempts to generalise and make recommendations run into difficulties on account of the absence of information about structures and the nature of the bonds in these compounds, even without mentioning the inadequate thermodynamic study and the complete absence of data on the kinetics of the formation and breakdown of complex vapour-phase species. However, although the facts are few, their treatment is already of practical and theoretical importance.

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MECHANISM OF REACTIONS OF ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

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