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Thermodynamic considerations of metal halide vapour complexes

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Certain metal halide vapour complexes of the type ABX_{m+n} increase the equilibrium vapour concentration of one or both of the component salts in the binary system (AX_m/BX_n). Such enhancement depends upon the free energy of complex formation, the saturated vapour pressure of the complexing salt and the melt activities, in a manner formulated here by means of a thermodynamic scheme. Certain trends in the periodic table are established.

Nomenclature

ϵ	enhancement term $= p^0 K_a$
ϵ'	enhancement term $= P^0 K_a$
F	enhancement
p	partial vapour pressure (atm)
p^0	saturated vapour pressure of monomer (atm)
P^0	total saturated vapour pressure exerted by a salt (atm)
ρ	vapour concentration of a species
ρ^0	vapour concentration of a species above the pure salt (mol m^{-3})
x	cation mole fraction
ΔH_a	enthalpy of complex formation from monomers
ΔH_b	vaporization enthalpy of AX_m
ΔH_c	vaporization enthalpy of BX_n
ΔH_d	vaporization enthalpy of ABX_{m+n}
ΔH_e	exchange enthalpy
ΔH_m	enthalpy of mixing in liquid pool
ΔV	change in coulombic potential energy
D_b	bridge bond strength
D_t	end bond strength

1. Introduction

The presence of dimers, trimers and higher order aggregates in the vapour phase above salt condensates is well established [1]. Binary salt systems may also contain mixed polymeric vapour species which are termed heterocomplexes [2]; thus for example the vapour in equilibrium with a sodium chloride/lead chloride melt is known to contain at least four vapour species, NaCl, Na_2Cl_2, $NaPbCl_3$ and $PbCl_2$ [3]. Their relative abundances will vary with temperature, the higher order aggregates being more abundant at low temperatures where the partial vapour pressure of the complex may exceed the saturated vapour pressure of sodium chloride.

$$p_{\mathrm{NaPbCl_3}} \geqslant p^0_{\mathrm{Na_2Cl_2}} + p^0_{\mathrm{NaCl}}$$

The total vapour concentration of sodium at such a temperature,

$$\rho_{\mathrm{Na}} = \rho_{\mathrm{NaCl}} + 2\rho_{\mathrm{Na_2Cl_2}} + \rho_{\mathrm{NaPbCl_3}}$$

where measured as a function of melt composition will then actually increase as the pure sodium chloride is diluted with lead chloride, passing through a maximum value.

This phenomenon, known as enhancement, is of considerable interest to, for instance, the manufacturers of electrical discharge lamps. They wish to increase the arc concentration of certain elements which have useful light-emitting properties, without increasing the lamp temperature which is limited by the thermal properties of the envelope. One possibility is to complex the salts of these metals (the alkali, alkaline earths and rare earths).

The magnitude of the likely enhancement can

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be predicted from the melt activities, the temperature, the vapour pressure of the complexing agent, and the free energy of complex formation, as described below.

2. Theory

Complex formation in the gas phase is generally exothermic and accompanied by a decrease in entropy, thus the equilibrium constant K_a for the reaction

$$AX_m(g) + BX_n(g) = ABX_{m+n}(g)$$

decreases as the temperature increases. In the simplest model these are the only gaseous species present. Their equilibria with each other and with the condensed phase are represented in the isothermal equilibrium box of Fig. 1. Kirchoff summations yield the relationships

$$\Delta\chi_a = (\Delta\chi_d - \Delta\chi_b - \Delta\chi_c) + \Delta\chi_m$$

where $\chi = H, S, G$.

Enhancement of the species A will occur provided its equilibrium vapour concentration above the mixed salt AX_m/BX_n (taking into account all the molecular forms) exceeds its equilibrium vapour concentration above the pure salt AX_m; i.e., if the ratio

$$F_A = (\rho_{ABX_{m+n}} + \rho_{AX_m})/\rho^0_{AX_m} \quad (1)$$

exceeds unity. The ideal gas law is applicable to dilute salt vapours however [4], so that Equation 1 may be rewritten in terms of the partial vapour pressures to give

$$F_A = (p_{ABX_{m+n}} + p_{AX_m})/p^0_{AX_m} \quad (2)$$

The activity equilibria in Fig. 1 can now be written as

$$K_a = p_{ABX_{m+n}}/p_{AX_m})/p^0_{BX_n}$$

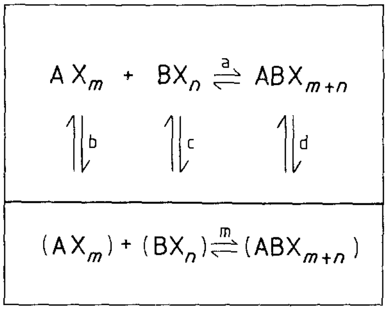


Figure 1 Isothermal equilibrium for $\Delta X_a = (\Delta X_d - \Delta X_b - \Delta X_c) + \Delta X_m$. $X = H$ (enthalpy), S (entropy) and G (free energy).

$$K_b = p^0_{AX_m}$$
$$K_c = p^0_{BX_n} \quad (3)$$
$$K_d = p^0_{ABX_{m+n}}$$
$$K_m = (p/p^0)_{ABX_{m+n}}/[(p/p^0)_{AX_m} \times (p/p^0)_{BX_n}]$$

Rewriting Equation 2 in terms of these equilibria:

$$F_A = a_{AX_m}(1 + a_{BX_n} \times p^0_{BX_n} \times K_a) \quad (4)$$
$$= a_{AX_m}(1 + a_{BX_n} \times \epsilon_A) \quad (5)$$

where the "enhancement term" $\epsilon_A = p^0_{BX_n}K_a$ Equation 4 dictates that for a large enhancement: (a) K_a should be large so that ΔG_a must be large and negative; (b) the vapour pressure of the complexing salt $p^0_{BX_n}$ should be high; and (c) the activities of the components should be close to, or above, their ideal Temkin values ($a_{AX_m} = x_A$; $a_{BX_n} = x_B$; for common anion halide mixtures).

If Temkin's law is obeyed in the melt, Equation 5 yields

$$F_A = (\epsilon + 1)x_A - \epsilon x_A^2 \quad (6)$$

F_A is plotted as a function of x_A in Fig. 2 for several values of ϵ_A. The higher the enhancement term, ϵ_A, the greater the enhancement F_A. For an ideal system enhancement ($F_A > 1$) occurs provided $\epsilon_A > 1$ with the maximum value at the melt composition $x_A = \epsilon + 1/2\epsilon$, (i.e. $x_A \rightarrow 0.5$ as $\epsilon \rightarrow \infty$). If the melt is non-ideal and the vapour phase more complicated than that described above, maximum enhancement may be obtained at some other melt composition.

The analysis described above raises some interesting questions:

(a) Can one define an activity for a species such as the complex ABX_{m+n} which does not exist as a pure compound?

(b) Can enhancement occur when the complex is absent from the condensed phase and, if so, by what mechanism is the salt of low volatility transported into the vapour? Karpenkos' work [5] suggests that such a circumstance occurs in the tin chloride/alkali metal chloride systems.

Much experimental evidence supports the view that enhancement occurs by virtue of hetercomplex formation. Such molecules have been detected by mass spectrometry and their free energies of formation, ΔG_a, have been measured. Vapour transport/condensate analysis techniques have been used to measure the enhancements F directly. These parameters are related, in the simplest systems, by Equation 4 . and, since

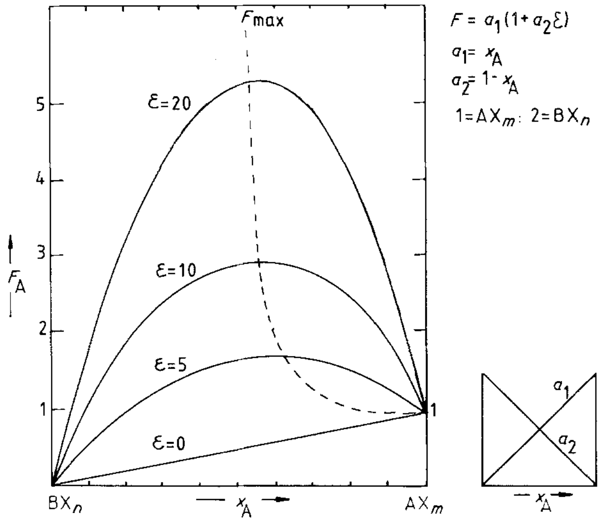


Figure 2 Enhancement as a function of melt composition for salts that mix ideally.

$K_a = \exp - \Delta G_a^0/RT$, the free energy of complex formation depends logarithmically upon the enhancement; i.e.

$$\Delta G_a^0 = -RT[\ln (F_A - a_{AX_m}) - \ln a_{AX_m} a_{BX_n} - \ln p^0_{BX_n}] \qquad (7)$$

so that an accurate value for ΔG_a^0 can be calculated from vapour transport results, provided that the activities are known.

Theory predicts that the enhancement may also vary considerably with temperature. Substituting $p^0_{BX_n} = \exp - \Delta G_c^0/RT$ into Equation 4, taking logarithms and differentiating with respect to temperature:

$$\mathrm{d} \ln F_A/\mathrm{d}T \fallingdotseq (\Delta H_c^0 + \Delta H_a^0)/RT^2 \qquad (8)$$

If, for example, the reaction enthalpy $\Delta H_a^0 = -200\,\mathrm{kJ\,mol^{-1}}$ while the vaporization enthalpy of the complexing salt BX_n, $\Delta H_c^0 = +150\,\mathrm{kJ\,mol^{-1}}$, Equation 8 yields $F(1050)/F(950) \fallingdotseq 0.55$; i.e. the enhancement is nearly halved in a 100 K interval.

In the following review enhancement terms like $\epsilon' = P^0 K_a$ are estimated from vapour pressures [6] and the free energies of complex formation. In addition the enthalpy of the reaction

$$\tfrac{1}{2}A_2X_{2m} + \tfrac{1}{2}B_2X_{2n} = ABX_{m+n}$$

(ΔH_e^0) is often measured, and this is quoted where appropriate.

The reaction enthalpy ΔH_a is related to this enthalpy ΔH_e by the expression

$$\Delta H_a = \tfrac{1}{2}(\Delta H_{d1} + \Delta H_{d2}) + \Delta H_e \qquad (9)$$

where ΔH_{d1} and ΔH_{d2} are the dimerization enthalpies of the component salts.

3. Review

3.1. Review of thermodynamic data

3.1.1. AX/BX (A, B both alkali metals)

The reaction enthalpies ΔH_e^0, determined by mass spectrometry, are negative and increase in magnitude with the difference in cation radius, $(r_A - r_B)$ (see Table I). Thus the complexes are more stable than the dimers of their component salts (the arithmetic mean enthalpy). This stabilization can be explained in part by the net change in coulombic potential energy of the cations during the exchange of dimers. Hastie [7] has shown that this energy

$$\Delta V_c = c[(r_A + r_B)^{-1} - (4r_A)^{-1} - (4r_B)^{-1}]$$

correlates with the exchange enthalpy, but he notes that higher order polarizations must be accounted for before quantitative predictions can be made.

The enhancement terms ϵ' can be calculated from the exchange enthalpies ΔH_e^0 as follows (the procedure is given in Table II): the reaction enthalpy ΔH_a^0 is calculated from ΔH_e^0 and the dimerization enthalpies ΔH_{d1} and ΔH_{d2} which are known [1]. The free energy of complex formation, ΔG_a^0, is now found by assuming $\Delta S_a^0 = -125.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$, a value recommended by Hastie [7], and finally the saturated vapour pressures of the salts are used to calculate the enhancement terms $\epsilon' = P^0 K_a$.

The resulting values are generally small, with the enhancement limited by the low vapour pressures of the alkali metal halides. Enhancement is unlikely for most of these systems.

TABLE IA Exchange reaction enthalpies for systems type AX/BX (A, B both alkali metals; X = F, Cl). Values of ΔH_e are given in kJ mol^{-1}

NaF	KF	RbF	CsF		Reference
−9.62		−12.55		LiF	[7]
	−6.28			NaF	
		−5.86		KF	
			−5.44	RbF	

TABLE IB Exchange reaction enthalpies for systems type AX/BX (A, B both alkali metals; X = F, Cl). Values of ΔH_e are given in kJ mol^{-1}

NaCl	KCl	RbCl	CsCl		Reference
			−28	LiCl	[8, 9]
	−6.7	−24	−22	NaCl	[11, 10, 10,]
		−3	−11	KCl	[10, 10]
			−4	RbCl	[10]

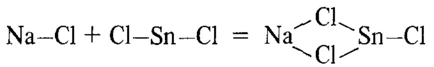
3.1.2. *AX/BX$_n$ (A = alkali metal; B = non-alkali metal)*

The data are present in Table III. The thermodynamic data for this class of system is generally given as ΔH_a^0 and ΔS_a^0, having been determined by mass spectrometry. There are some large discrepancies in the reported ΔG_a^0 values for certain systems which lead to disproportionate errors in the enhancement terms and thus the two values of ΔG_a^0 reported for the complex $LiBeF_3$; $\Delta G_a^0 = -125$ and -96 kJ mol^{-1}, yield $\epsilon'_{\mathrm{Li}} = 1023$ and 31 respectively.

For each system the enhancements of the two components are in an inverse ratio to their vapour pressures, e.g. $\epsilon'_{\mathrm{Li}}/\epsilon'_{\mathrm{Be}} = P^0_{\mathrm{BeF_2}}/P^0_{\mathrm{LiF}}$.

The stability of the complexes (ΔG_a^0) varies with the halide group, usually in the sequence $F > Cl > Br > I$, while the vapour pressures of the complexing salts usually increase in that sequence. The enhancement terms, a product of these two, in general decrease in this sequence with the loss in complex stability overriding the gain in complexing salt volatility. For example, the enhancement term for potassium in the KCl/$PbCl_2$ system [3] ($\Delta G_a^0 = -90$ kJ mol^{-1}; $P^0_{\mathrm{PbCl_2}} = 0.0588$ atm) $\epsilon'_{\mathrm{K}} = 2971$, whereas in the KBr/$PbBr_2$ system ($\Delta G_a^0 = -71$ kJ mol^{-1}; $P^0_{\mathrm{PbBr_2}} = 0.0931$ atm) $\epsilon'_{\mathrm{K}} = 478$. (In systems where one of the salts is a gas at 1000 K a nominal pressure of one atmosphere is assigned.)

The change in stability with halide group may be explained in terms of the bridge bonds thought to form in heterocomplexes since these are, on average, 20% stronger than end bonds [7]. Thus the reaction



$$\mathrm{Na{-}Cl + Cl{-}Sn{-}Cl = Na{<}^{Cl}_{Cl}{>}Sn{-}Cl}$$

will, on this basis, yield the enthalpy

TABLE II Calculation of the enhancement terms for the system AX/BX (A, B both alkali metals; X = fluoride, chloride)

Complex ABX_2	$-\Delta H_a$ (kJ mol^{-1})	$-\Delta S_a$ (J mol^{-1} K^{-1})	$-\Delta G_a$ (kJ mol^{-1})	$-\Delta H_e$ (kJ mol^{-1})	ϵ'_{A}	ϵ'_{B}	References
$LiNaF_2$	259.6	125.5	134.1	9.62	7.1×10^3	11.7	[7]
$LiRbF_2$	238.1	125.5	112.6	12.55	140	0.88	[7]
$NaKF_2$	233.3	125.5	107.8	6.28	29.7	298	[7]
$KRbF_2$	208.4	125.5	82.9	5.86	3.91	1.5	[7]
$RbCsF_2$	185.9	125.5	60.4	5.44	2.38	0.26	[7]
$LiCsCl_2$	214.5	125.5	89	28	59.9	401	[8, 9]
$NaKCl_2$	197.2	125.5	71.7	6.7	0.95	0.46	[11]
$NaRbCl_2$	208	125.5	82.5	24	7.75	1.66	[10]
$NaCsCl_2$	200	125.5	74.5	22	10.37	0.65	[10]
$KRbCl_2$	176.5	125.5	51	3	0.18	0.08	[10]
$KCsCl_2$	178.5	125.5	53	11	0.78	0.10	[10]
$RbCsCl_2$	165	125.5	39.5	4	0.16	0.05	[10]

TABLE III Calculation of the enhancement terms for the system AX/BX_n (A = alkali metal; B = non-alkali metal; X = F, Cl)

Complex ABX_{m+1}	$-\Delta H_a$ (kJ mol^{-1})	$-\Delta S_a$ (J mol^{-1} K^{-1})	$-\Delta G_a$ (kJ mol^{-1})	$-\Delta H_e$ (kJ mol^{-1})	ϵ'_A	ϵ'_B	References
Group IIA							
$LiBeF_3$	251	126	125	41.5	1023	3.92	[12]
$LiBeF_3$	222	126	96	12.5	31.2	0.12	[13]
$NaBeF_3$	218	88	130	17.5	1866	5.6	[14]
$NaBeF_3$	283	134	149	82.5	18326	55	[15]
$NaBeF_3$	281	126	155	80.5	38107	115	[16]
$NaBeCl_3$	226	96	130	75.5	6.2×10^6	418	[14]
$KBeCl_3$	201	100	101	44.5	1.9×10^5	32	[14]
$KMgCl_3$	243	130	113	54.5	422	137	[10]
Group III							
$LiAlF_4$	289	133	156	59	76.1	163.5	[17]
$LiAlF_4$	305	155	150	75	37	79.4	[18]
$NaAlF_4$	366	132	234	145	9.1×10^5	1.55×10^6	[19]
$KAlF_4$	351	126*	225	144	3.1×10^5	3.97×10^7	[20]
$CsAlF_4$	146	126*	20	39	0	0.02	[21]
$NaAlCl_4$	208	121	87	35.5	3.52×10^4	2.36	[22]
$NaAlCl_4$	209	126*	83	36.5	2.18×10^4	1.46	[23]
$NaAlCl_4$	213	126*	87	40.5	3.52×10^4	2.35	[7]
Group IVB							
$NaSnF_3$	251	79	172		9.8×10^8	887	[7]
$NaSnCl_3$	192	113	79	44	1.3×10^4	0.91	[5]
$NaSnBr_3$	167	109	58		1.1×10^3	0.28	[5]
$NaSnI_3$	155	109	46		254	0.15	[5]
$KSnF_3$	226	79	146		4.3×10^7	2.9×10^3	[7]
$KSnCl_3$	201	121	80	64	1.5×10^4	2.6	[5]
$KSnBr_3$	155	105	50		410	0.17	[5]
$KSnI_3$	146	105	41		140	0.12	[5]
$RbSnCl_3$	192	113	79	24	1.3×10^4	5.2	[5]
$RbSnBr_3$	155	105	50		410	0.21	[5]
$RbSnI_3$	151	109	42		157	0.13	[5]
$CsSnCl_3$	192	113	79	16	1.3×10^4	17.5	[5]
$CsSnBr_3$	151	100	50		410	0.45	[5]
$CsSnI_3$	155	113	42		157	0.27	[5]
$NaPbCl_3$	159	84	75		490	0.56	[3]
$KPnCl_3$	172	82	90		2971	8.53	[3]
$RbPbCl_3$	165	81	84		1443	9.51	[3]
$CsPbCl_3$	153	80	73		384	8.68	[3]
$KPbBr_3$	155	84	71		478	2.1	[3]
B = transition series							
$LiScCl_4$	237	147	90	33	146	5.1	[1]
$NaScCl_4$	243	149	93	41	101	25	[1]
$NaMnCl_3$	209	117	92	26	102	4.4	[24]
$NaFeCl_3$	216	121	95	41	9.2×10^4	6.3	[10]
$NaCoCl_3$	214	129	85	36	266	1.9	[25]
$NaScI_4$	167	109	58		11	0.7	[26]

*Estimated.

TABLE IVa The exchange reaction enthalpies for system type AX_m/BX_n (A, B non-alkali metals)

$$\tfrac{1}{2}A_2X_{2m} + \tfrac{1}{2}B_2X_{2m} = ABX_{m+n}$$

System ABX_{m+n}	$-\Delta H_e$ (kJ mol^{-1})	References
$AlGaCl_6$	− 2.9	[27]
$AlInCl_6$	− 7.5	[28]
$AlFeCl_6$	0	[29]
$AlUCl_6$	− 5.4	[30]
$GaInCl_6$	2.9	[31]
$InTlCl_5$	2.9	[1]
$InSnCl_5$	3.8	[1]
$InZnCl_5$	11.7	[1]
$TlPbCl_3$	14.2	[1]
$TlSnCl_3$	16.3	[1]
$TlCdCl_3$	7.1	[1]
$TlThCl_4$	6.3	[1]
$TlUCl_5$	12.1	[1]
$PbCdCl_4$	7.9	[1]
$PbThCl_6$	5.4	[1]
$EuLuCl_6$	5.4	[32]
$ThUCl_8$	3.8	[33]

$$\Delta H_a = 2D_b(\mathrm{NaCl}) - D_t(\mathrm{NaCl}) + 2D_b(\mathrm{SnCl_2}) - D_t(\mathrm{SnCl_2}) \quad (10)$$

or, if the complex has a triple bridge bond by

$$\Delta H_a = 3D_b(\mathrm{NaCl}) - D_t(\mathrm{NaCl}) + 3D_b(\mathrm{SnCl_2}) - 2D_t(\mathrm{SnCl_2}) \quad (11)$$

The bridge and terminal bond strengths have been determined from the heat of atomization of the monomers and dimers [7] and are $D_b(\mathrm{NaCl}) = -255$, $D_b(\mathrm{SnCl_2}) = -213$, $D_t(\mathrm{NaCl}) = -414$, $D_t(\mathrm{SnCl_2}) = -389$ kJ mol^{-1}.

Thus the enthalpy of reaction is

$$\Delta H_a \text{ (double bridge bond)} = -133 \text{ kJ mol}^{-1}$$

or

$$\Delta H_a \text{ (triple bridge bond)} = -212 \text{ kJ mol}^{-1},$$

compared with an experimental value due to Karpenko [5] of − 192 kJ mol^{-1}.

Furthermore the stabilization depends upon terms such as $2D_b - D_t$ and $3D_b - D_t$ (Equations 10 and 11) and these terms decrease in the sequence F, Cl, Br, I. For example [7] $(2D_b - D_t)$ NaF = − 121; NaCl = − 96 and LaF_3 = − 147; $LaCl_3$ = − 95 kJ mol^{-1}. Thus the bridge bond model explains the decrease in magnitude of the reaction enthalpy down the halogen series, and achieves some measure of quantitative accuracy.

Some very stable complexes and large enhancement terms are found in this group AX/BX_n (A = alkali metal; B = non-alkali metal), and some enhancements ($F > 1$) seem probable.

3.1.3. AX_m/BX_n (A, B non-alkali metals)

The exchange reaction enthalpies are reported in Table IV as are the free energies of complex formation, calculated as described above for complexes of the type ABX_2 (A, B = alkali metals). The free energies are very low and there is no possibility of enhancement in any of these systems.

4. Summary

The trends in complex stability between groups may be discerned from Fig. 3 where ΔG_a^0 (1000 K) has been plotted for all the chloride complexes. Complexes of the type $ABCl_{n+1}$ (A = alkali metal; B = non-alkali metal) are more stable than those formed by the interaction of two alkali metal halide monomers, or by two non-alkali metal halide monomers. Within this group the strongest complexes $ABCl_{n+1}$ are formed by the interaction of the vapours of the least volatile salts, i.e. B = alkali earth or rare earth. For example ΔG_a^0 for the alkali metal halide/rare earth halides, measured by Novikov *et al.* [34–46], lie between − 98 ($CsLuCl_4$) and − 157 ($LaNaCl_4$) kJ mol^{-1}. They were measured by a total vapour pressure

TABLE IVb Calculation of the free energy of complex formation from the exchange reaction enthalpy and dimerization enthalpies. System AX_m/BX_n (A, B non-alkali metals)

System ABX_{m+n}	ΔH_{d1} (kJ mol^{-1})	ΔH_{d2} (kJ mol^{-1})	ΔH_d av. (kJ mol^{-1})	ΔH_e (kJ mol^{-1})	ΔH_a (kJ mol^{-1})	ΔG_a (kJ mol^{-1})	References
$AlGaCl_6$	− 126	− 90	− 108	2.9	− 105.1	20.4	[27]
$AlInCl_6$	− 126	− 124	− 125	7.5	− 117.5	8	[28]
$AlFeCl_6$	− 126	− 148	− 137	0	− 137	− 11.5	[29]
$GaInCl_6$	− 90	− 124	− 107	− 2.9	− 109.9	15.6	[31]
$InSnCl_5$	− 124	− 95	− 109.5	− 3.8	− 113.3	12.2	[1]
$InZnCl_5$	− 124	− 111	− 117.5	11.7	− 129.2	− 3.7	[1]
$PbCdCl_4$	− 128	− 114	− 121	− 7.9	− 128.9	− 3.4	[1]

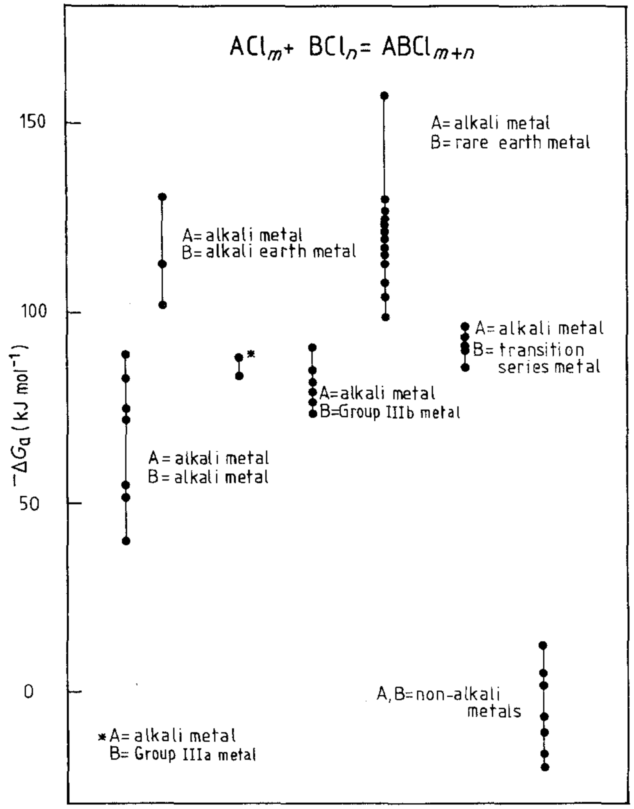


Figure 3 Free energy of formation of various gaseous metal chloride complexes at 1000 K.

condensate analysis technique and are reported separately in Table V.

It is unfortunate that the least volatile salts form the most stable complexes since large enhancement requires a volatile complexing agent. It appears that, in optimizing enhancement, there is a competition between complex stability and complexing salt volatility. In bonding terms this arises because low volatility salts are strongly bound in the condensed phase and require large energies for vaporization. They will therefore form strongly bound dimers (dimerization can be regarded as the first stage in condensation to an aggregate). Thus according to Equation 9 the reaction enthalpy will also be large and the complex stable.

5. Conclusions

Reactions of the type

$$AX_m(g) + BX_n(g) = ABX_{m+n}(g)$$

are exothermic and accompanied by a decrease in entropy, usually in the range 104 to 145 J mol^{-1} K^{-1}. The relative stability of the complexes may be gauged by comparing the free energies of complex formation at 1000 K. Those combinations where A is an alkali metal and B is not are the most stable and within the group the largest ΔG_a is found when the salt BX_n is of low volatility. Thus there is a competition between complex stability and complexing salt volatility when selecting systems for maximum enhancement.

Two kinds of system AX/PbX_2 and AX/DyX_3

TABLE V The free energy of formation at 1000 K of complexes type $ABCl_4$. (A = alkali metal, B = rare earth) Values of $-\Delta G_a$ are in kJ mol^{-1}

	Y	La	Ce	Pr	Nd	Gd	Dy	Ho	Lu
Li	103^{34}					126^{35}	112^{36}		106^{37}
Na	119^{38}	157^{39}			123^{44}			122^{40}	
K	121^{42}	129^{42}	122^{43}	155^{42}	115^{43}			117^{40}	
Cs					122^{44}		116^{45}	119^{44}	98^{45}

have been investigated to find out whether complex stability or complexing salt volatility is the more important in maximizing enhancement. The results of these experiments are described and discussed in other articles.

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