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# Metal halide vapour complexes: vapour transport and lamp experiments

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Stable vapour complexes of the type $ABX_{m+n}$ can sometimes increase the vapour concentration of a low volatility salt above the liquid pool. If the equilibrium concentration of A and/or B, in all their molecular forms above the binary melt $AX_m/BX_n$ exceed their values above their respective pure salts enhancement ($F > 1$) has occurred. Mass spectrometric data suggests that such enhancement may occur in two dissimilar systems NaCl/$PbCl_2$ ($F_{Na} > 1$) and NaCl/$DyCl_3$ ($F_{Dy} > 1$). Vapour transport and electrical discharge lamp experiments have been used to test this prediction by direct measurement of the enhancement and the results are reported here.

## 1. Introduction

A recent review of metal halide vapour complexes [1] showed that in a binary salt system $AX_m/BX_n$ that contains three vapour species $AX_m$, $BX_n$ and the complex $ABX_{m+n}$, enhancement of for example, A will occur provided $F_A > 1$ where

$$F_A = a_{AX_m}(1 + a_{BX_n} P^0_{BX_n} K_a) \quad (1)$$

$$= a_{AX_m}(1 + a_{BX_n} \epsilon) \quad (2)$$

and

$$F_B = a_{BX_n}(1 + a_{AX_m} P^0_{AX_m} K_a) \quad (3)$$

$a_{AX_m}$, $a_{BX_n}$ are the activities of the salts, $P^0_{BX_n}$ the saturated vapour pressure of the complexing salt $BX_n$ (monomer), and $K_a = \exp - \Delta Ga/RT$, the equilibrium constant for the vapour reaction

$$AX_m(g) + BX_n(g) = ABX_{m+n}(g) \quad (4)$$

The review concluded that in systems where $K_a$ is large, the vapour pressure of the complexing salt is low, and vice versa. Thus in selecting systems for optimum enhancement there is a competition between complex stability ($K_a$) and complexing salt volatility ($P^0_{BX_n}$).

To examine this hypothesis two systems were chosen for experimental work. In the first ACl/$PbCl_2$ (A = Li, Na, K) a volatile complexing agent, lead chloride, was partnered with a relatively low volatility alkali metal chloride. In the second ACl/$DyCl_3$ (A = Na, K) two salts of similar low volatility were partnered.

The equilibriated vapour was investigated by a combined Knudsen effusion/time of flight mass spectrometry technique [2]. The complex ions $APbCl_2^+$ and $ADyCl_3^+$ were found suggesting the presence of 1:1 vapour complexes. The reaction enthalpies were measured for Reaction 4 above and the free energies of complex formation deduced by assuming the reaction entropies are in both cases ($\Delta S_a = -125.5\ \text{J mol}^{-1}\,\text{K}^{-1}$). Enhancement terms were now calculated according to the equations

$$\epsilon_A = P^0_{BX_n} K_a, \qquad \epsilon_B = P^0_{AX_n} K_a \quad (5)$$

The results, presented in Table I suggest that the enhancements $F$ are likely to be in order

$$F_{Na}(NaCl/PbCl_2) > F_{Dy}(NaCl/DyCl_3) > F_{Na}(NaCl/DyCl_3), F_{Pb}(NaCl/PbCl_2)$$

given that the equimolar melt activities are unlikely to be less than $a = 0.1$. The large differences in the predicted sodium and lead enhancements in the $NaCl/PbCl_2$ system arise from the commensurate difference in volatility of the two components. In the $NaCl/DyCl_3$ system the free energy of complex formation is more favourable, but the low vapour pressure of the two salts indicate that only modest enhancement is likely.

The enhancements $F$ were measured directly

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TABLE I A summary of the mass spectrometric data showing the estimated free energies of complex formation and enhancement terms at 1000 K.

| System | $-\Delta H_a$ (kJ mol$^{-1}$) | $-\Delta S_a$ (J mol$^{-1}$K$^{-1}$) | $-\Delta G_a$ (kJ mol$^{-1}$) | $K_a$ (atm$^{-1}$) | $P^0$(NaCl)[d] (atm) | $P^0$(MCl$_n$) (atm) | $\epsilon_{Na}$[e] | $\epsilon_m$[f] |
|---|---|---|---|---|---|---|---|---|
| NaCl/PbCl$_2$[a] | 234 ± 28 | 125.5[c] | 108.5 | $4.7 \times 10^5$ | $4.8 \times 10^{-5}$ | $5.9 \times 10^{-2}$ | 27 600 | 22.5 |
| NaCl/DyCl$_3$[a] | 250 ± 32 | 125.5[c] | 124.5 | $3.2 \times 10^6$ | $4.8 \times 10^{-5}$ | $6.6 \times 10^{-6}$ | 21.2 | 154 |
| NaCl/PbCl$_2$[b] | 159 ± 4 | 80 | 79 | $1.3 \times 10^4$ | $4.8 \times 10^{-5}$ | $5.9 \times 10^{-2}$ | 794 | 0.65 |

[a] This work.
[b] Bloom's work.
[c] Estimated, see Schafer [11].
[d] $P^0_{NaCl} = P^0_{NaCl}(1-\alpha)/(1-\alpha/2)$, $\alpha = 0.59 P^0_{NaCl} = 8.3 \times 10^{-5}$ atm.
[e] $\epsilon_{Na} = P^0_{MCl_n} \times K_a$ (Equation 5).
[f] $\epsilon_M = P^0_{NaCl} \times K_a$ (Equation 5).

to check the validity of the theory and the enhancement equations by a vapour transport technique.

## 2. Experimental details

### 2.1. Materials and apparatus

The alkali metal chlorides and lead chloride were purchased as Analar grade reagents (BDH) and were used without further purification. Dysprosium trichloride was prepared from its oxide [2]. All subsequent handling and processing was conducted in a VAC systems dry box at Thorn Lighting, Leicester. The salt mixes were weighed out and melted into gold reaction boats.

The vapour transport apparatus, Fig. 1, consists of two concentric alumina tubes, the carrier gas tube and the flushing gas tube, which rest horizontally within a resistance-wound Kanthal furnace. The reaction boat is located inside the inner tube on a push rod assembly and can be inserted into the end of the inner tube which is coincident with the hot zone of the furnace.

At equilibrium the carrier gas, oxygen-free nitrogen, passes over the boat, is saturated with salt vapour, and passes through the capillary into the silica condensate tube, where it is collected. An inward leak is maintained at the interface between the condensate tube and the carrier gas tube by passing additional nitrogen through the flushing gas tube, ensuring that the salt-laden vapour is quantitatively convected into the condensate tube. The boat temperature is measured using a platinum–platinum 13% rhodium thermocouple which is also connected to a Eurotherm controller. Temperature differences along the boat were found to be less than 2° C at 1000 K and temperature control was within one degree.

Back diffusion is limited by the close fit between the silica cradle and the inner tube and forward diffusion by the capillary. These effects were modelled using the theories of Merten and Bell [3] and Kvande and Wahlbeck [4], with the nitrogen/salt interdiffusion coefficients estimated using Arnolds [5] equation. This calculation sug-

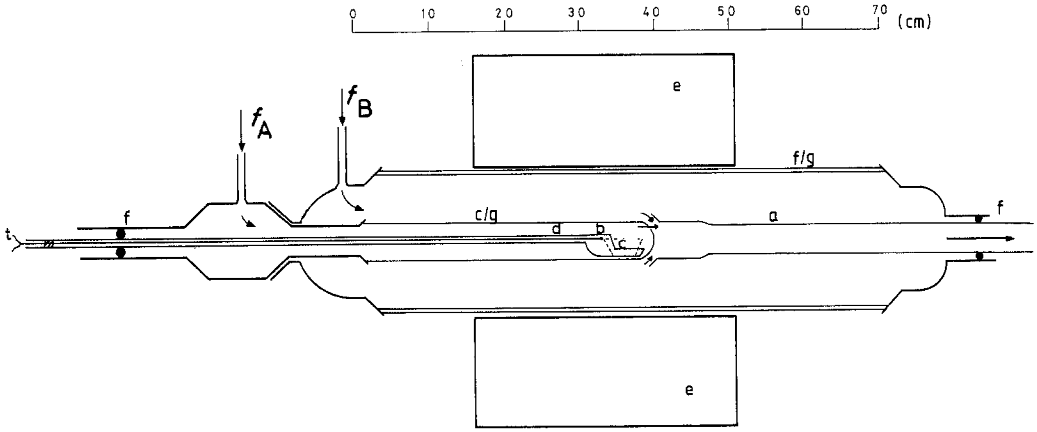

*Figure 1* The vapour transport apparatus. a = condensate tube, b = cradle, c = boat, d = silica cradle assembly, e = furnace, f = O-ring seal, f/g = flushing gas tube, c/g = carrier gas tube, t = thermocouple.

gested that the salt transport rate would be independent of flow rate provided that the room temperature flow rate ($f_A$) exceeded $10\,\mathrm{cm^3\,min^{-1}}$. Undersaturation may occur at high flow rates due to incomplete mixing in the gas stream or the inability of the salt to vaporize rapidly enough to saturate the gas [3]. This effect was calculated [6] and found to be insignificant provided $f_A > 30\,\mathrm{cm^3\,min^{-1}}$. Thus theoretical considerations suggested that the characteristic plateau in the transport rate/carrier gas flow rate plot would occur in the range $10 < f_A/\mathrm{cm^3\,min^{-1}} < 30$ as shown in Fig. 2.

### 2.2. Experimental procedure

The reaction boat was loaded into the cradle assembly inside a glove bag and with the gas trains flowing moved to the hot end of the tube. After reaching thermal equilibrium (10 min) a clean condensate tube was engaged to the carrier gas tube and timing commenced. On completion (2 to 10 h) the condensate tube was removed and washed with dilute nitric acid. The collected washings were diluted and then analysed for cation concentration by atomic absorption spectrophotometry.

The data for subsequent examination consists of: $T_R$ room temperature $T_E$, the boat temperature, $f_A$, the room temperature flow rate of gas; $\tau$ the duration of the experiment; $N_{A,B}$ the number of moles of cations transported.

The apparatus was first calibrated using sodium chloride and lead chloride separately. Having established the saturation plateau the saturated vapour pressure of dysprosium trichloride was measured at 1240 K and the binary mixes NaCl/PbCl$_2$ and NaCl/DyCl$_3$ then investigated.

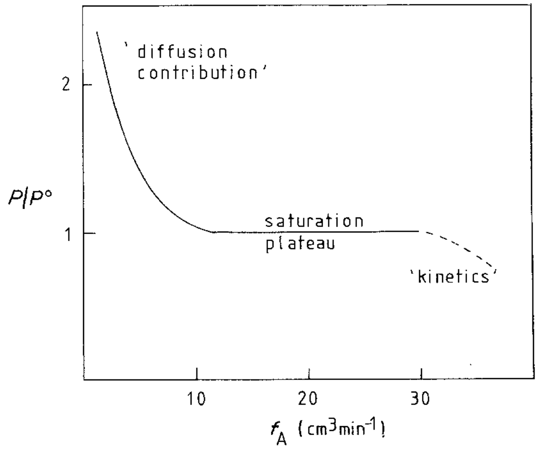

*Figure 2* The theoretically predicted calibration curve for the vapour transport apparatus. $P$ = measured pressure, $P^\circ$ = true equilibrium vapour pressure.

## 3. Results

### 3.1. Single component systems: PbCl$_2$, NaCl, DyCl$_3$

The saturated vapour pressure of lead chloride is deduced from the number of moles of lead in the condensate by application of the ideal gas law, yielding

$$P^0_{\mathrm{PbCl_2}} = N_{\mathrm{Pb}}RT_R/(A\Sigma V) \qquad (6)$$

where $T_R$ is the room temperature, $A$ the constant $1.01 \times 10^5\,\mathrm{N\,m^{-2}\,atm^{-1}}$ and

$$\Sigma V = V_{\text{carrier gas}} + V_{\text{salt}},$$

the total volume of the gas at room temperature.

The sodium chloride vapour contains dimeric species, hence the saturated vapour pressure $P^0_{\mathrm{NaCl}}(\text{total})$ is given by

$$P^0_{\mathrm{NaCl}}(\text{total}) = P^0_{\text{monomer}} + P^0_{\text{dimer}}, = (n^0_{\text{monomer}} + n^0_{\text{dimer}})RT_R/(A\Sigma V) \qquad (7)$$

The number of moles of monomer and dimer are found by simultaneous solution of the conservation equation

$$N_{\mathrm{Na}} = n^0_{\text{monomer}} + 2n^0_{\text{dimer}} \qquad (8)$$

and the dimerization equation

$$K_d = P^{0^2}_{\text{monomer}}/P^0_{\text{dimer}} = (n^{0^2}_{\text{monomer}}/n^0_{\text{dimer}})RT_R/(A\Sigma V) \qquad (9)$$

for the reaction

$$\mathrm{Na_2Cl_2(g)} = 2\,\mathrm{NaCl(g)}$$

$K_d$ is found using [7] $\Delta H = 202.8\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S = 121.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

The saturated vapour pressures of these salts were found for several carrier gas flow rates and the characteristic plateau in the calibration curves found. The combined results are shown in Fig. 3 where the mean plateau values have been used to normalize the ordinate values. This plot $P^0/P^0_{\text{mean}}$, plateau suggests that for both salts saturation occurs in the range of $12 < (f_A/\mathrm{cm^3\,min^{-1}}) < 30$, which agrees well with the theoretical prediction.

The saturated vapour pressure of sodium chloride was now measured over a series of temperatures using an appropriate carrier gas flow rate. The resulting values shown in Fig. 4 are in good agreement with the literature [8]. The vapour

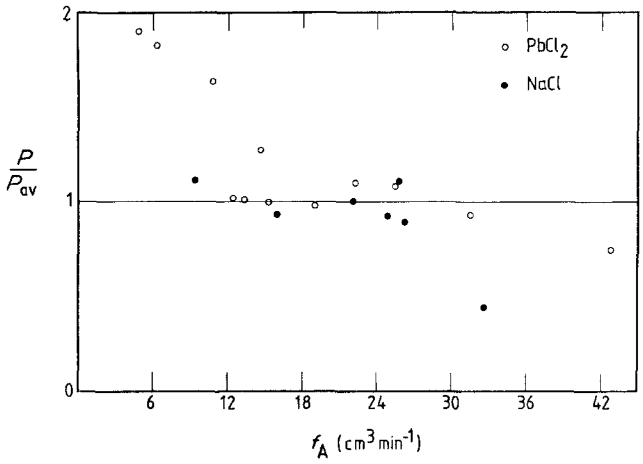

*Figure 3* Combined calibration curves showing the saturation plateau.

pressure of dysprosium trichloride (for which the equations are identical to lead chloride) measured at 1240 K has the value $P^0_{DyCl_3} = 1.94 \pm 0.34$ torr which is in fair agreement with Moriarty's [9] value of 2.94 torr. This discrepancy may arise from the difficulties inherent in handling such a hygroscopic material or the difficulties experienced in analyzing for dysprosium ion by atomic absorption spectrophotometry.

## 3.2. Binary component systems

Mass spectrometry suggests that in the two binary systems investigated NaCl/MCl$_n$ (M = Pb, Dy) the vapour consists essentially of four species NaCl, Na$_2$Cl$_2$, MCl$_n$ and NaMCl$_{n+1}$.

The number of moles transported may be written $n_1 = n$ (NaMCl$_{n+1}$); $n_2 = n$ (MCl$_n$); $n_3 = n$ (NaCl); $n_4 = n$ (Na$_2$Cl$_2$). The vapour equilibria are

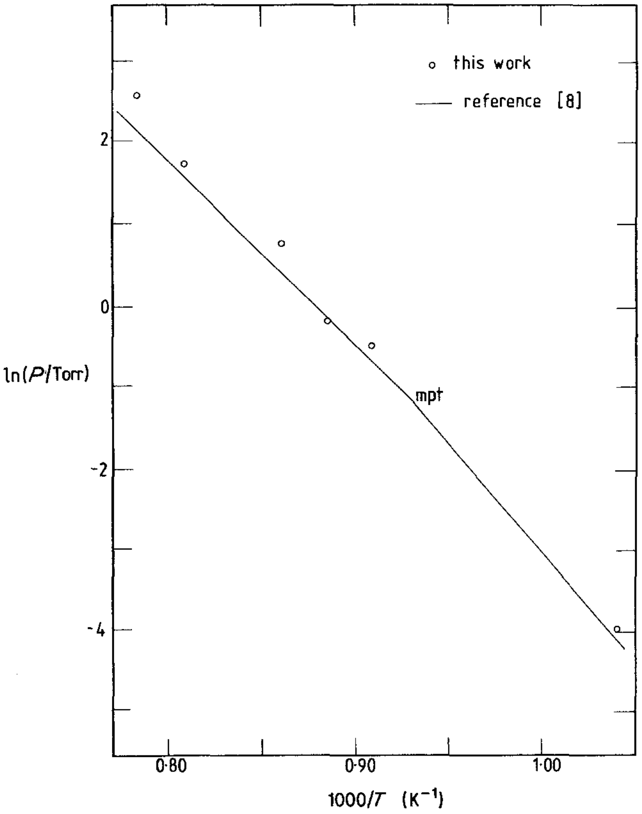

*Figure 4* Vapour pressure of sodium chloride by vapour transport.

$$MCl_n + NaCl = NaMCl_{n+1} \qquad K_a$$
$$Na_2Cl_2 = 2\,NaCl \qquad K_d$$

of which only $K_d$ is known [7].

Characterization of the vapour involves solving the set of six equations

$$K_d = (n_3^2/n_4)D \qquad (10)$$

$$K_a = n_1/(n_2 n_3 D) \qquad (11)$$

$$N_{Na} = n_1 + n_3 + 2n_4 \qquad (12)$$

$$N_M = n_1 + n_2 \qquad (13)$$

$$a_2 = a_{MCl_n} = n_2/n_2^0 \qquad (14)$$

and

$$a_3 = a_{NaCl,monomer} = n_2/n_3^0 \qquad (15)$$

where $D$ is the constant $RT/(1.01 \times 10^5 \Sigma V)$, $N$ refers to the total number of moles of the cation Na or M transported, inclusive of all its molecular forms, and $a_2$, $a_3$ are the activities of the components in the melts. $n_2^0$ refers to the number of moles of $MCl_n$ that would have been transported had the pure salt $MCl_n$ been used, thus $n_{2,3}^0 > n_{2,3}$.

These six equations contain seven unknowns: $n_1$ to $n_4$, $K_a$, $a_2$ and $a_3$, and their solution requires some assumption about $K_a$ or about the activities $a_2, a_3$ or one of the values $n_1$ to $n_4$.

### 3.3. Sodium chloride/lead chloride

This system was investigated at 960 K over a range of compositions. At higher temperatures the rapid evaporation of the lead chloride brought about unacceptable changes in melt composition, and at lower temperatures the small sodium chloride transport rate rendered condensate analysis difficult.

The data are presented in Table II. Nearly all the sodium is being transported as the complex and in Fig. 5 the approximation, $n_1 \simeq N_{Na}$ has been used to plot the vapour pressure of the complex against melt composition. The broad maximum around the equimolar composition is consistent with a complex of 1:1 stoichiometry. This allows the approximate solution of Equations 10–15.

Given

$$n_1 \simeq N_{Na} \qquad (16)$$

Equation 13 may be written

$$n_2 \simeq N_{Pb} - N_{Na} \qquad (17)$$

and the partial vapour pressures of complex and of lead chloride by the ideal gas law $P_i = n_i D$, as

$$P_1 \simeq N_{Na} D \text{ (complex)} \qquad (18)$$

$$P_2 \simeq (N_{Pb} - N_{Na}) D \text{ (lead chloride)} \qquad (19)$$

$\Delta G_a^0$, the free energy of complex formation, may now be found for

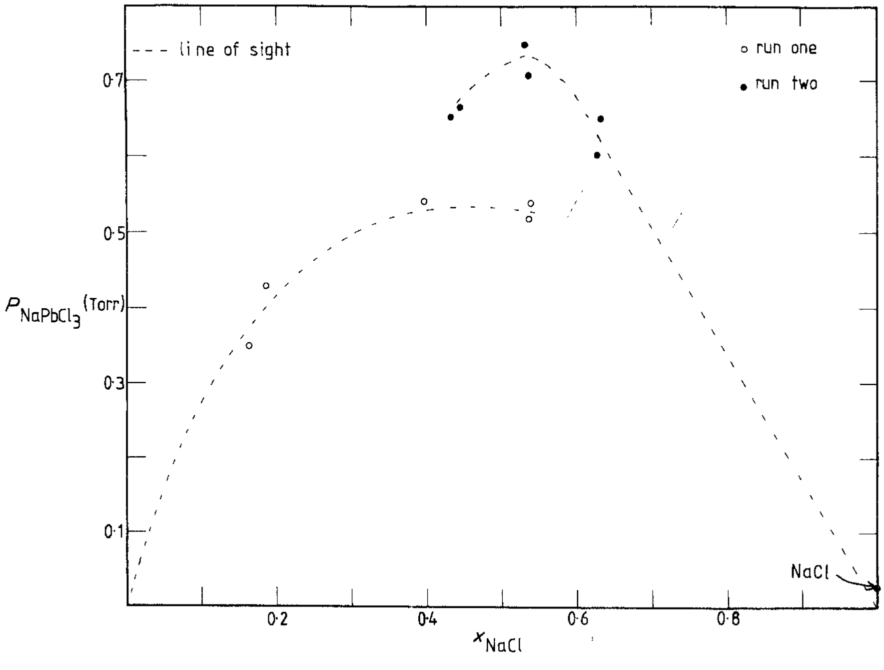

*Figure 5* The vapour pressure of the complex $NaPbCl_3$ as a function of melt composition.

TABLE II Results for the sodium chloride/lead chloride system. Vapour transport data for the binary system $NaCl/PbCl_2$ at 960 K, over a range of melt compositions

| Quantity | Units | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_{NaCl}$ | | 0.191 | 0.396 | 0.164 | 0.537 | 0.537 | 0.573 | 0.666 | 0.624 | 0.623 | 0.437 | 0.439 | 0.532 | 0.531 |
| $f_A$ | $cm^3\ min^{-1}$ | 25.00 | 24.88 | 24.88 | 24.88 | 24.88 | 25 | 25 | 24.875 | 24.875 | 24.875 | 24.625 | 24.875 | 24.875 |
| $\tau$ | min | 67 | 120 | 62 | 120 | 120 | 120 | 120 | 126 | 120 | 124 | 120 | 123 | 120 |
| $T_E$ | K | 960 | 960 | 960 | 960 | 960 | 960 | 960 | 960 | 960 | 960 | 960 | 960 | 960 |
| $T_R$ | K | 298 | 298 | 298 | 298 | 298 | 298 | 298 | 295.5 | 295 | 296.5 | 296.5 | 295 | 295 |
| $N_{Na} \times 10^3$ | mol | 1.35 | 1.84 | 1.40 | 1.18 | 1.11 | 1.25 | 0.85 | 1.722 | 1.661 | 2.460 | 2.585 | 2.154 | 2.093 |
| $N_{Pb} \times 10^5$ | mol | 3.90 | 8.79 | 2.93 | 8.79 | 8.79 | 21.49 | 14.66 | 10.47 | 10.80 | 11.07 | 10.75 | 12.64 | 11.80 |
| $P_1$ | Torr | 0.425 | 0.541 | 0.346 | 0.541 | 0.544 | 1.324 | 0.904 | 0.609 | 0.659 | 0.653 | 0.660 | 0.749 | 0.717 |
| $P_2^{(u)}$ | Torr | 14.73 | 11.32 | 16.55 | 7.258 | 5.778 | 7.699 | 5.244 | 10.02 | 10.13 | 14.51 | 15.88 | 12.77 | 12.72 |
| $P_2^{(c)}$ | Torr | 14.30 | 10.78 | 16.20 | 6.717 | 6.322 | 6.375 | 4.339 | 9.41 | 9.47 | 13.85 | 15.22 | 12.02 | 12.00 |
| $P_1/P_2P_3^0$ | atm | 2284 | 3851 | 1641 | 6179 | 6602 | 15 937 | 15 999 | 4970 | 5338 | 3617 | 3330 | 4785 | 4586 |
| $-RT \ln P_1/P_2P_3^0$ | $J\ mol^{-1}$ | 61 695 | 65 864 | 59 059 | 69 636 | 70 164 | 77 194 | 77 225 | 67 899 | 68 469 | 65 364 | 64 704 | 67 596 | 67 257 |
| $-RT \ln x$ | $J\ mol^{-1}$ | 13 165 | 7 390 | 14 423 | 4 960 | 4 442 | 3 762 | 3 243 | 3 762 | 3 775 | 6 604 | 6 568 | 5 035 | 5 035 |
| $-\Delta G_a^{0\prime}$ | $J\ mol^{-1}$ | 74 860 | 73 254 | 73 482 | 74 596 | 74 606 | 80 956 | 80 468 | 71 661 | 72 244 | 71 968 | 71 272 | 72 631 | 72 292 |

$P_2^{(u)}$ the partial pressure of lead chloride, uncorrected for the presence of the complex; $P_2^{(c)}$ the partial pressure of lead chloride, corrected for the presence of the complex.

$$K_a = a_1/a_2a_3 = P_1/P_2P_3 = P_1/P_2a_3P_3^0 \quad (20)$$

hence

$$\Delta G_a = -RT(\ln P_1/P_2P_3^0 - \ln a_3) \quad (21)$$

The activities are referred to standard states of 1 atm and for dilute salt vapours the vapour pressure may be taken as equal to the fugacity, hence $a = (P/1\,\text{atm})$. $P_1$ and $P_2$ are given by Equations 18 and 19 and $P_3^0$ is found from vapour pressure data. $a_3$ is unknown but $a_2$, the activity of the lead chloride, may be reliably estimated from Equation 19. $a_2 = P_2/P_2^0$ is plotted against composition in Fig. 6. The system is close to ideal for this component and thus for the other, so $a_3$ is approximated by $X_{NaCl}$. This procedure, which is set out in Table II, leads to the result.

$$\Delta G_a^0(960\,\text{K}) = -74.2 \pm 3\,\text{kJ mol}^{-1}$$

$$\Delta G_a^0(1000\,\text{K}) = -69.2 \pm 3\,\text{kJ mol}^{-1}$$

$$(\Delta S_a = -125.5\,\text{J mol}^{-1}\text{K}^{-1})$$

This value lies just outside the error limits on the mass spectrometric data, and must be regarded as more accurate.

The enhancement of sodium can now be calculated according to the equation

$$F_{Na} = n_1 + n_3 + 2n_4/n_3^0 + 2n_4^0 = 21 \pm 2 \quad (22)$$

This would represent a significant increase in the luminous intensity of a sodium chloride-doped metal halide discharge lamp.

The enhancement Equation 1 can be rearranged as a quadratic in the activity $a$, by writing $a_1 = a_2 = a$ at the equimolar composition, i.e.

$$a^2P_2^0K + a - F = 0 \quad (23)$$

Substituting the results given above, $F = 21$; $K(960) = 10\,949$; $P_2^0(960) = 0.0295$ atm yields $a = 0.25$. Thus the analysis is self-consistent.

Bloom [10] has studied the NaCl/PbCl$_2$ by vapour transport but found only about two-fold enhancement at 1071 K. At this temperature $P^0_{PbCl_2} = 123.6$ torr, $P^0_{NaCl} = 0.58$ torr. At the composition $X_{NaCl} = 0.491$ he found $P_{PbCl_2} = 40.58$ torr; $P_{NaPbCl_3} = 0.93$ torr, thus $a_{PbCl_2} = 0.33$. At the same time he states that the free energy of complex formation measured by mass spectrometry,

$$\Delta G_a^0 = -87.8\,\text{kJ mol}^{-1}$$

which yields

$$K_a = 10^{4.28}\,\text{atm}^{-1}$$

Given $K_a = P_1/P_2P_3\,\text{atm}^{-1}$ one can deduce that $P_{NaCl} = P_3 = 0.000\,914$ torr, i.e. that $a_{NaCl} = 0.0016$. This is very unlikely given that $a_{PbCl_2} = 0.33$, and hence the values quoted for $F$ and $\Delta G_a$ appear incompatible both with one another and with the enhancement observed in this work.

## 3.4. Sodium chloride/dysprosium trichloride (1238 K)

This system was investigated at one temperature, and melt composition $X_{NaCl} = 0.555$. The data are presented in Table III. The average dysprosium and sodium enhancements are $2.76 \pm 0.70$ and $0.93 \pm 0.28$. $n_1$ to $n_4$ are all of similar magnitude, hence solution of Equations 10 to 15 requires an assumption about $a_2$ or $K_a$. In both instances the limiting conditions are that $0 < a_2 < 1$; $n_1 < N_{Dy}$ and $n_1 < N_{Na}$.

Equations 10, 12, 13, 14 and 15 yield a quadratic in $n_3$ containing $a_2$

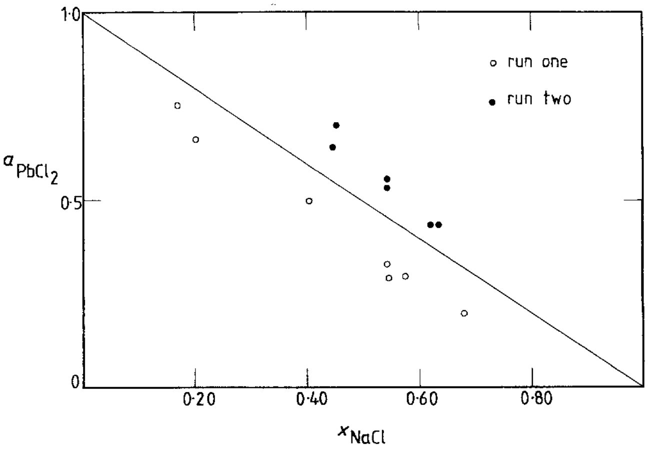

*Figure 6* The activity of lead chloride in the system NaCl/PbCl$_2$.

TABLE III Results for the sodium chloride/dysprosium trichloride system. Vapour transport data for the binary system $NaCl/DyCl_3$ at 1238 K (equimolar melts) – gold sample boats. Sample $NaCl/DyCl_3$; $x_{NaCl} = 0.555$

| Quantity | Experiment | | | | | Units |
|---|---|---|---|---|---|---|
| | F | G | H | I | J | |
| $f_A$ | 24.63 | 24.63 | 26.00 | 25.63 | 28.75 | $cm^3 min^{-1}$ |
| $\tau$ | 60 | 60 | 30 | 36 | 44 | min |
| $T_E$ | 1238 | 1238 | 1238 | 1238 | 1238 | K |
| $T_R$ | 296 | 296 | 296 | 296 | 296 | K |
| $N_{Na} \times 10^4$ | 5.997 | 3.578 | 2.811 | 4.92 | 7.02 | mol |
| $N_{Dy} \times 10^4$ | 2.468 | 2.730 | 2.481 | 2.78 | 4.37 | mol |
| $n_2^0 \times 10^4$ | 1.471 | 1.096 | 0.779 | 0.924 | 1.269 | mol |
| $n_3^0 \times 10^4$ | 2.695 | 2.685 | 1.4525 | 1.692 | 2.323 | mol |
| $n_4^0 \times 10^4$ | 1.985 | 1.979 | 1.050 | 1.246 | 1.712 | mol |
| $N_{Na}^0 \times 10^4$ | 6.665 | 6.643 | 3.525 | 4.184 | 5.745 | mol |
| $D$ | 16.24 | 16.34 | 30.79 | 25.94 | 18.91 | $atm\,mol^{-1}$ |
| $F_{Dy}$ | 1.68 | 2.49 | 3.19 | 3.01 | 3.44 | |
| $F_{Na}$ | 0.90 | 0.54 | 0.80 | 1.18 | 1.22 | |

$$n_3^2(2D/K_d) + n_3 + (N_{Dy} - N_{Na} - a_2 n_2^0) = 0 \qquad (24)$$

which may be solved yielding $n_2$ and thus $n_1$, $n_2$, $n_4$ and $K_a$ as a function of $a_2$. Alternatively Equations 10 to 15 may be solved by eliminating $a_2$, $n_2$, $n_3$, $n_4$ to yield a cubic in $n_1$, which may be solved for various values of $K_a$, i.e.

$$n_1^3 + Fn_1^2 + Gn_1 + H = 0 \qquad (25)$$

where

$$F = 2/(K_a^2 K_d D) - N_{Na} - 2N_{Dy} - 1/(K_a D)$$
$$G = 2N_{Na}N_{Dy} + N_{Dy}^2 + N_{Dy}/(K_a D)$$
$$H = N_{Na} \times N_{Dy}^2$$

The resulting values of $a_2$ were plotted as a function of $K_a$. Two such examples are shown in Fig. 7. The fraction of dysprosium transported as the complex $R = n_1/(n_1 + n_2)$ is plotted together with $a_2$ (the activity of $DyCl_3$), both as a function of $K_a$. As $K_a$ increases and complex formation becomes more favourable the ratio $R$ increases, that is most of the dysprosium in the vapour is in the form of the complex and so $a_2$ decreases. The collected activity plots are shown in Fig. 8 with a tie line at $a_2 = 0.5$. If this is the true activity of the melts then the experimental errors lead to an equilibrium constant in the range $867 < K_a/atm^{-1} < 3670$ (at 1238 K). If the true activity is lower then $K_a$ assumes higher values. The scatter in results may be due to the handling and analytical problems experienced. If the dysprosium chloride is contaminated with moisture it forms the oxychloride on heating, and it would be preferable to have the vapour transport apparatus appended to a dry box. Dysprosium ion requires $2000\,\mu g\,ml^{-1}$ of potasium ion as an ionization buffer for atomic absorption spectrophotometry results to be reproducible to ten per cent. Assuming ideal mixing $\Delta G_a^0(1238\,K)$ can be evaluated

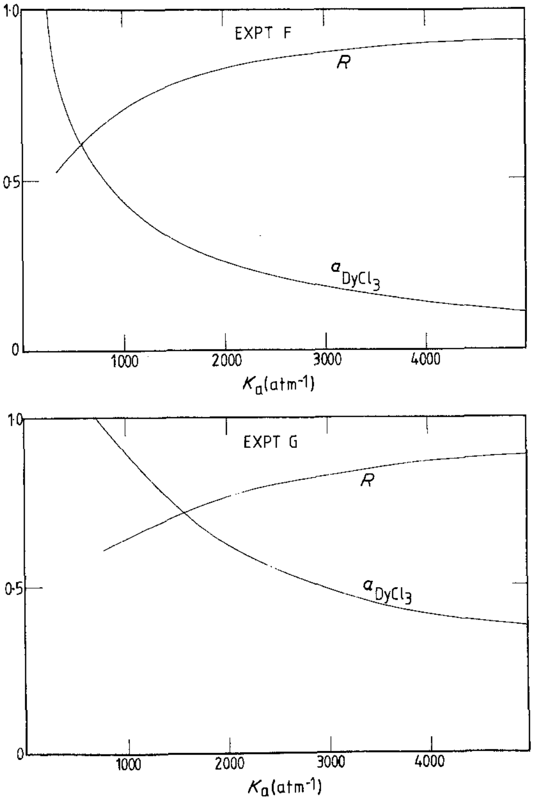

*Figure 7* The activity and complex ratio as a function of $K_a$.

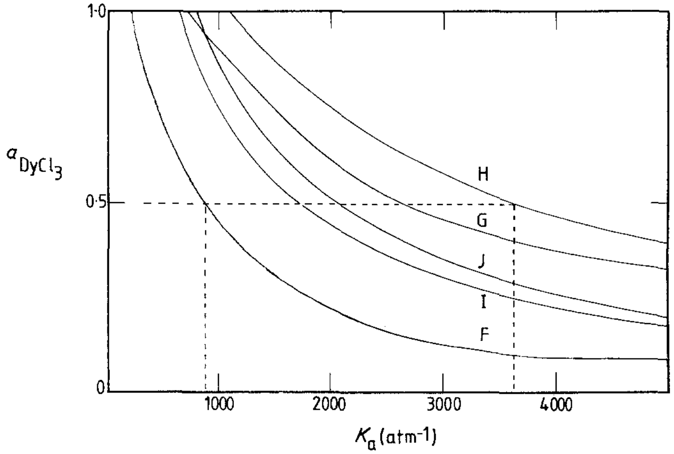

*Figure 8* The combined activity results for Experiments F to J.

and its value, $-76.9 \pm 8\,kJ\,mol^{-1}$ corrected to 1000 K using $\Delta S_a^0 = -150.6\,J\,mol^{-1}K^{-1}$ [11]. The result $\Delta G_a^0(1000\,K) = -112.7 \pm 8\,kJ\,mol^{-1}$ implies $\Delta H_a^0 = -263.3\,kJ\,mol^{-1}$. This free energy is in good agreement with Novikov's [12, 13] data for the lithium and caesium complexes: $\Delta G_a^0$ $(1000\,K) = -114\,kJ\,mol^{-1}$. The value of the reaction enthalpy agrees with that found by mass spectrometry [2] ($\Delta H_a^0 = -251.6 \pm 32\,kJ\,mol^{-1}$).

The observed enhancements are temperature dependent and can be corrected to 1000 K by writing [1]

$$d \ln F_{Dy}/dT = (\Delta H^0_{evaporation,\,NaCl} + \Delta H_a^0)/RT^2 \tag{25}$$

and

$$d \ln F_{Na}/dT = (\Delta H^0_{evaporation,\,DyCl_3} + \Delta H_a)/RT^2 \tag{26}$$

The evaporation and reaction enthalpies, measured by mass spectrometry [2], are $\Delta H^0_{evaporation,\,NaCl} = +167.1 \pm 11.8$, $\Delta H^0_{evaporation,\,DyCl_3} = +223.2 \pm 10$, and $\Delta H_a^0 = -251.6 \pm 32\,kJ\,mol^{-1}$. Thus the corrected enhancements are $F_{Na}(1000\,K) = 1.8$ and $F_{Dy}(1000\,K) = 19.3$. A drop in temperature of $\sim 238\,K$ increases the enhancement of dysprosium seven-fold. This trend was predicted by observing the relative changes in ion intensities of the complex $NaDyCl_3^+$ and the ion $DyCl_2^+$ ($DyCl_3$) in the mass spectrometry experiments.

### 3.5. Lamp experiments

The enhancements found in the NaCl/$DyCl_3$ system were further tested by dosing three electrical discharge mercury lamps with sodium chloride, dysprosium chloride and an equimolar sodium chloride/dysprosium chloride mix, respectively. The resulting spectra, shown in Fig. 9, contain emission lines from the mercury in all three cases, and emission lines from the respective metals. Both the sodium and dysprosium lines increase in intensity in the third lamp with the multi-line emission spectrum of dysprosium appearing. The enhancement factors were estimated as $F_{Na} > 4$ and $F_{Dy} > 8$ and so were consistent with the vapour transport results.

## 4. Conclusions

Vapour transport experiments yield direct quantitative values for the enhancement(s) in a

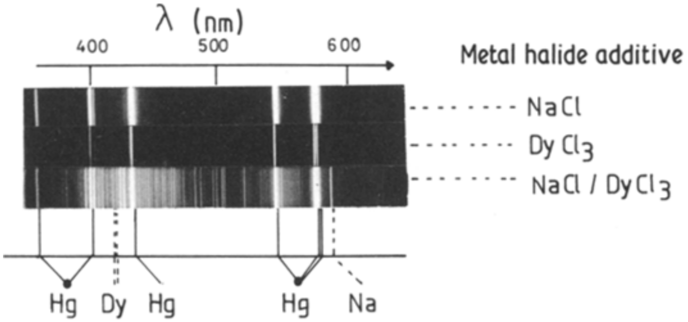

*Figure 9* The spectra from three mercury/metal halide discharge lamps.

system from which accurate free energies may be calculated provided the melt activities are known.

Enhancement of a species in the vapour requires both a large equilibrium constant for complex formation and a volatile complexing agent. However, since the most stable complexes (e.g. $NaDyCl_4$) are formed from relatively involatile ionic salts, these requirements are incompatible.

The two types of system studied here give similar enhancements. In the $NaCl/DyCl_3$ system the combination of two involatile salts yields a stable complex with $K_a(1000\,K) = 7.76 \times 10^5$ $atm^{-1}$, but the enhancements are limited by the low vapour pressures of NaCl and $DyCl_3$ to $F_{Na}$ $(1000\,K) = 1.8$; $F_{Dy}(1000\,K) = 19.3$. In the $NaCl/PbCl_2$ system the complex is less stable with $K_a$ $(1000\,K) = 4.1 \times 10^3\,atm^{-1}$, but the high vapour pressure of lead chloride allows it to act as an effective complexing agent and the sodium enhancement, corrected to 1000 K, is $F_{Na} = 11.4$. In the latter type of system one will only observe enhancement of the low volatility component (Na).

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