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Stability of Gaseous Complexes between Two- and Three-Valent Metal Halides

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The formation of gaseous complexes according to $MX_2(s) + 2LX_3(g) = ML_2X_8(g)$ was measured for the following compounds (in parentheses are mean temperature; method of investigation): $MgFe_2Cl_8(g)$, $\log K = 4150/T - 4.59$ (885 K; transpiration, chemical transport); $CaFe_2Cl_8(g)$, $\log K = 2660/T - 4.56$ (930 K; transpiration, chemical transport); $SrFe_2Cl_8(g)$, $\log K \simeq 2960/T - 4.51$ (1010 K; chemical transport); $BaFe_2Cl_8(g)$, $\log K \simeq 2250/T - 4.52$ (970 K; chemical transport); $CoGa_2Cl_8(g)$, $\log K \simeq 1860/T - 4.74$ (670 K; VIS spectroscopy); $CoAl_2Br_8(g)$, $\log K = 3500/T - 4.79$ (610 K; transpiration, VIS spectroscopy); $CuAl_2Cl_8(g)$, $\log K = 4450/T - 4.84$ (555 K; transpiration, VIS spectroscopy). The stability of gaseous complexes is discussed in terms of a simple thermodynamic model.

Introduction

During the last few years, there has been an increasing interest in gaseous complexes of metal halides (see ref 1–8 in ref 1). Most of the recent research has dealt with gaseous complexes formed between chlorides of bivalent metals and aluminium or ferric chloride as shown in reaction 1, where M

$$MX_2(s) + 2LX_3(g) \rightleftharpoons ML_2X_8(g) \qquad (1)$$

= alkaline earth metal, transition metal; L = Fe, Al; X = Cl.

Because we were interested in stability trends, we investigated the formation of the following gaseous complexes: $MgFe_2Cl_8(g)$, $CaFe_2Cl_8(g)$, $SrFe_2Cl_8(g)$, $BaFe_2Cl_8(g)$, $CoGa_2Cl_8(g)$, $CoAl_2Br_8(g)$, $CuAl_2Cl_8(g)$.

Methods and Computations

Chemicals. Anhydrous $FeCl_3$, $CoBr_2$, and MCl_2 (M = Mg, Ca, Sr, Ba) were prepared from analytical grade hydrated salts by standard procedures.[2] Commercial anhydrous $AlCl_3$ was purified by subliming it under dynamic vacuum from an $AlCl_3$–charcoal mixture.[3] Anhydrous $GaCl_3$ was supplied by courtesy of the Alusuisse Co., Neuhausen, Switzerland.

Transpiration. The equilibrium constants of reaction 1 for the formation of $MgFe_2Cl_8(g)$, $CaFe_2Cl_8(g)$, and $CuAl_2Cl_8(g)$ were measured by transpiration with equipment described elsewhere.[13,14] A stream of argon or nitrogen first passed through solid LCl_3 (140–250 °C) and then through $MgCl_2$ (575–650 °C), $CaCl_2$ (600–715 °C), or $CuCl_2$ (230–330 °C). The salt vapors entrained with the inert gas were condensed upstream and the condensates were analyzed by atomic absorption or (and) chelatometry.

In the determination of the stability of $CoAl_2Br_8(g)$, $AlBr_3$ was generated in situ by passing the inert gas first through liquid Br_2 at 0 °C and then through aluminum shot (450–550 °C).

The amount of inert carrier gas passing through the salts was measured with a calibrated gas meter and the flow rate was read from a Fisher-Porter flowmeter. In the range of flow rates used (approximately 7–80 $cm^3\ min^{-1}$) the equilibrium constants of reaction 1 were independent of the flow rate, proving that equilibrium between flowing gases and $MX_2(s)$ was established.

At the equilibrium temperature the volume V_{tot} of all the gases passing through the transpiration apparatus is

$$V_{tot} = V_{carrier\ gas} + V_{L_2X_6} + V_{LX_3} + V_{complex} + V_{MX_2} \qquad (2)$$

The relative magnitudes of these volumes are

$$V_{carrier} \gg V_{L_2X_6} > V_{LX_3} > V_{complex} \gg V_{MX_2} \qquad (3)$$

and consequently

$$V_{tot} \simeq \left[n_{carrier} + \frac{n_{L,tot}}{2}\right]\frac{RT}{p_{barom}} \qquad (4)$$

where n is the number of moles, $R = 0.08205$ l. atm $mol^{-1}\ deg^{-1}$, T is the equilibrium temperature (K), and p_{barom} is the atmospheric pressure (0.923 ± 0.013 atm). $n_{carrier}$ is calculated from the measured volume of the carrier gas while $n_{L,tot}$ is obtained from the analysis of the entrained and afterward condensed L_2X_6. The vapor pressure p_c of the gaseous complex follows from

$$p_c = \frac{n_{MX_2}RT}{V_{tot}} - p_{MX_2} \qquad (5)$$

where n_{MX_2} is known from the analysis of the entrained MX_2 and p_{MX_2} is taken from the literature.[4,5] In most of the experiments $p_c \gg p_{MX_2}$.

If the mass balance

$$n_{LX_3,tot} = 2n_{L_2X_6} + n_{LX_3} + 2n_{ML_2X_8} \qquad (6)$$

is combined with the perfect gas law and with the dissociation equilibrium of $L_2X_6(g)$ (Al_2Cl_6,[6] Al_2Br_6,[5] Fe_2Cl_6[7]), eq 7 is obtained

$$p_{LX} = \frac{-K_{diss}}{4} + \left[\left(\frac{K_{diss}}{4}\right)^2 + \frac{K_{diss}n_{L,tot}p_{barom}}{2n_{carrier} + n_{L,tot}} - K_{diss}p_c\right] \qquad (7)$$

which allows us to calculate p_{LX_3}.

As only a small fraction of the total amount of LX_3 is tied up in the complex, its stoichiometry, assumed to be ML_2X_8 in eq 6, has almost no effect on p_{LX_3}. Furthermore the system is buffered with

Table I. Entrainment Measurements of the Equilibrium $MX_2(s) + 2LX_3(g) = ML_2X_8(g)$

T, K	K, atm^{-1}	T, K	K, atm^{-1}
$MgFe_2Cl_8$		$CaFe_2Cl_8$	
848	1.88	873	2.50×10^{-2}
873	1.32	933	2.24×10^{-2}
923	0.93	988	1.50×10^{-2}
$CoAl_2Br_8$		$CuAl_2Cl_8$	
573	7.63	503	124.9×10^{2}
598	7.00	555	17.59×10^{2}
623	6.73	603	4.10×10^{2}
653	6.27		

respect to p_{LX_3} by the dissociation equilibrium of $L_2X_6(g)$.

With p_c from eq 5 and p_{LX_3} from eq 7 the equilibrium constant of reaction 1 can be calculated

$$K = p_{ML_2X_8}/(p_{LX_3})^2 \tag{8}$$

Results are summarized in Table I while more detailed information is presented in Tables II–IV.[45]

VIS Spectroscopy. The spectra of $CoGa_2Cl_8(g)$, $CuAl_2Cl_8(g)$, and $CoAl_2Br_8(g)$ [$=ML_2X_8(g)$] were recorded with a single-beam, double-prism Zeiss PMQ2 spectrophotometer modified for high-temperature measurements.[13] Quartz cells of 2-cm diameter and 10-cm optical path length were charged in a drybox with $CoCl_2$ and $GaCl_3$ or $CuCl_2$ and $AlCl_3$ or $CoBr_2$ and $AlBr_3$ and sealed at $p < 10^{-4}$ Torr. The difference of absorbance between sample and reference cell (=baseline) was measured at room temperature and assumed not to vary with temperature.

The molar absorptivity ϵ of $ML_2X_8(g)$ was determined by measuring the absorbance A in cells containing no solid or liquid MX_2. After this measurement, the amount of MX_2 in the cells was determined by atomic absorption and ϵ was calculated using eq 9 where A is the

$$\epsilon = AV/n_{MX_2}l \tag{9}$$

absorbance, V is the volume of the cell (l.), n_{MX_2} is the number of moles of $CoCl_2$, $CuCl_2$, or $CoBr_2$, and l is the optical path length (10 cm).

To determine the equilibrium constant of reaction 1 cells containing gaseous LX_3 and an excess of solid MX_2 were used. The partial pressure of the gaseous complex, p_c, was calculated from the absorbance by eq 10. The partial pressure of LX_3 was calculated from

$$p_c = ART/\epsilon l \tag{10}$$

the analytical data $n_{LX_3,\text{tot}}$, p_c, V_{cell}, and T using eq 11. To derive

$$p_{LX_3} = \frac{-K_{\text{diss}}}{4} + \left[\left(\frac{K_{\text{diss}}}{4}\right)^2 + K_{\text{diss}}\left(\frac{RTn_{LX_3,\text{tot}}}{2V_{\text{cell}}} - p_c\right)\right]^{1/2} \tag{11}$$

eq 11 the same assumptions have to be made as in the derivation of eq 7.

$CuAl_2Cl_8(g)$. As the spectrum was measured in a chlorine atmosphere to avoid decomposition of $CuCl_2$[32] (this precaution was later found to be necessary only above ~650 K), only the long-wavelength part of the spectrum was recorded. It showed a broad maximum at 850 nm compatible with a $CuCl_3$ as well a $CuCl_4$ chromophore.[23] According to a recent Raman spectroscopy study[11] $CuAl_2Cl_8(g)$ has the structure shown in Figure 1.

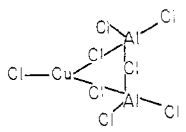


Figure 1. Proposed structure[11] of $CuAl_2Cl_8(g)$.

In the temperature range covered by our measurements (490–650 K) the molar absorptivity did not depend on temperature, $\epsilon_{850\text{nm}}$ 100.35 M^{-1} cm^{-1} (Table V[45]). Four optical cells (path length 10 cm) containing an excess of solid $CuCl_2$, approximately 1 atm of Cl_2, and various amounts of $AlCl_3$ (64.8–171.0 mg) were heated and cooled slowly in the furnace of the spectrophotometer while their absorbance at 850 nm was recorded. Identical absorbances were observed in the heating and cooling cycle. For each cell the absorbance at 493.1, 523.1, 553.1, 583.1, and 613.1 K was extrapolated from an $A = f(T)$ graph. By use of eq 10 to calculate $p_{CuAl_2Cl_8}$ ($=p_c$) and eq 11 to calculate p_{AlCl_3}, the equilibrium constant (eq 8) was calculated. Results are shown in Tables V[45] and VI.

Table VI. Spectophotometric Measurements of the Equilibrium $MX_2(s) + 2LX_3(g) = ML_2X_8(g)$

T, K	K, atm^{-1}	T, K	K, atm^{-1}
$CuAl_2Cl_8$		$CoAl_2Br_8$	
493	13 804	543	70.3
523	3 950	558	44.4
553	1 360	573	27.2
583	525	588	17.8
613	232	603	11.7
		618	7.9
$CoGa_2Cl_8$		633	5.42
646	1.63×10^{-2}	663	2.78
673	1.07×10^{-2}	683	1.90
700	0.86×10^{-2}	713	1.07

$CoAl_2Br_8(g)$. The molar absorptivity of $CoAl_2Br_8(g)$ depends appreciably on temperature: $\epsilon_{700\text{nm}} = 302 - 0.167T$ M^{-1} cm^{-1} (Table VII[45]).

Three cells containing gaseous aluminum bromide and an excess of solid cobalt bromide were heated and cooled while their absorbance was recorded. These measurements were evaluated as described above for $CuAl_2Cl_8(g)$. Results are summarized in Tables VI and VII.[45]

It should be mentioned that too large an excess of aluminum bromide resulted in formation of a liquid phase and gave very steep $\log A = f(T^{-1})$ plots. From analogous observations in similar systems ($CuIn_2Cl_8(g)$,[43] $CoIn_2Cl_8(g)$,[44] $CuAl_2Cl_8(g)$[43]) we conclude that in this type of experiment excessively steep $\log A = f(T^{-1})$ plots indicate the formation of a liquid phase from which the evaporation of a gaseous complex apparently is a highly endothermic process.

$CoGa_2Cl_8(g)$. The stability constant of $CoGa_2Cl_8(g)$ was determined in much the same way as those of $CuAl_2Cl_8(g)$ and $CoAl_2Br_8(g)$ mentioned above, but the result is less accurate. Measurements of the equilibrium constants in two different samples agreed within a factor of 2 only (Table IX[45]).

In the meantime a more detailed investigation of the system $CoCl_2/GaCl_3$ has been published by Anundskas et al.[9] and our results agree reasonably well with theirs (Table XIII).

Chemical Transport. Pyrex or quartz ampules of 1.5–3 cm diameter and 12–22 cm length were charged in a drybox with a few hundred milligrams of anhydrous MCl_2 (M = Mg, Ca, Sr, Ba), while $FeCl_3$ was sublimed into the ampule. The ampules were left for one to several days in a two-zone furnace fed from a PID controller. Transport always occurred from the hot to the cold end of the ampule (ΔT = 95–170 K). At the end of the experiment the transport agent was condensed at the source end of the ampule (hot during transport), and the amount of MCl_2 transported as well as the amount of transport agent was determined by atomic absorption or chelatometry.

The transport equilibrium is

$$MCl_2(s) + 2FeCl_3(g) = MFe_2Cl_8(g) \tag{12}$$

If the transport is diffusion controlled, the amount of MCl_2 transported is related to experimental parameters by eq 13, as discussed by

$$m = \Delta p_c \frac{qtD}{sRT} \tag{13}$$

Schäfer;[10] m is the number of moles of MCl_2 transported from T_2 to T_1, Δp_c is the pressure difference between the hot (T_2) and cold (T_1) ends of the ampule (atm), T is the mean temperature in the ampule [$(T_2 + T_1)/2$], D is the diffusion coefficient (cm^2 s^{-1}), q is the section area of the ampule (cm^2), t is the duration of transport (s), s is the length of the ampule (cm), and R = 82 cm^3 atm deg^{-1} mol^{-1}.

If the temperature dependence of the transport equilibrium (13) and the temperature difference between the hot and the cold ends of the ampule are not too small, then

$$p_c(T_1) << p_c(T_2)$$

Table X. Chemical Transport of $\mathrm{MCl_2}$ with $\mathrm{FeCl_3}$ by Equilibrium 12

$\mathrm{MCl_2}$	T_2, K	K_{T_2},[a] atm^{-1}	K_{T_2}(adjusted),[b] atm^{-1}
$\mathrm{MgCl_2}$	798	13.8	2.7
$\mathrm{CaCl_2}$	768	87×10^{-2}	17.4×10^{-2}
$\mathrm{CaCl_2}$	1017	8.7×10^{-2}	1.74×10^{-2}
$\mathrm{CaCl_2}$	1033	4.6×10^{-2}	0.92×10^{-2}
$\mathrm{SrCl_2}$	1000	0.076	1.5×10^{-2}
$\mathrm{SrCl_2}$	1018	0.228	4.6×10^{-2}
$\mathrm{BaCl_2}$	1003	0.027	5.4×10^{-2}

[a] Calculated with a diffusion coefficient estimated according to ref 38. [b] See text.

and consequently

$$\Delta p_c = p_c(T_2) \tag{14}$$

m, q, t, s, and T can easily be measured and therefore all of the parameters, except D, which are needed to determine p_c ($\simeq \Delta p_c$) by eq 13 from a transport experiment are known. As $p_{\mathrm{FeCl_3}}$ can be calculated from the amount of ferric chloride in the ampule, the volume of the ampule, and the dissociation constant of $\mathrm{Fe_2Cl_6(g)}$, the diffusion coefficient D is the only missing piece of data needed to determine the equilibrium constant of reaction 12 from chemical transport experiments. If the diffusion coefficient of $\mathrm{MFe_2Cl_8(g)}$ in $\mathrm{FeCl_3(g)}$ is calculated following the procedure used by Jona and Mandel[38] (Table XI[45]), the resulting stability constants of $\mathrm{MgFe_2Cl_8(g)}$ and $\mathrm{CaFe_2Cl_8(g)}$ are, on the average, around 5 times larger than the ones obtained from the transpiration experiments. Under the conditions of our experiments it has been observed[10] that convection may very well speed up the gas motion, and this can be taken into account by choosing in eq 13 a larger diffusion coefficient than the one estimated from molecular dimensions. As the convective contribution to the gas motion depends mainly on factors which are similar in all of our experiments (temperature, ampule size, pressure), it seems justified to apply the empirical correction factor of 5 also to the equilibrium constant of $\mathrm{SrFe_2Cl_8(g)}$ and $\mathrm{BaFe_2Cl_8(g)}$ (K(adjusted) in Tables X and XI[45]). The results of the chemical transport experiments are summarized in Table X while more detailed experimental information is collected in Table XI.[45]

Stoichiometry of Gaseous Complexes. In the reaction

$$m\mathrm{MX}_b(\mathrm{s}) + h\mathrm{LX}_3(\mathrm{g}) = \mathrm{M}_m\mathrm{L}_h\mathrm{X}_{mb+3h}(\mathrm{g}) \tag{1a}$$

the case $m > 1$ has only been observed for metal chlorides which are known for their tendency to form polymer vapors such as $\mathrm{BeCl_2}$, CuCl, and TlCl.[41] h has been found[42] to assume integer values 1–4, whereby the most abundant complex is always the one with $h = b$. For $m = 1$ the logarithmic form of the mass action law of equilibrium 1a is

$$\log p_c = \log K + h \log p_{\mathrm{LX_3}} \tag{1b}$$

Equation 1b can be used to determine h and $\log K$ by plotting $\log p_c$ vs. $\log p_{\mathrm{LX_3}}$. However, if the system is governed by two or more simultaneous equilibria with different h's, h will not be a constant but it will be a function of $p_{\mathrm{LX_3}}$.[13] Previous studies[6,13,16] have shown that gaseous complexes with $h > b$ are formed to an appreciable extent at $p_{\mathrm{LX_3}} + p_{\mathrm{L_2X_6}} > 1$ atm only. As shown in Table XII, those experiments which allow us to evaluate h were all performed at rather low pressures and therefore, in equilibrium with $\mathrm{MX_2(s)}$, complexes with $h > 2$ will play a minor role if any. The formation of small amounts of complexes with $h = 1$ and the formation of polymer species $(\mathrm{ML}_h\mathrm{X}_{b+3h})_n$ cannot be excluded, but adding all of the evidence it seems safe to say that the equilibria studied are described adequately by reaction 1.

h can be determined from eq 1b with reasonable accuracy only if p_c and $p_{\mathrm{LX_3}}$ embrace, at one temperature, an appreciable range of pressures. Log K could be determined by eq 1b from the same plot as h, but after knowing the integer value of h, we obtain more accurate values of K by evaluating individual data points and averaging the results.

Accuracy of Thermodynamic Data. The accuracy of the equilibrium constant K is influenced by the accuracy of the dissociation constant K_{diss} of $\mathrm{L_2X_6(g)}$ but we shall assume that errors associated with K_{diss} are negligibly small.

It is well-known[4] that the determination of equilibrium constants is less subject to errors than the determination of their temperature dependence which is needed to calculate the second-law enthalpy and entropy values. We therefore decided to estimate the entropy of reaction 1 and to combine this estimate with measured equilibrium constants to find the third-law enthalpy.

Table XII. Stoichiometry of the Reaction $\mathrm{MX_2(s)} + n\mathrm{LX_3(g)} = \mathrm{ML}_n\mathrm{X}_{2+3n}$

M	L	X	Method	$P_{\mathrm{LX_3}} + P_{\mathrm{L_2X_6}}$, atm	No. of data points evaluated	n
Cu	Al	Cl	Transpiration	0.1	15	2.03 ± 0.03
Cu	Al	Cl	Optical	0.6	16	1.96 ± 0.17
Mg	Fe	Cl	Transpiration	0.1	6	1.90 ± 0.69
Ca	Fe	Cl	Transpiration	0.1	6	1.49 ± 0.67
Co	Al	Br	Transpiration	0.1	32	*a*
Co	Al	Br	Optical	1	9	1.90 ± 0.26

[a] Range of pressures is too small.

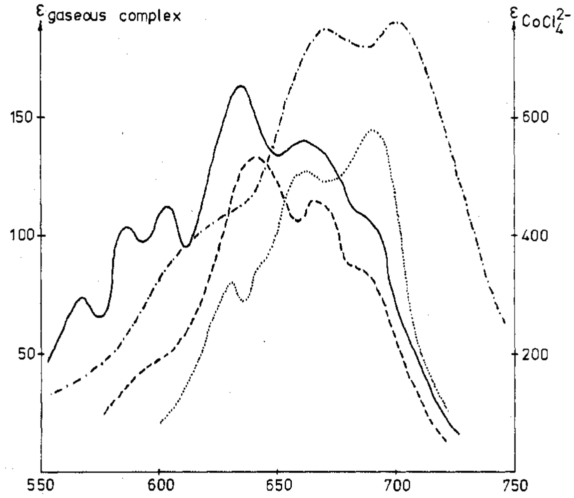


Figure 2. Spectra of (—) $\mathrm{CoAl_2Cl_8(g)}$, (- · · · · ·) $\mathrm{CoAl_2Br_8(g)}$, (- - -) $\mathrm{CoGa_2Cl_8(g)}$, and (· · · ·) $\mathrm{CoCl_4^{2-}(aq)}$.

The entropy of reaction 1 is estimated by first considering reaction 1c where the translational entropy depends only little on mole masses,

$$\mathrm{MX_2(g)} + 2\mathrm{LX_3(g)} = \mathrm{ML_2X_8(g)} \tag{1c}$$

$\Delta S_{\mathrm{transl}}(1\mathrm{c}) \simeq -78$ eu. Unfortunately geometry and vibrational structure of the gaseous complexes are not known, but if we assume that they are related to $\mathrm{MX_2(g)}$ and $\mathrm{LX_3(g)}$, $\Delta S_{\mathrm{rot}}(1\mathrm{c})$ and $\Delta S_{\mathrm{vibr}}(1\mathrm{c})$ will not depend much on mole masses either. We find $\Delta S_{\mathrm{rot}}(1\mathrm{c}) \simeq -35$ eu, $\Delta S_{\mathrm{vibr}}(1\mathrm{c}) \simeq 46$ eu; thus $\Delta S_{298}(1\mathrm{c}) \simeq -67$ eu. One could also estimate $\Delta S(1\mathrm{c})$ on the basis of the following assumptions. Formation of the gaseous complex according to reaction 1c means forming two four-membered rings (see eq 1d), and ΔS of such a reaction should be about twice the entropy of dimerization of gaseous metal halides for which an average of -32 eu (at 298 K) has been deduced from the work of Hastie;[17] thus $\Delta S_{298}(1\mathrm{c}) \simeq -64$ eu. With the averages $\Delta S_{298}(1\mathrm{c}) \simeq -65$ eu and $\Delta S_{\mathrm{subl,MX_2}} \simeq 43$ eu (from literature[4,5,33]), $\Delta S_{298}(1) \simeq 43 - 65 \simeq -22$ eu is obtained. Dewing[16] has found for a series of similar reactions $\Delta S_{298} \simeq -23.7$ eu. This latter value together with $\Delta C_p \simeq 2.5$ cal mol^{-1} K^{-1} [16] was used to calculate the third-law enthalpy of the reactions investigated.

The data in Table XIII show that for the formation of $\mathrm{CuAl_2Cl_8(g)}$ third-law and second-law enthalpies agree within the limits of error. Where the formation of the complexes has been studied by two independent methods, there is closer agreement between third-law than between second-law enthalpies. We therefore are confident that the third-law thermodynamic parameters shown in Table XIII describe the equilibria adequately.

Discussion

Absorption Spectra of $\mathrm{CoL_2X_8(g)}$. In Figure 2 the spectra of $\mathrm{CoGa_2Cl_8(g)}$, $\mathrm{CoAl_2Br_8(g)}$, $\mathrm{CoAl_2Cl_8(g)}$, and $\mathrm{CoCl_4^{2-}(aq)}$ are shown for comparison. Due to the small values of ab-

Table XIII. Enthalpy and Entropy of the Formation of Gaseous Complexes According to $MX_2(s) + 2LX_3(g) = ML_2X_8(g)$

			Second law[a]		Third law; $\Delta S_{298} = -23.7$ cal mol^{-1} deg^{-1}		
Complex	Method	T_{av}, K	ΔH at T_{av}, kcal mol^{-1}	ΔS at T_{av}, cal mol^{-1} K^{-1}	ΔH at T_{av}, kcal mol^{-1}	ΔS at T_{av}, cal mol^{-1} K^{-1}	ΔH_{298},[c] kcal mol^{-1}
$MgFe_2Cl_8$	Transpiration	885	−14.3 ± 4.8	−15.7 ± 5.5	−19.0	−21.0	−20.4
$MgFe_2Cl_8$	Chem transport	798			−18.5	−21.2	−19.8
$CaFe_2Cl_8$	Transpiration	930	−7.4 ± 5.7	−15.7 ± 6.1	−12.2	−20.9	−13.8
$CaFe_2Cl_8$	Chem transport	940			−12.7	−20.8	−14.3
$SrFe_2Cl_8$	Chem transport	1010			−13.6	−20.6	−15.4
$BaFe_2Cl_8$	Chem transport	1000			−10.3	−20.7	−12.1
$CoAl_2Br_8$	Transpiration	613	−1.8 ± 0.3	1.0 ± 0.5	−15.8	−21.9	−16.6
$CoAl_2Br_8$	Spectroscopy	600	−19.5 ± 0.4	−27.5 ± 0.7	−16.2	−21.9	−17.0
$CuAl_2Cl_8$	Transpiration	555	−20.6 ± 1.7	−22.3 ± 3.1	−20.5	−22.1	−21.1
$CuAl_2Cl_8$	Spectroscopy	553	−20.5 ± 0.3	−22.6 ± 0.5	−20.2	−22.2	−20.8
$CoGa_2Cl_8$	Spectroscopy	673	−11.3 ± 16	−25.8 ± 25	−8.5	−21.7	−9.5
$CoGa_2Cl_8$	Ref 9	673	−10.5	−23.5	−9.3	−21.7	−10.2

[a] Systematic errors are not considered. The level of confidence is twice the standard deviation of the least-squares fit to the linear plot log $K = f(T^{-1})$. [b] Calculated from $\Delta S_{298} = -23.7$ cal mol^{-1} deg^{-1} with $\Delta C_p = 2.5$ cal mol^{-1} K^{-1}. [c] Calculated from third-law ΔH at T_{av} with $\Delta C_p = 2.5$ cal mol^{-1} K^{-1}.

sorbance observed in measuring the spectrum of $CoGa_2Cl_8(g)$ it is not surprising that much of the fine structure seen in $CoAl_2Cl_8(g)$ is lost in the $CoGa_2Cl_8(g)$ spectrum. Nevertheless the resemblance of the four spectra is close enough to suggest a tetrahedral or nearly tetrahedral CoX_4 chromophore in all four cases. The following points favor this suggestion.

(a) The intensity of the main absorption band is a much better criterion than its position to distinguish between tetrahedral $CoCl_4$ and octahedral $CoCl_6$ chromophores.[12] The oscillator strengths, $f_{CoCl_4^{2-}(aq)} \simeq 5.9 \times 10^{-3}$, $f_{CoAl_2Br_8(g)} \simeq 2.3 \times 10^{-3}$, $f_{CoGa_2Cl_8(g)} \simeq 2.4 \times 10^{-3}$,[9] and $f_{CoAl_2Br_8(g)} \simeq 2.4 \times 10^{-3}$, have the same order of magnitude while a decrease by 1 order of magnitude would be expected in going from tetrahedral to octahedral coordination of Co(II).[39]

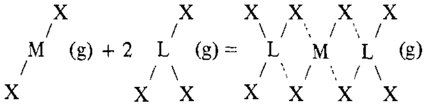
(b) Theory[46] predicts that with increasing temperature the absorption band of an octahedral chromophore such as $CoCl_6$ should gain intensity and should shift to longer wavelength. VCl_6 in $VAl_2Cl_8(g)$ has been shown[40] to follow the prediction of the theory; however, no such feature has been observed in either $CoAl_2Cl_8(g)$,[13] $CoGa_2Cl_8(g)$, or $CoAl_2Br_8(g)$. On the contrary, on increasing temperature the molar extinction coefficients are slightly decreasing without any noticable increase of the half-width of the absorption bands.

(c) Due to size and polarizability of the ligands, tetrahedral coordination around the cobalt is certainly favored if one replaces chloride by bromide, but the measured oscillator strengths for $CoAl_2Cl_8(g)$ and $CoAl_2Br_8(g)$ are almost the same, indicating a similar coordination geometry in both cases.

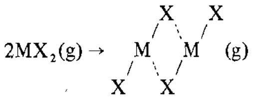
(d) As the spectrum of $CoCl_2$ dissolved in molten $AlCl_3$ has been interpreted[12] as originating from an octahedral $CoCl_6$ chromophore despite its rather large oscillator strength ($f \simeq 0.97 \times 10^{-3}$), it seems not unlikely that the high ligand concentration in $AlCl_3$ melt could cause a slight rearrangement of the tetrahedral coordination sphere of cobalt into an octahedral one without causing an appreciable change in the optical properties. Furthermore, higher coordination numbers in solids or melts as compared to solutions or gases are a common phenomenon.

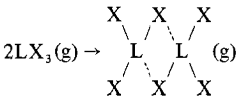
It has recently been suggested by Papatheodorou[15] that equilibrium between tetrahedral ($CoCl_4$) and octahedral ($CoCl_6$) chomophores could exist in gaseous $CoAl_2Cl_8(g)$ but this possibility has been questioned by Anundskas et al.[9]

Thermodynamics of the Formation of Gaseous Complexes. Hastie[17,47] has discussed ways to estimate the enthalpy of the homogeneous formation of 1:1 mixed gaseous metal halides from the enthalpy of dimerization of the constituents. It is very attractive to extend this scheme to the heterogeneous reaction 1 because, as discussed above, ΔS of reaction 1 does not depend much on M and L and therefore, if the free energies of reaction 1 are different for different M's and L's, this difference could be attributed mainly to the enthalpy. To estimate the enthalpy of reaction 1 one might first look at the homogeneous reaction 1d. In the course of this reaction two


(1d)

L---X and two M---X bridging bonds are formed. We may assume that the energy of formation of each pair of bridging bonds is similar to the dimerization energy of the respective individual halides


$\Delta H_{d,MX_2}$


$\Delta H_{d,LX_3}$

Then

$$\Delta H_{react,1d} \simeq \Delta H_{d,MX_2} + \Delta H_{d,LX_3} \quad (15)$$

and the enthalpy of formation of the gaseous complex in the course of reaction 1 would be given by eq 16. This model

$$\Delta H_{f,compl} \simeq \Delta H_{d,LX_3} + \Delta H_{d,MX_2} + \Delta H_{subl,MX_2} \quad (16)$$

to calculate $\Delta H_{f,compl}$ is based on a structure of $ML_2X_8(g)$ which apparently is the one most frequently adopted[41] but not the only possible one.[11,13,15,40] Furthermore the model does not take into account that, according to a recent publication by Hastie,[47] there is a net gain of stability in addition to the sum of the dimerization energies if the gaseous complexes are formed from two halides of different metals with different oxidation states. Therefore $\Delta H_{f,compl}$ calculated according to eq 16 should indicate the lower limit of the stability gain of reaction 1.

Tables XIV[45] and XV[45] list dimerization and sublimation enthalpies for various metal halides while in Table XVI calculated and experimental enthalpies for gaseous complexes are compared.

Although the dimerization enthalpies of the heavier alkali earth chlorides are more negative than the dimerization enthalpies of most other halides of bivalent metals, the stabilities of $CaFe_2Cl_8(g)$, $SrFe_2Cl_8(g)$, and $BaFe_2Cl_8(g)$ are not very

Table XVI. Thermodynamic Data for $MX_x(s) + nLX_y(g) = ML_nX_{ny+x}(g)$; $\Delta H_{f,compl} \simeq (x/2)\Delta H_{d,MX_x} + (n/2)\Delta H_{d,LX_y} + \Delta H_{subl,MX_x}$

	$\Delta H_{f,compl}$, kcal mol^{-1}; $T = 298$ K					
	$LX_y = FeCl_3$, $n = 2$			$LX_y = AlCl_3$, $n = 2$		
MX_x	ΔH_{calcd}	ΔH_{exptl}	Ref	ΔH_{calcd}	ΔH_{exptl}	Ref
$MgCl_2$	−18.3	−20.4	This work	−13.1	−17.7	16
$CaCl_2$	−12.7	−13.8	This work	−7.5	−25.7	
$SrCl_2$	−15.6	−15.4	This work	−10.4		
$BaCl_2$	−12.9	−12.1	This work	−7.7		
$CrCl_2$	−21.7			−16.5	−20.0	22
$MnCl_2$	−21.3	−20.4	16	−16.1	−17.3	16
$FeCl_2$	−27.4			−22.2		
$CoCl_2$	−15.1	−21.0	16	−9.9	−19.5	13
$NiCl_2$	−11.0	−18.4	16	−5.8	−15.3	16
$CuCl_2$	−28.6			−21.4	−21.0	This work
$CdCl_2$		−20.8	16			
$PdCl_2$					−21.3	36
$PtCl_2$					−19.0	37

$ML_nX_{ny+x}(g)$	T, K	ΔH_{calcd}, kcal mol^{-1}	ΔH_{exptl}, kcal mol^{-1}	Ref	$ML_nX_{ny+x}(g)$	T, K	ΔH_{calcd}, kcal mol^{-1}	ΔH_{exptl}, kcal mol^{-1}	Ref
$CoAl_2Br_8$[a]	298	−12.7	−16.8	This work	$NdAl_3Cl_{12}$	800	−42	−34	6
$NiAl_2Br_8$[a]	298	−4.3	−10.0	35	$NaAlCl_4$	1000	+14.1	+3	34
$CoGa_2Cl_8$[a]	298	−1.1	−9.5	This work	$NaFeCl_4$	1000	+11.7	+4	27

[a] ΔH_{exptl} of the formation of $ML_2X_8(g)$ at 298 K was calculated from the references using the average equilibrium constant K_T at mean temperature T, $\Delta S_{298} = -23.7$ cal mol^{-1} K^{-1}, and $\Delta C_p = 2.5$ cal mol^{-1} K^{-1}: $\Delta H_{exptl} = T(2.5 \ln (T/298) - 23.7 - 1.987 \ln K_T) + 2.5(298 - T)$.

high, because the sublimation enthalpies of the heavier alkaline earth chlorides are large and positive. On the opposite side, the sublimation enthalpies of $PdCl_2$, $CdCl_2$, and (probably) $PtCl_2$ are small leading to high stabilities for $PdAl_2Cl_8(g)$, $PtAl_2Cl_8(g)$, and $CdFe_2Cl_8(g)$. Within the transition metal chlorides $FeCl_2$ and $CuCl_2$ should form the most stable complexes with $FeCl_3$ or $AlCl_3$. The formation constant of $FeAl_2Cl_8(g)$ has been shown[1] by chemical transport to be particularly large. Although we investigated $CuAl_2Cl_8(g)$ to verify its predicted high stability, we later found[11] that it very probably has a unique structure (Figure 1) which makes our scheme of thermodynamic estimation inapplicable.

Our model assumes fourfold coordination of M while $CrAl_2Cl_8(g)$,[22] $NiAl_2Cl_8(g)$,[36] and $CoAl_2Cl_8(g)$[15] have been proposed to contain an octahedral MCl_6 chromophore. Perhaps the two additional M–Cl bonds ($AlCl_4$ coordinating with a face instead of an edge) add to the stability of the complex and this could be the reason for the substantial difference between ΔH_{exptl} and ΔH_{calcd} of these compounds. No explanation can be offered for the large difference between ΔH_{exptl} and ΔH_{calcd} in the case of $CaAl_2Cl_8(g)$, but it might be mentioned that $CaCl_2$ and $AlCl_3$ form very stable liquid phases.[1]

From eq 16 and ΔH_d of $Al_2Cl_6(g)$ and $Fe_2Cl_6(g)$[5] it would follow that $\Delta H_{MAl_2Cl_8(g)} - \Delta H_{MFe_2Cl_8(g)} = +5.2$ kcal mol^{-1}. The average value observed, excluding $CaAl_2Cl_8(g)$, is 2.5 kcal mol^{-1}. As the dimerization enthalpy of $AlCl_3(g)$ is less negative than that of $FeCl_3(g)$, gaseous complexes with $AlCl_3$ are less stable than the ones with $FeCl_3(g)$. This however does not imply that the equilibrium pressure of $MAl_2Cl_8(g)$ is smaller than the equilibrium pressure of $MFe_2Cl_8(g)$ if the total amounts of ferric chloride and aluminum chloride in the gas phase are equal, because the more positive dimerization enthalpy of $AlCl_3(g)$ results in a comparatively higher monomer pressure which, with respect to the equilibrium pressure of $ML_2Cl_8(g)$, more than outweighs the lower stability. This is illustrated in Table XVII.

Table XVII. Pressure Data for the System $MCl_2(s) + 2LCl_3(g) = ML_2Cl_8(g)$[a]

	L = Fe		L = Al	
MCl_2	K_{700}, atm^{-1}	p_c, atm	K_{700}, atm^{-1}	p_c, atm
$MgCl_2$	22.0	1.22×10^{-2}	3.16	5.80×10^{-2}
$CaCl_2$	0.19	1.07×10^{-4}	0.45	8.67×10^{-3}
$MnCl_2$	22.0	1.22×10^{-2}	2.37	4.4×10^{-2}
$CoCl_2$	33.9	1.86×10^{-2}	11.53	0.189
$NiCl_2$	5.23	2.91×10^{-3}	0.56	1.07×10^{-2}
$CuCl_2$			33.9	0.43

[a] Closed system; 1 mol of LCl_3/22.4 l.; 700 K.

Stabilities of Gaseous Complexes with Halides Other Than $AlCl_3$ or $FeCl_3$. So far there are few data of stabilities of gaseous complexes of metal bromides. From the proposed method to estimate stabilities one would predict that the stabilities of bromide gaseous complexes would be similar to those of the chlorides because (a) ΔH_d of LX_3 depends only weakly on X and (b) ΔH_d of MX_2 is in general more positive for X = Br than for X = Cl but this adverse effect to the stability of the gaseous complex is counterbalanced by a smaller sublimation enthalpy of the MBr_2.

Due to their lone electron pair, group 5 trichlorides (QCl_3 = PCl_3, $AsCl_3$, or $SbCl_3$) have virtually no tendency to dimerize; i.e., their enthalpy of dimerization is very small. Consequently, gaseous complexes of group 5 trichlorides with MCl_2 will be very unstable although compounds of the type $MQCl_5$ are known in the solid state and in solution.[18] The low stability of $MCl_2(QCl_3)_x(g)$ complexes is illustrated by the fact that $CoCl_2(s)$ could not be transported with PCl_3, $AsCl_3$, or $SbCl_3$,[19] indicating[1] an equilibrium constant smaller than 10^{-4}. $TiCl_4$, VCl_4, and $SnCl_4$ are coordinatively saturated; therefore they have virtually no tendency to dimerize and they do not form gaseous complexes with MCl_2. $NbCl_5$ and $TaCl_5$ do exist as dimers in solution[18] but in the gaseous state dimerization is probably negligible. This is in the line with the very low transport rate observed in the chemical transport of $CrCl_3(s)$ with $NbCl_5(g)$.[1] $CoCl_2$ could not be transported with $NbCl_5(g)$,[19] and according to Kroshunov et al.[21] neither $NbCl_5$ nor $TaCl_5$ forms gaseous complexes with $FeCl_2$.

The dimerization enthalpy of $GaCl_3(g)$ is appreciably less negative than that of $AlCl_3(g)$, and consequently $MGa_2Cl_8(g)$ complexes should be less stable than $MAl_2Cl_8(g)$. This has been verified for the case of $CoGa_2Cl_8(g)$ (Table XVI).

Conclusion

It appears that the right order of magnitude of the stability of gaseous complexes formed between low-volatility and high-volatility metal halides can be rationalized by a rather simple thermodynamic model which correlates dimerization enthalpies of individual metal halides to the stabilities of their gaseous complexes assuming a constant entropy contribution (third law). Postulated relative stabilities of gaseous complexes containing MX_2 and $AlCl_3$, $AlBr_3$, $GaCl_3$, or $FeCl_3$ have been verified by experiments of our own as well as by stability constants reported in the literature. Furthermore the model can be used to interpret the instability of gaseous complexes containing a group 4 tetrahalide or a group 5 trihalide as the volatile partner. It is therefore felt that the model could be useful in predicting stabilities of gaseous complexes in not yet investigated systems.

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Registry No. $MgFe_2Cl_8$, 60840-49-5; $CaFe_2Cl_8$, 44006-14-6; $SrFe_2Cl_8$, 60840-50-8; $BaFe_2Cl_8$, 44006-13-5; $CoAl_2Br_8$, 60873-91-8; $CuAl_2Cl_8$, 58915-60-9; $CoGa_2Cl_8$, 59217-71-9; $MgCl_2$, 7786-30-3; $CaCl_2$, 10043-52-4; $SrCl_2$, 10476-85-4; $BaCl_2$, 10361-37-2; $CoBr_2$, 7789-43-7; $CuCl_2$, 7447-39-4; $CoCl_2$, 7646-79-9; $FeCl_3$, 7705-08-0; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3.

Supplementary Material Available: Tables II–V, VII–IX, XI, XIV, and XV containing experimental data such as extinctions, volumes, results of chemical analysis, etc., which allow the reader to reevaluate the themodynamic data contained in the tables appearing in full in this paper (9 pages). Ordering information is given on any current masthead page.

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Preparation of Magnesium Zinc Hydrides. $MgZnH_4$ and $Mg(ZnH_3)_2$

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Magnesium bis(trihydridozincate) [$Mg(ZnH_3)_2$] and magnesium tetrahydridozincate ($MgZnH_4$) have been synthesized by two different preparative routes. One method involves the reaction of dimethylmagnesium with dimethylzinc in 1:2 and 1:1 molar ratios in ether followed by addition of $LiAlH_4$ to the so-called soluble "ate" complexes resulting in the precipitation of the insoluble hydrides $Mg(ZnH_3)_2$ and $MgZnH_4$. The other method involves the metathetical reaction of $MgBr_2$ with $LiZn(CH_3)_3$ in a 1:2 molar ratio and with $Li_2Zn(CH_3)_4$ in a 1:1 molar ratio to form the "ate" complexes followed by addition of $LiAlH_4$ resulting in the precipitation of $Mg(ZnH_3)_2$ and $MgZnH_4$, respectively. The new hydrides were characterized by DTA–TGA, x-ray powder diffraction and elemental analysis. Detailed infrared and NMR investigations of the so-called "ate" complexes ($MgZn(CH_3)_4$ and $Mg[Zn(CH_3)_3]_2$) revealed that these compounds are better described by more complex equilibria. Proton NMR spectra of the "ate" complexes were obtained over a wide temperature range giving some information as to their composition in solution.

Introduction

During the last few years we have been engaged in a general study of the preparation and characterization of complex metal hydrides of zinc,[1] magnesium,[2] copper,[3] and beryllium.[4] The preparation of these compounds involves the reduction of an ether-soluble "ate" complex ($M_nM'_mR_{2m+n}$) with either $LiAlH_4$ or AlH_3. This reaction results in the precipitation of the insoluble hydride ($M_nM'_mH_{2m+n}$), leaving in solution the