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NEW APPROACHES TO THE STUDY OF LANTHANIDE/ACTINIDE CHLORIDE-- ALUMINUM CHLORIDE VAOPR PHASE COMPLEXES

by

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NEW APPROACHES TO THE STUDY OF LANTHANIDE/ACTINIDE CHLORIDE - ALUMINUM CHLORIDE VAPOR PHASE COMPLEXES*

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Recent interest in vapor phase complexes of lanthanide and actinide halides with aluminum halides has been focused on their dynamic optical properties, since these systems have potential as optical gain media. In addition, their thermodynamic properties indicate that elemental separation by chemical transport is potentially viable. The reaction for gas complexation is generally written as follows for lanthanide chlorides and aluminum chloride

$$mLnCl_y(c) + nAl_2Cl_6(g) \rightleftarrows Ln_mAl_{2n}Cl_{6n+my}(g). \qquad (1)$$

Vapor phase studies over a condensed solid phase (in all cases $LnCl_3$ or $AnCl_y$) have been made for the Nd^{+3} (1), Sm^{+3} (2), Ho^{+3} (3), U^{+4} and U^{+5} (4) systems. Vapor phase studies over a condensed liquid phase are more complicated and have been discussed for the Eu^{+2} system (5). The present discussion will be limited to the pressure-temperature region of solid-vapor equilibrium.

Equilibrium studies of reaction (1) are made to establish the temperature and Al_2Cl_6 pressure dependence of the vapor density of complexed lanthanide or actinide ions (1-5). The stoichiometric coefficient, n, is then derived from the isothermal pressure dependence of the complexed metal ion density. If n is temperature dependent, then more than one vapor species exist in the measurement region. The value of m cannot be calculated from data of this type, but a value of 1 is in agreement with mass spectro-

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scopic studies of transition metal chloroaluminate vapor complexes (6) and is consistent with our results.

A variety of direct and indirect methods have been used to determine vapor densities of complexed metal ions in transition metal systems (6), but the spectrophotometric technique has been used exclusively for the lanthanides and actinides. Unfortunately, the stoichiometries inferred from the vapor density information derived from these experiments are contradictory for the lanthanides (1-3). In the $NdCl_3(Al_2Cl_6)_n$ system n varies from 1.85 to 1.65, while in the $SmCl_3(Al_2Cl_6)_n$ system n is reported to be invariant with temperature and equal to 1.5. This type of deviation in chemistry is unusual for two similar lighter lanthanides. These and other discrepancies have prompted us to re-evaluate the application of the spectrophotometric technique to these systems and to develop a technique for vapor density measurements which circumvents some of the problems associated with optical experiments.

SPECTROPHOTOMETRIC TECHNIQUE

This method relates the optical absorbance of the system to the vapor density of complexed metal ions. The implicit assumption in this analysis is that the optical absorption of the measured bands follows Beer's law over the entire range of temperatures and group IIIB halide pressures used to study the system. Unfortunately, for many lanthanide systems this is not the case (2,3,7). Several authors have treated the temperature dependence of the molar absorptivity by empirically deriving an equation to express the dependence (2,5). This approach is fundamentally flawed. Three effects, which are considered to contribute to the deviations (from Beer's law), are (1) the temperature dependence of the natural line width, (2) the temperature dependence of the population distribution within the ligand field components of the ground J-manifold and (3) changes in the absorption spectrum due to the existence of several complex molecular species whose vapor density distributions are functions of temperature and complexing agent pressure (8). To overcome these effects, integration over the entire absorption band is performed.

The fundamental equation for the spectrophotometric analysis is

$$\frac{\ln 10}{\ell} \int_{\text{band}} A(\sigma)\,d\sigma = \frac{\pi e^2}{mc^2} \sum_n \rho_n \overline{f_n} \,, \qquad (2)$$

in which ℓ is the optical path length, $A(\sigma)$ is the observed optical absorbance at wavenumber σ, e and m are the charge and mass of the electron respectively, c is the velocity of light, ρ_n is the vapor density of the nth complexed species and $\overline{f_n}$ is the average oscillator strength of the nth complexed species for transitions between two J-manifolds (11). Eq. (2) should be used to relate optical absorbance data to the vapor density of complexed metal ions. In essence this approach relates the vapor density to the area under the peak due to the particular f-f transition being probed instead of to the peak height at a specific wavelength. In practice the optical experiments are done in a manner similar to that reported in the literature (1,2). The pressure and temperature dependence of the effective oscillator strength, $f^*(T,P_D)$, is determined in experiments with a known total vapor density of complexed metal ions (unsaturated cell). Then the pressure and temperature dependence of the vapor density is determined in cells with excess metal halide (saturated cell)

$$\rho_T(T,P_D) = \sum_n \rho_n(T,P_D) = \frac{mc^2}{\pi e^2}\,\frac{1}{f^*(T,P_D)}\,\frac{\ln 10}{\ell}\int_{band} A(\sigma)d\sigma \ . \qquad (3)$$

Because this technique measures the product of the vapor density and the oscillator strength, two assumptions were necessary. The oscillator strengths of the various species must be independent of temperature and the relative vapor densities of multiple species for saturated and unsaturated cells must be identical. To test these assumptions and to provide information when the spectrophotometric technique is not applicable, a technique for direct measurement of vapor densities of complexed metal ions was developed.

RADIOACTIVE TECHNIQUE

This method of complexed metal ion density measurement involves labelling the metal ions of interest with a radioactive isotope whose decay leads to γ-ray emission. The vapor density is conveniently monitored by γ-counting (usually >0.4 MeV γ-radiation) in a specified energy range (the energy integral of the γ-ray spectrum). The applicability of this technique was evaluated during studies of the $TbCl_3$-$AlCl_3$ system using tracer $^{160}TbCl_3$. The sample vessel was loaded with $TbCl_3$ and $AlCl_3$ and was placed in a furnace surrounded except for a detection slot by a shield of lead bricks. The end of the tube opposite to that monitored by the detector was kept at a lower temperature by ca. 20°K. The nonvolatilized portion of $TbCl_3(s)$ thus remained out of the detection field. Vapor equilibrium was established over the condensed phase. A suitable detector was used to monitor the γ-activity in the hot end of the sample vessel. The signals were fed through an amplifier/discriminator to a pulse height analyzer. Thus, in principal more than one characteristic γ-ray in a mixture could be monitored. The measured count rate was proportional to the density of Tb atoms in the vapor plus any background noise. The equation which relates vapor density to count rate is

$$\rho = \frac{4\pi R^2}{\bar{\varepsilon}\ A^* V_D\ f_o}\ \frac{e^{(\ln 2)t/T_{1/2}}}{I_\gamma}\ P \qquad (4)$$

in which R is the distance from sample to detector, A* is the effective detector area, V_D is the volume of the vessel sampled by the detector, $\bar{\varepsilon}$ is the effective detector efficiency, f_o is the initial amount of radioactive isotope, $e^{(\ln 2)t/T_{1/2}}$ considers the isotopes radioactive decay with time, I_γ is the probability per unit time of radioactive decay, and P is the count rate (9). Experiments are carried out in a manner similar to optical experiments. Unsaturated cells of known total complexed metal ion density are examined to calibrate the counting geometry (R, $\bar{\varepsilon}$, f_o, A* and V_D). Then saturated cells are studied to determine the temperature and complex agent pressure dependence of the vapor density. The greatest strength of this technique is that it is a direct measure of the complexed metal ion density and is not dependent upon the chemistry of the system. Accurate measurements of multi-species vapor systems can be readily accomplished. The accuracy and precision of the data are superior to data obtained by optical experiments (9). The tracer method is applicable to systems, such as $TbCl_3$-$AlCl_3$, which are not amenable to study by the spectrophotometric technique. In situations where both methods are available complementary data will be available to aid in characterization of the vapor system. A complete thermodynamic analysis of the $TbCl_3$-$AlCl_3$ system is currently underway using the tracer technique.

ANALYSIS OF THERMODYNAMIC PROPERTIES

From the temperature and pressure dependence of vapor density data, the identity and apparent thermodynamic formation parameters for the vapor complex species are inferred. The apparent equilibrium quotient for reaction (1) is written

$$K^* = P_C/P_D^{n^*} \qquad (5)$$

where the condensed phase is a solid. If n* is a non integer temperature dependent variable, then multiple vapor species exist. The prior method of analysis (1,5,10) involved fitting vapor pressure information to an appropriate two species model using a nonlinear least squares program. The data was not considered adequate for consideration of more complex models, but this assumption was not tested. The drawback of this approach is that it forces the data into a preconceived picture, the validity of which cannot be reliably tested. Instead of relying on this approach, a systematic method of data analysis has been developed (11).

Taking the natural logarithm of eq. (5) yields

$$\ln P_C = \ln K^* + n^* \ln P_D\ . \qquad (6)$$

A series of isothermal plots of ln P_C vs. ln P_D data yield K* and n* values as a function of temperature. In a multiple species system the vapor pressure can be expressed as

$$P_C = \sum_{m=0}^{B} K_m P_D^{m/2} \tag{7}$$

where B is twice the oxidation state of the metal ion in the halide and m = 2n. Possible m values can be chosen by considering the range of n values derived in the measurement region from ln P_C vs. ln P_D plots with the largest m value being derived by extrapolation to low temperature. For a two species model eq. (7) is written

$$P_C = K_{m_1} P_D^{m_1/2} + K_{m_2} P_D^{m_2/2} \tag{8}$$

where $m_1 > m_2$. Dividing both sides by $P_D^{m_1/2}$ yields

$$P_C/P_D^{m_1/2} = K_{m_1} + K_{m_2}/P_D^{(m_1-m_2)/2} \tag{9}$$

with the choice of $1/P_D^{(m_1-m_2)/2}$ as independent variable being arbitrary. Isothermal plots based upon eq. (9) indicate the temperature dependence of the equilibrium quotients K_{m_1} and K_{m_2}. If the natural logarithm of these quotients are well behaved straight line functions of 1/T(K) (ln $K_m = A_m e^{-B_m/T}$), then the two species model will adequately reproduce the vapor pressure data. If there are deviations from straight line behavior for all possible values of m_1 and m_2, then a three species model can be tested with the proposed third species being dependent upon the nature of the deviation of the previous model.

$$P_C = K_{m_1} P_D^{m_1/2} + K_{m_2} P_D^{m_2/2} + K_{m_3} P_D^{m_3/2} \tag{10}$$

For example, in the $HoCl_3(AlCl_3)_x$ system (3), the data indicate that a previously unreported higher temperature species, $HoAl_2Cl_9$, makes a 20% contribution to the total vapor density at 750 K and 2 atm of dimer pressure. Re-analysis of the Nd^{+3} system also led us to infer the existence of this lower molecular weight species at higher temperature (11). Examination of temperature dependent optical spectra indicates that spectral changes of the $^5I_8$ to $^5G_6$ transition of Ho^{+3} are consistent with this interpretation (3).

CONCLUSIONS

The spectrophotometric technique for vapor density measurements of complexed metal ions has been reformulated to account for temperature dependent effects and multi-species systems. Analysis of vapor pressure information indicates that the $NdCl_3$-$AlCl_3$ and $HoCl_3$-$AlCl_3$ systems are adequately explained by the existence of three vapor species. The two higher molecular weight complexes $LnAl_4Cl_{15}$ and $LnAl_3Cl_{12}$ were first proposed by Øye and Gruen. The newly identified higher temperature species, $HoAl_2Cl_9$, contributes significantly to the vapor density above 750 K and below 3 atm of dimer pressure. In view of the consistency of the Nd^{+3} (1) and Ho^{+3} (3) chemistry the data for the Sm^{+3} system (2) should be viewed with reservation. A new method for vapor density measurements involving use of radioactive tracers has been discussed in terms of its applicability to the study of $(Ln,An)Cl_3(AlCl_3)_x$ systems.

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T:Q1 ACTINIDE COMPLEXES;PHASE STUDIES

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systems.

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EDB	☑	ALD	☐		☐
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EPA	☐	RIP	☐		☐
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