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PHYSICAL INORGANIC CHEMISTRY
ANNUAL REPORT

July 1975—June 1976

by

M. Blander, L. A. Curtiss, C. C. Hsu, G. H. Kucera,
J. J. Marr, G. N. Papatheodorou, T. A. Renner,
M. L. Saboungi, F. A. Cafasso, and L. Burris

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ABSTRACT

The thermal conductivity of acetonitrile vapor has been measured at temperatures between 338 and 387 K and pressures between 100 and 1050 Torr. The pressure dependence of the thermal conductivities indicates the presence of dimeric vapor species with an association constant given by $RT \ln K_2 (\text{atm}^{-1}) = 5002 - 21.15 T$. Molecular orbital studies of hydrogen-bonded methyl alcohol vapor complexes indicate that, as with water, the cyclic tetramer is especially stable, in agreement with conclusions reached from our thermal conductivity measurements. Preliminary calculations on trifluoroethanol indicate that its dimer is more stable than that of methanol. Molecular dynamics calculations have been utilized to calculate the second-order coefficient of conformal ionic solution (CIS) theory. The results indicate that the repulsive part of the pair potential most commonly used for calculations on molten salts is inaccurate and that our calculation of the CIS coefficient provides a sensitive test of pair potentials. Laser-Raman spectra of molten solutions of YCl_3 in CsCl , KCl and LiCl were obtained and compared with spectra of solids of known structure. The spectra at low concentrations of YCl_3 ($X_{\text{YCl}_3} < 0.25$) indicate an octahedrally coordinated YCl_6^{3-} species. Raman and infrared spectra of claudetite and arsenolite were measured and compared with the spectra of vitreous and liquid As_2O_3 , as well as with the As_4O_6 vapor molecules. The spectrum of claudetite has some resemblance to that of vitreous and liquid As_2O_3 . Raman spectra of arsenous oxide indicate that the dimeric As_2O_3 species is present. The Raman spectra of aluminum chloride vapor (AlCl_3 and Al_2Cl_6 vapor molecules), provided nine new bands not observed before and permitted a more complete assignment and analysis of the structure of the species to be made. The Raman spectra of In(I) , In(II) and In(III) chlorides indicate the presence of InCl , In(I)In(III)Cl_4 (In_2Cl_4), InCl_3 , and In_2Cl_6 species in the vapors. Resonance Raman spectra of the vapor complex PdAl_2Cl_8 indicate that the Pd is surrounded by four Cl^- ions in a square planar configuration. The spectra of CuAl_2Cl_8 indicate preferential resonance Raman coupling for certain fundamentals. Measurements of CoAl_2Br_8 indicate that, for the reaction $\text{CoBr}_2(\text{s}) + \text{Al}_2\text{Br}_6 \rightleftharpoons \text{CoAl}_2\text{Br}_8$, the equilibrium constant, K , is given by $R \ln K = -9.4 + 9.9/T$. Measurements of dilute solutions of lithium in molten Al-Sn alloys

have been analyzed in terms of a generalized quasi-lattice theory. A new expression that took into account the properties of the solvent was deduced for the energetics of forming associated solution species. The resultant equations fit the experimental measurements very closely and appear to provide a more accurate description of the solution thermodynamics than previous theories. Emf measurements of molten Li-Pb alloys indicate large negative deviations from ideal solution behavior, characteristic of alloys that exhibit a partially ionic behavior. Calculations have been made of the phase diagrams of the binary systems Li-Mg, Li-Al, Li-Ca, Mg-Al and Ca-Mg which check the self-consistency of available phase diagrams; provide additional thermodynamic information on compounds, solid solutions and transformations; and help to more fully define the phase diagram. The results are to be used to construct ternary phase diagrams *a priori*. Calculations of condensation from a solar nebula were made with the imposition of nucleation constraints and kinetic constraints on the formation of MgSiO_3 and SiO_2 . The results indicate that the chemistry of enstatite chondrites is similar to that of the condensate at $\sim 10^{-2}$ atm; of ordinary chondrites, to that of the condensate at $\sim 10^{-3}$ atm; and of carbonaceous chondrites to that of condensates from the nebular gas at $\leq 10^{-4}$ atm.

SUMMARY

Physical Properties of Associating Gases

Thermal Conductivity of Associating Gases. Thermal conductivities of acetonitrile were measured at temperatures ranging from 338 to 387 K and pressures between 100 and 1050 Torr. The almost linear pressure dependence of the thermal conductivities indicates the presence of dimeric molecules with an association constant, K_2 , given by the expression

$$RT \ln K_2 (\text{atm}^{-1}) = 5002 - 21.15 T$$

The limiting thermal conductivities at zero pressure, λ_1 , are given by the expression

$$\lambda_1 \times 10^5 (\text{cal/cm sec K}) = -7.948 + 0.5900 T^{1/2}$$

At saturation, the fraction of dimeric species ranges from 0.023 at 338 K to 0.037 at 387 K.

Molecular Orbital Studies of Hydrogen-Bonded Complexes. *Ab initio* molecular orbital calculations of the structures and binding of hydrogen-bonded polymers of methyl alcohol have been made. Cyclic polymers appear to be more stable than linear species. The calculated stability of the cyclic tetramer is high ($-\Delta H_4 = 23.5\text{--}28.4$ kcal/mol), thus lending support to the conclusions reached from our thermal conductivity measurements, which indicate the presence of a tetrameric species ($-\Delta H_4 = 23.9$ kcal/mol). Preliminary calculations on trifluoroethanol indicate that its dimers are more stable than those of methanol.

Chemistry of Molten Salts and Their Vapors

Some Thermodynamic Properties of Binary Chloride Mixtures by Molecular Dynamics Computation. The second-order coefficient of the conformational ionic solution (CIS) theory was calculated using a molecular dynamics technique. The calculations are very sensitive to the form of the repulsive part of the pair potentials used in the calculations, and thus provide a sensitive test of pair potentials. One of the most widely used pair potentials, the Tosi-Fumi potential, does not lead to results consistent with measurements, whereas the potential of Michielsen *et al.* appears to be reasonable.

Raman Spectroscopic Studies

Raman Spectroscopic Studies of Yttrium(III) Chloride-Alkali Chloride Mixtures. The Raman spectra of molten $\text{YCl}_3\text{-ACl}$ ($A = \text{Cs, K, Li}$) mixtures have been measured at different compositions and temperatures up to 890°C . The Raman spectra of polycrystalline $\text{Cs}_2\text{NaYCl}_6$ and YCl_3 were also measured from 25°C to temperatures above their melting points. The factor group analysis of crystalline $\text{Cs}_2\text{NaYCl}_6$ was used to identify the three Raman-active modes of the YCl_6^{3-} octahedra. For liquid mixtures rich in ACl , the spectra are consistent with the presence of YCl_6^{3-} octahedra.

Raman Spectra of Amorphous Materials. Infrared absorption and polarized Raman spectra of monoclinic As_2O_3 and the Raman spectrum of cubic As_2O_3 have been recorded. The layered monoclinic phase, claudetite, exhibited rigid layer modes of Raman shifts of 30, 38, and 49 cm^{-1} , and numerous Davydov doublets, all of which appeared as a consequence of weak layer-layer coupling. Recurring bands in the crystalline and amorphous phases of As_2O_3 are noted and structural similarities between the different phases are evident by vibrational features that are comparable in frequency and symmetry. Accordingly, the layered structure in As_2O_3 glass is inferred.

Salt Vapor Studies

Raman Spectra of Arsenic Oxide. Polarized Raman spectra of As_4O_6 vapors were obtained. Vibrational interaction has been observed in two of the fundamentals. A new assignment of the fundamentals assuming a T_d molecular geometry is given. A band at 409 cm^{-1} is attributed to Fermi resonance.

Raman Spectra of Aluminum Chloride. Raman spectra of the aluminum chloride dimer-monomer equilibrium species:

were obtained in the temperature range from 200 to 900°C . Nine new bands and a new temperature-dependent doublet at 339 cm^{-1} were found.

Raman Spectra of Indium(I), (II) and (III) Chlorides. Raman spectra of vapors over indium chlorides with Cl/In ratios of 1, 2 and 3 were obtained at temperatures up to 900°C . For indium trichloride, the spectra were representative of two species in equilibrium:

The vapor over liquid InCl shows a vibrational-rotational structure of a symmetric top diatomic molecule. The spectra of vapors over liquid InCl₂ are attributed to InCl₃(g) and InCl(g) species in equilibrium:

Resonance Raman Spectra of PdAl₂Cl₈ and CuAl₂Cl₈. Raman spectra were obtained of gaseous complex species formed according to the reactions:

The intensities of the Raman bands depend on the excitation frequency and show resonance enhancement of certain symmetric fundamentals. The absorption spectrum of CuAl₂Cl₈(g) was also obtained.

Spectra and Thermodynamics of the Cobalt Bromide-Aluminum Bromide Gaseous Complexes. A new experimental setup for light absorption measurements at temperatures up to 1200°C is described. The reaction of solid Co(II) bromide with gaseous aluminum bromide to form deep-green gaseous complex(es) has been investigated spectrophotometrically in the range from 550 to 900 K and pressures up to 2 atm. Thermodynamic considerations suggest the reaction:

$$\Delta H = 9.9 \text{ kcal/mol}, \Delta S = 9.4 \text{ e.u.}$$

The electronic absorption spectra are discussed in terms of the possible coordination of Co(II) in the gaseous molecule(s). Spectroscopic and thermodynamic considerations suggest that the predominant absorbing species in the gas phase is Co(AlBr₄)₂ molecules having the Co(II) in a close-to-octahedral coordination. The volatility enhancement ratios of cobalt(II) halide in the presence of various "acidic" A₂X₆ gases are calculated and compared. At temperatures below 750 K, aluminum bromide is a better gas-complexing agent than aluminum chloride for the respective cobalt halides.

Thermodynamic Properties of Alloys

Electromotive Force Measurements and Interpretation of the Activity Coefficients of Dilute Solutions of Lithium in Molten Aluminum-Tin Alloys. Activity coefficients of dilute solutions of Li in Al-Sn alloys were measured using an emf technique. The concentration dependence of the activity coefficients was analyzed in terms of a generalized quasi-lattice theory based on the presence of species Li[Sn₁, Al_{Z-1}], where Z is a coordination number. The results were accurately described when a new expression that took into account the deviations from ideality of the solvent was used for the energetics of the formation of such species. The new expression led to a better description of the results than prior theories.

Electromotive Force Measurements in Molten Li-Pb Alloys. Emf measurements of the activities of Li in Li-Pb alloys indicate large negative deviations from ideal solution behavior, with the excess chemical potential of Li at infinite dilution being -11.098 kcal mol⁻¹. The "S"-shaped concentration

dependence of $\ln \gamma_{Li}$ is characteristic of partly ionic alloys in which electrons are transferred from Li to Pb atoms.

Computation of Phase Diagrams. Phase diagrams of the five binary systems Li-Mg, Li-Al, Li-Ca, Mg-Al, and Ca-Mg were calculated theoretically, using a very few points on the measured phase diagrams. The calculations served to check the self-consistency of the measured phase diagrams and helped to define and extend the phase diagrams to unmeasured regions. In addition, the calculations provided additional thermodynamic information on the stability of compounds, on solid solutions, and on solid-solid transformations. The parameters used to calculate the binary diagrams will be used to calculate ternary phase diagrams *a priori*.

Meteoritic Studies

The NASA computer program of Gordon and McBride was used to calculate condensates from a solar nebula. Nucleation constraints predicted from nucleation theory and known kinetic constraints on the formation of $MgSiO_3$ and SiO_2 were imposed on the equilibria involved. The results indicate that the condensates will be fairly close to equilibrium at nebular pressures of 10^{-2} atm. At pressures of $\sim 10^{-3}$ atm, the condensates depart from equilibrium and resemble ordinary chondrites. At pressures of $\sim 10^{-4}$ atm, there are large departures from equilibrium, and the condensates resemble carbonaceous chondrites.

I. PHYSICAL PROPERTIES OF ASSOCIATING GASES (M. Blander)

Associating gases have physical properties that make them potentially useful as working fluids in power cycles. In addition, several materials that have been used or proposed for use as power-cycle working fluids form associated vapor species whose properties have not been adequately investigated. Measurements and calculations of the thermophysical properties of such gaseous materials are under way to determine the stabilities of the aggregated vapor species and properties of the gases and to obtain data needed for potential applications as working fluids.

A. Thermal Conductivity of Associating Gases (T. A. Renner)

Acetonitrile and substituted nitriles are thermally stable materials that have potential uses as working fluids. The thermal conductivity of acetonitrile vapor has been measured between 338 K and 387 K in the pressure range from 100 to 1050 Torr. A modified thick hot-wire cell method was employed; the cell consisted of a soft-glass tube 10 cm in length with an ID of 0.5 cm. A uniform platinum wire of 0.51-mm diameter was mounted under slight tension along the axis of the cylinder by fusing it into the glass at each end of the tube. A regulated constant current of 1.0 A was passed through the wire to produce a radial and an axial thermal gradient in the acetonitrile vapor. The pressure in the cell was continuously monitored with a thin-film strain-gage pressure transducer calibrated against a mercury manometer.

The thermal conductivity cell was calibrated against reference gases of known conductivity, namely, helium, nitrogen, argon, and krypton. The voltage drop across the cell wire was found to vary linearly with the reciprocal of the thermal conductivity of the reference gases and may be expressed as follows:

$$V = A + B/\lambda \quad (1)$$

where V is the voltage drop, λ is the thermal conductivity, and A and B are constants to be determined by calibration. The precision of the data obtained by this technique was approximately $\pm 0.5\%$.

The experimental thermal conductivities of acetonitrile are shown in Fig. 1 for the four temperatures studied. The data were fitted by a least-squares minimization technique to an equation of the form

$$\lambda = \lambda_f + \lambda_R \quad (2)$$

where λ_f is the "frozen" conductivity (i.e., the thermal conductivity of a system of equilibrium composition not undergoing any chemical reaction), and λ_R is the enhancement of the thermal conductivity due to the formation of acetonitrile dimers. When the vapor is considered to be a mixture of monomers and dimers, λ_f may be represented by the relationship known as the Wassiljewa equation,¹

Fig. 1. Thermal Conductivities of Acetonitrile as a Function of Pressure

$$\lambda_f = \frac{\lambda_1}{(1 + A_{12} x_2/x_1)} + \frac{\lambda_2}{(1 + A_{21} x_1/x_2)} \quad (3)$$

where λ_1 and λ_2 are the thermal conductivities of monomers and dimers, respectively, x_1 and x_2 are the corresponding mole fractions, and A_{12} and A_{21} are numerical parameters. A_{12} and A_{21} were calculated from a relationship given by Mason and Saxena,²

$$A_{ij} = \frac{k}{2\sqrt{2}} \left[\frac{M_j}{M_i(M_i + M_j)} \right]^{1/2} \frac{(M_i^{1/4}\eta_j^{1/2} + M_j^{1/4}\eta_i^{1/2})^2}{\eta_j} \quad (4)$$

in which η_1 is the viscosity and M_1 is the molecular weight of species 1, and $k = 1.065$. The thermal conductivity and viscosity of the dimer, λ_2 and η_2 , may be calculated in terms of λ_1 and η_1 , respectively, from the kinetic theory of gases.³ The mole fraction $x_1 = p_1/p$ and $x_2 = p_2/p = K_2 p_1^2/p$, where p_1 is the partial pressure of monomer, p_2 is the partial pressure of dimer, p is the total pressure, and K_2 is the equilibrium constant for the reaction $2\text{CH}_3\text{CN} \rightleftharpoons (\text{CH}_3\text{CN})_2$. Upon substitution of these quantities in Eq. 3, λ_f may then be written,

$$\lambda_f = (a + bT^{1/2}) \left[\frac{1}{(1 + 1.5702 K_2 p_1)} + \frac{0.9290 K_2 p_1}{(K_2 p_1 + 0.6994)} \right] \quad (5)$$

where $\lambda_1 = (a + bT^{1/2})$ and a and b are constants to be determined from the experimental data.

The increase in thermal conductivity due to dimer formation, λ_R , is given by the relationship derived by Butler and Brokaw,⁴

$$\lambda_R = \left(\frac{pD_{12}}{RT} \right) \frac{\Delta H_2^2}{RT^2} \frac{K_2 P_1}{(1 + 2K_2 P_1)^2} \quad (6)$$

in which pD_{12} is the product of the pressure and the binary diffusion coefficient between monomers and dimers, ΔH_2 is the enthalpy of dimer formation, R is the gas constant, and T is the absolute temperature. The term pD_{12} may be calculated from equations developed in Hirschfelder, Curtiss, and Bird:³

$$pD_{12} = pD_{11} \left(\frac{3}{4} \right)^{1/2} \left(\frac{\sigma_{11}}{\sigma_{12}} \right)^2 \quad (7)$$

and

$$pD_{11} = \frac{6}{5} \left(\frac{R}{M_1} \right) A_{11}^* T \eta_1 \quad (8)$$

where σ_{11} and σ_{12} are size parameters characteristic of monomer-monomer and monomer-dimer interactions, respectively. These have been estimated by assuming that the molecular volume of the dimer is twice that of the monomer and that $\sigma_{12} = (\sigma_1 + \sigma_1)/2$, where $\sigma_2^3 = 2\sigma_1^3$. The parameter σ_1 was determined by the method of Fuller, Schettler, and Giddings⁵ ($\sigma_1 = 3.547$). The term A_{11}^* is a ratio of two collision integrals that is very nearly equal to unity for this case.

In fitting the experimental thermal conductivity data to Eq. 2, a , b , and K_2 (hence, ΔH_2 and ΔS_2) were treated as adjustable parameters; these were obtained by employing the SIMPLEX version of the Fortran subroutine STEPIT, available through the Quantum Chemistry Program Exchange (QCPE).⁶

$$RT \ln K_2 (\text{atm}^{-1}) = 5002 - 21.15 T \quad (9)$$

$$a = -7.948 \times 10^{-5}$$

$$b = 0.5900 \times 10^{-5} \text{ cal}/(\text{cm})(\text{sec})(\text{k}^{3/2})$$

The thermal conductivity of acetonitrile vapor, calculated from the best fit of data with Eq. 2, is also plotted as a function of pressure in Fig. 1.

For each of the four temperatures of this study, values of p_2 and x_2 evaluated at the saturation pressure are presented in Table 1.

There is an extremely small upward curvature in the plots of experimental points shown in Fig. 1. This would seem to indicate the presence of another associated species higher than the dimer in acetonitrile vapor. Attempts to separate the contribution of this species to the thermal conductivity from the contributions of monomer and dimer were not successful because of the small amount of this n-mer present. The magnitude of the effect of this n-mer on the measured thermal conductivity is smaller than the precision of our data,

Table 1. Thermodynamic Data Deduced from Thermal Conductivities

T, K	$10^2 K_2$, atm ⁻¹	$p_{\text{sat.}}$, Torr	p_2 , Torr	x_2
387.3	1.58	1927	72	0.037
372.2	2.06	1275	41	0.032
361.2	2.53	925	27	0.029
338.4	4.05	442	10	0.023

making the task of separation impossible. For practical purposes, the vapor of acetonitrile may be considered to be a mixture of monomers and dimers over the temperature and pressure ranges covered.

B. Molecular Orbital Studies of Hydrogen-Bonded Complexes
(L. A. Curtiss)

Ab initio molecular orbital calculations of the structures and binding energies of several hydrogen-bonded complexes have been carried out. The purpose of these calculations is to help explain the results of the thermal conductivity measurements on associating gases, including why certain species are observed and the possible structures of the complex. In addition, it is hoped that the results of these calculations can be used to help identify gases with molecular complexes having large enthalpies of formation and large degrees of association since these complexes might be good working fluids and good subjects for further thermal conductivity measurements.

The theoretical calculations use the GAUSSIAN 70 set of computer programs developed by Professor John Pople's group at Carnegie-Mellon University.⁷ This set of programs uses linear combinations of atomic orbitals (LCAO) to obtain self-consistent field (SCF) solutions to the Hartree-Fock equations for molecules. This procedure is easily extended to hydrogen-bonded complexes. For those complexes involving first-row atoms (C, N, O, F), the minimal STO-3G basis set has been found to give reasonable results⁸ and is relatively inexpensive in computer time.

Thermal conductivity measurements on methanol in the gas phase indicate that the tetrameric species is present.⁹ A recent theoretical study by Del Bene and Pople¹⁰ of the stabilities of the water polymers (H₂O)_n (n = 2, 3, 4, 5, 6) found that the largest increase in stability occurred when the tetramer was formed. To determine whether this is also true for the associated methanol species, we have carried out molecular orbital calculations on the series (CH₃OH)_n (n = 2, 3, 4, 5).

The geometry of the methanol dimer (Fig. 2a) has been determined by Del Bene¹¹ to be very similar to that of the water dimer. Using the assumption that the water and methanol polymers have similar structures, we have calculated the binding energies of the methanol polymers with structures similar to the water polymers. Dimer and tetramer structures are illustrated in Fig. 2. The binding energies for the most stable structures for which n = 2, 3, 4, 5

Fig. 2. Geometry of Methanol Dimer (a) and Tetramers (b)

are given in Table 2. As in the case of the water polymers, the cyclic structures for $n > 2$ are more stable than the chain structures.

The geometry of the methanol tetramer was partially optimized to test the hypothesis that the structures of the methanol polymers are similar to those of the water polymers. The results in Table 3 indicate that this hypothesis is valid.

The experimental and theoretical enthalpies of formation ΔH_{1n}° for the reaction

are compared in Table 4. The experimental values are from the thermal conductivity measurements on methanol vapor. In order to calculate the same theoretically, ΔH_{1n}° must be partitioned as follows:¹²

Table 2. Theoretical Binding Energies ΔE_{elec} for the Methanol Polymers Using the STO-3G Basis Set (in kcal/mol)

Polymer	Chain	Cyclic
(CH ₃ OH) ₂	-5.5	---
(CH ₃ OH) ₃	-14.7	-15.4
(CH ₃ OH) ₄	-21.0	-35.3
(CH ₃ OH) ₅	-34.7	-48.3

Table 3. Optimized Geometrical Parameters for (H₂O)₄ and (CH₃OH)₄

Polymer	R(Å) ^a	α ^b	γ ^c
(H ₂ O) ₄	2.47	61°	8°
(CH ₃ OH) ₄	2.50	59°	8°

^aHydrogen bond length.

^bThe angle that the C-O bonds make with the plane containing the four oxygen atoms in Fig. 2.

^cThe angle that the O-H bond makes with the O-O line between a pair of hydrogen-bonded molecules.

Table 4. Theoretical and Experimental Enthalpies of Formation for (CH₃OH)_n (in kcal/mol)

Polymer	ΔE_{elec}	Theory (at 325°C)			Experimental ΔH_{ln}
		ΔE_{vib} ^a	[$\Delta E_{\text{trans}} + \Delta E_{\text{rot}} + \Delta(PV)$]	$\Delta H_{\text{ln}}^{\circ}$ ^a	
(CH ₃ OH) ₂	-5.5	4.9	-2.58	-3.3	<4.0
(CH ₃ OH) ₃	-15.4	9.8(14.7)	-5.17	-10.8(-5.9)	--
(CH ₃ OH) ₄	-35.3	14.7(19.6)	-7.75	-28.4(-23.5)	23.9
(CH ₃ OH) ₅	-48.3	19.6(24.5)	-10.30	-39.0(-34.1)	--

^aThe numbers in parentheses are a higher estimate.

$$\Delta H_{1n}^{\circ} = \Delta E^{\circ} + \Delta(PV) = \Delta E_{\text{trans}}^{\circ} + \Delta E_{\text{rot}}^{\circ} + \Delta E_{\text{vib}}^{\circ} + \Delta E_{\text{elec}}^{\circ} + \Delta(PV) \quad (11)$$

When $RT/2$ is allotted to each translational and rotational degree of freedom, ΔH_{1n}° becomes

$$\Delta H_{12}^{\circ} = -4 RT + \Delta E_{\text{vib}12}^{\circ} + \Delta E_{\text{elec}12}^{\circ} \quad (12)$$

$$\Delta H_{13}^{\circ} = -8 RT + \Delta E_{\text{vib}13}^{\circ} + \Delta E_{\text{elec}13}^{\circ} \quad (13)$$

$$\Delta H_{14}^{\circ} = -12 RT + \Delta E_{\text{vib}14}^{\circ} + \Delta E_{\text{elec}14}^{\circ} \quad (14)$$

$$\Delta H_{15}^{\circ} = -16 RT + \Delta E_{\text{vib}15}^{\circ} + \Delta E_{\text{elec}15}^{\circ} \quad (15)$$

The contribution of the vibrations to the internal energy is determined from the relationship¹³

$$\Delta E_{\text{vib}}(T) = E_{\text{vib}}^{\circ}(0) + N \sum_i \frac{h\nu_i}{e^{h\nu_i/kT} - 1} \quad (16)$$

where $E_{\text{vib}}^{\circ}(0) = 1/2(N h \sum_i \nu_i)$ (17)

and the ν_i are the vibrational frequencies, and the summation is over the number of vibrational degrees of freedom.

$\Delta E_{\text{vib}}^{\circ}$ can be divided into contributions from intermolecular and intramolecular frequencies as follows:

$$\Delta E_{\text{vib}}^{\circ} = \Delta E_{\text{intra}}^{\circ} + \Delta E_{\text{inter}}^{\circ}$$

Generally, the intermolecular frequencies are not available for the polymeric species of molecules and one must resort to theoretical estimates of $\Delta E_{\text{vib}}^{\circ}$. Using a theoretical calculation of the intermolecular frequencies of the water dimer,¹⁴ we have estimated $\Delta E_{\text{vib}}^{\circ}$ for the methanol polymers and have obtained the ΔH° presented in Table 4.

The presence of dimer in the vapor was not detected in the thermal conductivity measurements; this would indicate that its enthalpy of formation is less than 4 kcal/mol. This is confirmed by the theoretical prediction of approximately 3.3 kcal/mol for ΔH_{12} at 325 K. Also, the value of ΔH_{14} found for the methanol tetramer falls in the range predicted for the value by theory.

The change in binding energy of the polymer as the number of methanol molecules in it increases is illustrated in Fig. 3. The maximum increase in stability occurs in going from the trimer to the tetramer. This result seems to explain why the thermal conductivity measurements on methanol detect the presence of mainly tetrameric species in the vapor.

Fig. 3. Stabilities of Gas Phase Water and Methanol Polymers, Calculated Using *ab initio* Molecular Orbital Theory

Molecular orbital calculations are also being carried out on trifluoroethanol (TFE) dimers to help understand the results of thermal conductivity measurements presently being made on TFE vapor. TFE is a working fluid that has been used in steam engines. A knowledge of the type of hydrogen bonding occurring in its vapor is important for thermal calculations and may help to identify other working fluids.

TFE differs from methanol and ethanol in that TFE has several rotational isomers, two of which are illustrated in Fig. 4. The gauche isomer has an intramolecular hydrogen bond that stabilizes it by about 3 kcal/mol¹⁵ over the trans isomer, which has a structure similar to ethanol. The existence of the gauche isomer creates the possibility of a stable bridged dimer, as well as a linear dimer similar to that found for methanol. These two types of structures are illustrated in Fig. 5.

Initially, the linear hydrogen-bonded structures of TFE and the OH...O form were considered and found to have a binding energy of 5.8 kcal/mol and the F...HO form to have a binding energy of 2.6 kcal/mol. Still to be investigated are the bridged structures. The fact that there are at least two dimer structures and that one of these is more stable than the methanol dimer leads to the expectation that TFE will be significantly more dimerized than methyl alcohol.

Fig. 4. Equilibrium between the Trans and Gauche Forms of 2,2,2 Trifluoroethanol

Fig. 5. Possible Dimer Structures for 2,2,2 Trifluoroethanol

II. CHEMISTRY OF MOLTEN SALTS AND THEIR VAPORS (M. Blander)

Molten salts and their vapors are used or have potential uses in a variety of technologies in which energy is produced or consumed such as in coal conversion, the production of fuel from wastes, batteries, nuclear fuel processing, aluminum production, vapor lamps, lasers, and metal purification. We have continued our fundamental studies of the thermodynamic and spectroscopic properties of molten salts and have increased our effort on the spectroscopic studies of salt vapors. Binary-salt vapor compounds often are extremely stable, which makes them potentially promising for use in chemical processing and in various other technologies.

A. Some Thermodynamic Properties of Binary Chloride Mixtures by Molecular Dynamics Computation (M. L. Saboungi and A. Rahman*)

In recent years, Monte-Carlo (MC) and molecular dynamics (MD) methods have been widely used to investigate the dynamics and thermodynamics of computer simulated alkali-halides.¹⁶ However, to our knowledge, there have been only two machine simulations of ionic liquid mixtures.^{17,18} Unfortunately, the conclusions drawn from these investigations did not provide information on the mixing process as precise as might be expected from a numerical method.

We report here on MD computations of the Helmholtz excess free energy of mixing of binary chloride solutions. The equations used to describe the thermodynamics of the system are the second-order equations derived from the conformal ionic solution (CIS) theory. Qualitatively, the CIS theory has proven to give reliable predictions:^{19,20} the form of the calculated thermodynamic functions agree with available data. A quantitative test remains to be performed.

1. General Considerations on the CIS Theory

An attractive feature of the CIS theory resides in the fact that the thermodynamic properties of the binary mixtures are related only to those of the reference salt. For a binary mixture, AX-BX, three perturbation calculations are carried out, generating property data for the two pure salts, AX and BX, and the mixture from a reference salt with the same common anion. The resultant Helmholtz excess free energy of mixing, ΔA_m^E , is expressed as:²¹

$$\Delta A_m^E = a(T,V)(\lambda_1 - \lambda_2)^2 X_1 X_2 \quad (19)$$

Contributions up to only second-order terms in $(\lambda_1 - 1)$ are included in the above equation. The perturbation parameter λ_i ($i = 1, 2$) is defined as $\lambda_i = d_0/d_i$, with d_0 and d_i being the characteristic sum of the anion-cation radii of the reference salt and of the i th salt, respectively; λ_i is used to scale the repulsive part of the pair potential. The quantity X_i represents the ionic fraction of the cation in the i th salt. The binary interaction coefficient can be written as:²¹

* Solid State Science Division, ANL.

$$a(T,V) = \frac{kT}{2} \left[\frac{N^3 D + N^3 (N-1) F}{Z'} - \left(\frac{A}{Z'} \right)^2 \right] \quad (20)$$

where k is the Boltzmann constant and N is Avogadro's number. Using the same notation as in Ref. 21, one obtains

$$Z' = \int \dots \int \exp(-U_0/kT) (d\tau)^{2N} \quad (21)$$

$$A = \frac{N^2}{kT} Z' \langle \phi_{ca} \rangle \quad (22)$$

$$D = \left(\frac{1}{kT} \right)^2 Z' \langle \phi_{ca} \phi_{c'a'} \rangle \quad (23)$$

$$F = \left(\frac{1}{kT} \right)^2 Z' \langle \phi_{ca} \phi_{c'a'} \rangle \quad (24)$$

The quantity U_0 refers to the total potential energy of the reference salt, c to a cation, a to an anion, $d\tau$ to a volume element in configurational space, and the function $\phi_{ca} = (\partial u_{ca}^{\text{rep}} / \partial \lambda_1)_{\lambda_1=1}$, where u_{ca}^{rep} represents the repulsive part of the pair potential. All these integrals can be calculated solely from properties of the reference salt. For any function Q of the coordinates, $\langle Q \rangle$ designates:

$$\langle Q \rangle = \frac{1}{Z'} \int \dots \int Q \exp(-U_0/kT) (d\tau)^{2N} \quad (25)$$

We have shown that, to a good approximation, Eq. 20 can be written as:²²

$$a(T,V) = \frac{N^2}{2kT(N-1)} [\langle E_c \rangle^2 - \langle E_c^2 \rangle] \quad (26)$$

with

$$E_c = \sum_{a=1}^N \phi_{ca} \quad (27)$$

According to Eq. 26, the second-order contributions to ΔA_m^E must always be negative. The same conclusion holds for the second-order contributions to the enthalpy of mixing, ΔH_m . In fact, a second-order perturbation calculation gives:

$$\Delta H_m = a'(T,P) (\lambda_1 - \lambda_2)^2 X_1 X_2 \quad (28)$$

The difference between $a(T,V)$ and $a'(T,P)$ is proportional to the excess entropy of mixing, ΔS_m^E , which is generally small.²³ Therefore,

$$a'(T,P) \cong a(T,V) \quad (29)$$

One can conclude from Eqs. 26, 28, and 29 that ΔH_m should be negative. The sign is in agreement with the calorimetric observations. In particular, at a 50%-50% composition, the variations of ΔH_m for chloride mixtures are linear in $(\lambda_1 - \lambda_2)^2$ and the reported slope is negative.²⁴

2. Combination of the CIS Theory and MD Techniques

Molten KCl was simulated by the method of MD computations.²⁵ Our model consisted of 216 particles enclosed in a cube of size $L = 20.607 \text{ \AA}$ (mass density, $1.528 \text{ g}\cdot\text{cm}^{-3}$).

Firstly, calculations were made for the case where the particles interacted according to the empirical Tosi-Fumi pair potential²⁶ derived from an extensive analysis of the properties of solid alkali-halides:

$$u_{ij} = \frac{z_i z_j}{4\pi\epsilon_0} e^2 r^{-1} + b_{ij} \exp[B_{ij}(d_{ij} - r)] + C_{ij} r^{-6} + D_{ij} r^{-8} \quad (30)$$

where z_K is the charge of the ion K ; e , the electron charge; ϵ_0 , the vacuum permittivity; r , the distance between the two particles; d_{ij} , the characteristic size parameter; b_{ij} and B_{ij} are constants defining the repulsive interaction; and C_{ij} and D_{ij} are, respectively, the coefficients for dipole-dipole and dipole-quadrupole interactions. The values for KCl are given in Table 5.^{26,27}

Table 5. Values of the Coefficients of the Pair Potentials According to Tosi-Fumi²⁶ and to Michielsen *et al.*,²⁸ for KCl

A. Tosi-Fumi Potential²⁶ (Eq. 30)

	b_{ij} (10^{-12} erg)	B_{ij} ($\text{\AA}^{-1}$)	d_{ij} ($\text{\AA}$)	C_{ij} ($10^{-12} \text{ erg \AA}^6$)	D_{ij} ($10^{-12} \text{ erg \AA}^8$)
cc	0.423	2.97	2.926	-24.3	-24.0
ca	0.338	2.97	3.048	-48.0	-73.0
aa	0.253	2.97	3.170	-124.5	-250.0

B. Michielsen *et al.* Potential²⁸ (Eq. 31; $m = 1$, $n = 4$)

	b_{ij} ($10^{-12} \text{ erg \AA}^4$)	B_{ij} ($\text{\AA}^{-1}$)	d_{ij} ($\text{\AA}$)	C_{ij} ($10^{-12} \text{ erg \AA}^6$)	D_{ij} ($10^{-12} \text{ erg \AA}^8$)
cc	35.2	1.44	3.01	-213.0	-505.0
ca	35.2	1.44	3.147	-110.0	-353.0
aa	35.2	1.44	3.26	-156.0	-626.0

C. Michielsen *et al.* Potential²⁸ (Eq. 31; $m = 1$, $n = 6$)

	b_{ij} ($10^{-12} \text{ erg \AA}^6$)	B_{ij} ($\text{\AA}^{-1}$)	d_{ij} ($\text{\AA}$)	C_{ij} ($10^{-12} \text{ erg \AA}^6$)	D_{ij} ($10^{-12} \text{ erg \AA}^8$)
cc	355.0	0.747	3.01	-213.0	-505.0
ca	355.0	0.747	3.147	-110.0	-353.0
aa	355.0	0.747	3.26	-156.0	-626.0

Secondly, calculations were made when the particles interacted according to a recent empirical pair potential suggested by Michielsen *et al.*²⁸

$$u_{ij} = \frac{z_i z_j}{4\pi\epsilon_0} e^2 r^{-1} + b_{ij} r^{-n} \exp [B_{ij}(d_{ij}^m - r^m)] + C_{ij} r^{-6} + D_{ij} r^{-8} \quad (31)$$

where m and n are integers ranging from 0 to 10. In this new form, the repulsive contribution is less "soft" and the London-van der Waals dispersion energy is larger than in the Tosi-Fumi potential. The coefficients b_{ij} and B_{ij} become adjustable parameters which can be determined for every combination of m and n . It has been proven that, for $m = 1$ (according to quantum mechanical considerations; for very close collisions m should be unity), the best values for n range from 4 to 6.²⁸ In this study, we arbitrarily chose $n = 4$ and $n = 6$. The corresponding values of the coefficients²⁸ in Eq. 31 for KCl are given in Table 5. The values selected by Michielsen *et al.*²⁸ for C_{ij} and D_{ij} are those calculated by Ladd.²⁹

Depending on the form of the pair potential used [*i.e.*, Eq. 30 or 31, with $m = 1$ and $n = 4$ or $n = 6$], the respective expressions for E_c , as defined in Eq. 27, are as follows:

$$E_c = - \sum_{a=1}^N b_{ca} B_{ca} d_{ca} \exp [B_{ca}(d_{ca} - r)] \quad (32)$$

or

$$E_c = - \sum_{a=1}^N b_{ca} B_{ca} d_{ca} r^{-4} \exp [B_{ca}(d_{ca} - r)] \quad (33)$$

or

$$E_c = - \sum_{a=1}^N b_{ca} B_{ca} d_{ca} r^{-6} \exp [B_{ca}(d_{ca} - r)] \quad (34)$$

In the above equations, b_{ca} and B_{ca} have different values (see Table 5). From Eqs. 32, 33, and 34, the averages of E_c and E_c^2 were calculated using about 10,000 configurations. The values derived for $a(T,V)$ were as follows:

- (1) Using the Tosi-Fumi potential (Eq. 30), $a(T,V) = -1320$ kcal mol⁻¹.
- (2) Using the Michielsen *et al.* potential (Eq. 31), with $m = 1$ and $n = 4$, $a(T,V) = -465$ kcal mol⁻¹.
- (3) Using the Michielsen *et al.* potential, with $m = 1$, and $n = 6$, $a(T,V) = -120$ kcal mol⁻¹.

3. Discussion

The values calculated for $a(T,V)$ depend strongly on the effective pair potential used. This result is surprising since the values of the total potential energy and the repulsive potential energy for each proposed pair potential do not differ significantly. Furthermore, the radial distribution functions for the cation-cation pair, g_{++} ; for the anion-anion pair, g_{--} ; and for the cation-anion pairs g_{+-} depend weakly on the pair potential. In Table 6, for the purpose of comparison, the coordinates of the extrema of g_{++} , g_{+-} and g_{--} , as well as the values of r for which these functions are equal to unity, are listed for the three pair potentials.

Table 6. Some Characteristics of the Radial Distribution Functions g_{--} , g_{++} and g_{+-} for Different Models of the Pair Potentials

<u>Pair Anion-Anion</u>								
	r^a	$r(1)^b$	$r_{\max}^c$	$g_{--}^{\max c}$	$r(1)$	$r_{\min}^d$	$g_{--}^{\min d}$	$r(1)$
Tosi-Fumi (Eq. 30)	2.90	3.83	4.45	1.75	5.77	6.80	0.690	7.97
Michielsen <i>et al.</i> (Eq. 31; $m=1$, $n=4$)	2.90	3.84	4.48	1.77	5.81	6.85	0.690	7.97
Michielsen <i>et al.</i> (Eq. 31; $m=1$, $n=6$)	2.95	3.83	4.40	1.77	5.87	6.75	0.680	7.88
<u>Pair Cation-Cation</u>								
	r^a	$r(1)$	$r_{\max}$	$g_{++}^{\max}$	$r(1)$	$r_{\min}$	$g_{++}^{\min}$	$r(1)$
Tosi-Fumi (Eq. 30)	2.95	3.81	4.45	1.72	5.90	6.85	0.710	7.92
Michielsen <i>et al.</i> (Eq. 31; $m=1$, $n=4$)	2.95	3.82	4.45	1.77	5.87	6.90	0.690	7.90
Michielsen <i>et al.</i> (Eq. 31; $m=1$, $n=6$)	3.05	3.86	4.45	1.80	5.80	6.95	0.700	7.92
<u>Pair Cation-Anion</u>								
	r^a	$r(1)$	$r_{\max}$	$g_{+-}^{\max}$	$r(1)$	$r_{\min}$	$g_{+-}^{\min}$	$r(1)$
Tosi-Fumi (Eq. 30)	2.30	2.59	2.95	3.82	3.68	4.55	0.474	5.95
Michielsen <i>et al.</i> (Eq. 31; $m=1$, $n=4$)	2.35	2.61	2.95	3.89	3.71	4.55	0.464	5.96
Michielsen <i>et al.</i> (Eq. 31; $m=1$, $n=6$)	2.40	2.64	3.00	3.94	3.72	4.60	0.450	5.95

^a r^a denotes the distance of closest approach.

^b $r(1)$ denotes the distance which corresponds to $g_{ij} = 1$.

^c $r_{\max}$ and $g_{ij}^{\max}$ denote the position and height of the main peak.

^d $r_{\min}$ and $g_{ij}^{\min}$ denote the position and depth of the first minimum.

It appears clear that in the case of molten KCl (this investigation) and of molten NaCl (Michielsen *et al.* investigation²⁸), there is little difference between these properties of molten pure salts computed using either the model of Tosi-Fumi or the model of Michielsen *et al.* The coefficient $a(T,V)$ is more sensitive to the form of the repulsive part of the pair potential than the other properties examined. This observation led us to the following question: Is it possible to use the CIS theory and MD results as one criterion for the suitability of the repulsive contribution to an empirical pair potential? Such a test could be performed by comparing the calculated and observed values of $a(T,V)$ for a class of binary mixtures, which, in this case, are chloride mixtures. According to the calorimetric results,²⁴ the enthalpy of mixing of binary alkali-halide mixtures at the 50-50 composition varies linearly with $(1/d_1 - 1/d_2)^2$, within the experimental uncertainties. Using the Pauling ionic radii, Kleppa and his co-workers²⁴ obtained:

$$4 \Delta H_m(50-50) = -340 \left(\frac{1}{d_1} - \frac{1}{d_2} \right)^2$$

which leads to $a(T,V) = -37 \text{ kcal mol}^{-1}$. Blander³⁰ reworked the same data but with a different self-consistent set of ionic radii. He found that each class of binary mixtures (*i.e.*, chloride mixtures, bromide mixtures, etc.) defines a different slope. The value of $a(T,V)$ obtained for chloride mixtures is $-130 \text{ kcal mol}^{-1}$.³⁰ Another set of ionic radii suggested by Melnichak and Kleppa³¹ would undoubtedly lead to different values for $a(T,V)$.

Despite these differences in the interpretation of the results, it is obvious that the value for $a(T,V)$ computed according to the Tosi-Fumi potential is much too far from the experimental values to be physically meaningful. On the other hand, the values obtained using the Michielsen *et al.* potential are reasonably close to the experimental values; for $n = 6$, the agreement with the value obtained by Blander is good (Table 7).

Table 7. Comparison Between the Values of $a(T,V)$ Calculated for Different Pair Potentials and the Experimental Data

Model Used	$a(T,V)$, kcal mol ⁻¹
Tosi-Fumi Potential ²⁶	-1320
Michielsen <i>et al.</i> Potential ²⁸ ($m = 1, n = 4$)	-465
Michielsen <i>et al.</i> Potential ²⁸ ($m = 1, n = 6$)	-120
Experimental Data	-37 ^a ; -130 ^b

^aBased on data of Kleppa and co-workers, Ref. 24.

^bBased on calculations of Blander, Ref. 30.

Consequently, one can use the combination of the CIS theory and numerical methods as a sensitive test of the repulsive contribution of a given pair potential.²²

B. Raman Spectroscopic Studies

1. Raman Spectra of Yttrium(III) Chloride-Alkali Chloride Mixtures (G. N. Papatheodorou)

The structural (Raman)^{32,33} and thermodynamic^{34,35,36} properties of some molten lanthanide chloride-alkali chloride mixtures have been recently reported. Due to a regular progression of ionic radii and polarizabilities of the lanthanide ions, it is, in general, possible to predict the chemical properties of the lanthanide compounds from the properties of compounds of the first and the last members (*i.e.*, La^{+3} and Lu^{+3}). A possible alternative to the rare and expensive compounds of Lu^{+3} are the Y^{+3} compounds.³⁷ Thus, the purpose for studying the YCl_3 -ACl molten-salt mixtures is to establish the systematics of the structural and thermodynamic³⁸ properties of the lanthanide chloride-alkali chloride systems and, to some extent, to approximate similar properties of some mixtures involving actinide chlorides.

The laser Raman system for which the optics were described in the preceding report in this series (ANL-75-46) was used to obtain the Raman spectra of a variety of YCl_3 -ACl mixtures at different temperatures (Table 8). Raman spectral changes of solid $\text{Cs}_2\text{NaYCl}_6$, Cs_3YCl_6 , K_3YCl_6 , $\text{CsY}_3\text{Cl}_{10}$, and YCl_3 from room temperature to temperatures above the melting point were also obtained. The mixtures were contained in fused silica tubes (4-mm OD and 20 mm long) which were always placed in a fixed position inside the high-temperature compartment. The spectra obtained by this technique permitted measurements (within 5%) of the relative Raman spectral intensities of mixtures of different compositions at different temperatures.

Figure 6 gives an example of the spectra obtained for $\text{Cs}_2\text{NaYCl}_6$ solid and liquid. The distribution of the normal modes of $\text{Cs}_2\text{NaMCl}_6$ crystals (where M is any trivalent cation), containing discreet MCl_6^{3-} octahedra, are described in Table 9, and an assignment of the vibrational frequencies of $\text{Cs}_2\text{NaYCl}_6$ is presented. The observed Raman changes with temperature and upon melting (Fig. 6) are interpreted as indicating that the internal modes of the solid (*i.e.*, the YCl_6^{3-} octahedral modes) are preserved in the liquid.

For all ACl- YCl_3 melts at high ACl concentrations ($X_{\text{YCl}_3} < 0.25$), the Raman spectra are similar to the liquid spectra shown in Figs. 6 and 7 and are characterized by a strong polarized band P at $\sim 260 \text{ cm}^{-1}$ and depolarized bands with frequencies near the ν_1 and ν_5 frequencies of the YCl_6^{3-} octahedron. This indicates the existence of octahedral species in these melts.

In melts containing more than 25% YCl_3 , a new polarized band D (Fig. 7) appears in the spectra; this band shifts continuously and rapidly to higher energies with increasing YCl_3 concentrations. The frequency shift is accounted for by assuming a continuous distortion of the YCl_6^{3-} octahedra by neighboring yttrium ions in the melt. The continuous frequency shift of the D band implies that the structural changes are better described in physical terms than in "chemical" terms.³⁹

Table 8. Main Raman Frequencies Observed in the $\text{YCl}_3\text{-AlCl}_3$ Mixtures at Different Compositions and Temperatures

System, % YCl ₃	Temperature, °C	Main Frequencies, cm ⁻¹				
CsCl-YCl ₃						
10%	700		255	(113) ^b		
	800		252	(114)		
25%	820 ^a		260	126		
	890		258	(112)		
45%	600		282	(255)		
	700		287	(260)		
	800		292	(263)		
75%	600 ^a	350	285	254	174	91 69
	650	(311)		252		
	750	(303)		255		
KCl-YCl ₃						
10%	700		260	(112)		
	800		256	(110)		
15%	700		259	(112)		
	800		255	(115)		
20%	750		259	(111)		
	800		256	(112)		
25%	750 ^a		265	125		
	810		261	(110)		
30%	800		264	(110)		
45%	450		280	(250)		
	600		282	(248)		
	700		283	(250)		
	800		282	(245)		
60%	600		(295)	254		
	700		(294)	262		
	800		(291)	264		
75%	630	(315)		253		
	700	(317)		254		
	800	(316)		255		
100%	710	(350)		255		
	800	(351)		248		
LiCl-YCl ₃						
45%	500		253			
	600		254			
	700		257			
	800		256			

^aSolid.

^bNumbers in parentheses indicate shoulder bands and estimated frequencies with an error of 10 cm^{-1} .

Fig. 6.

Raman Spectra of Polycrystalline and Molten $\text{Cs}_2\text{NaYCl}_6$. $\lambda = 514.5 \text{ nm}$; slits $\sim 7 \text{ cm}^{-1}$; $t = 1 \text{ sec}$; scan rate 1.25 nm/min ; * grating ghost

2. Raman Spectra of Amorphous Materials (E. J. Flynn,* S. A. Solin,* and G. N. Papatheodorou)

Bulk amorphous solids constitute a bridge between the solid and liquid states of matter and their study contributes to the understanding of the microscopic and macroscopic properties of molten materials. Any chemical compound that can be studied in the crystalline, glassy, liquid, and gaseous states is of particular interest, because correlations of the vibrational modes in the different phases can provide detailed information on fundamental molecular and ionic interactions. One such compound, arsenic oxide, exists in two crystalline modifications, claudetite and arsenolite, forms a transparent bulk glass, melts under low pressures, and easily forms dimeric As_4O_6 gas. In this work, we report the polarized Raman and infrared[†] (IR) absorption spectra of claudetite and the Raman spectra of arsenolite.

* Department of Physics, University of Chicago.

[†] We thank Gerald Reedy for his help and advice in recording the infrared data.

Table 9. Distribution of Normal Modes for $\text{Cs}_2\text{NaMCl}_6$ Solids

Crystallographic Information

Space Group	$\text{Fm}\bar{3}\text{m}(\text{O}_h^5)$
Molecules per Unit Cell	4
Lattice Points	4
Molecules per Bravais Lattice	1

Molecular Ionic Crystals; $3N = 30$ normal modes

Correlation Diagram:

	Point Group	Site Group	Factor Group
MCl_6^{3-}	O_h $\left. \begin{matrix} \text{A}_{1g}, \text{E}_g, \text{F}_{2g} \\ \text{F}_{1u}, \text{F}_{2u} \end{matrix} \right\}$	O_h $\left. \begin{matrix} \text{A}_{1g}, \text{E}_g, \text{F}_{2g} \\ 2\text{F}_{1u}, \text{F}_{2u} \end{matrix} \right\}$	O_h $\left. \begin{matrix} \text{A}_{1g}, \text{E}_g, \text{F}_{2g} \\ 2\text{F}_{1u}, \text{F}_{2u} \end{matrix} \right\}$
Na; 1(b)		O_h $\text{F}_{1u} \longrightarrow$	F_{1u}
Cs; 2(c)		T_d $\text{F}_2 \longrightarrow$	F_{1u} F_{2g}
MCl_6^{3-} ; 1(a) (external)		O_h $\text{F}_{1u} \longrightarrow$	O_h F_{1u}
MCl_6^{3-} (librations)		O_h $\text{F}_{1g} \longrightarrow$	O_h F_{1g}

Assignment of Raman
Frequencies (cm^{-1}) of Solid
 $\text{Cs}_2\text{NaYCl}_6$; $T = 25^\circ\text{C}$

$$\nu_1(\text{A}_{1g}) = 285; \nu_2(\text{E}_g) = 223;$$

$$\nu_5(\text{F}_{2g}) = 128^a$$

$$\nu_{\text{acoustic}}(\text{F}_{2g}) = 47$$

$$\Gamma_{3N} = \Gamma_{\text{acoustic}} + \Gamma_{\text{external}} + \Gamma_{\text{libration}} + \Gamma_{\text{internal}}$$

$$\Gamma_{\text{acoustic}} = \text{F}_{1u}(\text{IR}); \Gamma_{\text{external}} = \text{F}_{2g}(\text{R}) + 2\text{F}_{1u}(\text{IR})$$

$$\Gamma_{\text{libration}} = \text{F}_{1g}(\text{IA}); \Gamma_{\text{internal}} = \text{A}_{1g}(\text{R}) + \text{E}_g(\text{R}) + \text{F}_{2g}(\text{R}) \\ + 2\text{F}_{1u}(\text{IR}) + \text{F}_{2u}(\text{IA})$$

^aNote that $\nu_1^2 \approx \nu_2^2 + 3/2 \nu_5^2$, which makes the assignment unique without depolarization measurements.

Fig. 7.

Raman Spectra of Molten KCl-YCl₃ Mixtures at 800°C. $\lambda = 514.5$ nm; slits ~ 5 cm⁻¹; $t = 1$ sec; scan rate 0.6 nm/min. Numbers in parentheses give the Raman intensity of the ~ 260 cm⁻¹ band relative to the intensity of the same band at $x_{\text{YCl}_3} = 0.2$

Claudetite is a biaxial layered material (C_{2h}^5 -P2₁M) having strong interlayer bonding characteristics and weak layer-layer coupling inherent to Davydov splitting and low-frequency rigid-layer modes. The crystal (C_{2h}) and layer (C_s) point groups can be correlated according to the diagram:

Therefore, when the layer-layer forces are taken into account; the structure splits the A' and A'' modes to pairs of Raman-active and IR-active modes. The external mode $A'' + 2A'$ gives rise to three Raman-active rigid-layer modes and three rigid translations ($\alpha\text{Bu} + \text{Au}$). Table 10 lists the Raman and IR frequencies measured in claudetite. For nearly every Raman frequency, a Davydov partner can be found in the infrared. Polarization Raman measurements have shown that the three low-frequency Raman lines at 30, 38 and 49 cm^{-1} , for which no Davydov component has been found in the IR, are most clearly resolved in the $y(xy)x$ configuration. This fact decisively locates the rigid-layer modes at these three lowest Raman active modes. The remaining frequencies in Table 10 correspond to 20 (out of the expected 27) Davydov doublets.

Table 10. Davydov Splitting in Claudetite. The Raman and infrared frequencies were recorded in wave numbers to within 2 cm^{-1} .

Raman	Infrared	Raman	Infrared
30	...	285	285
38	...	331	327
49	...	357	353
72	62	426	...
87	89	461	460
114	117	501	500
174	...	544	543
192	202	633	637
217	226	773	...
236	...	818	825
248	244	869	865
260	257		

Arsenolite is cubic ($O_h^4\text{-Fd}3m$), and its measured Raman spectrum is in complete agreement with the published results of Beattie *et al.*⁴⁰ and Brumbach *et al.*⁴¹ The Raman spectra of arsenolite and the other four phases of arsenic oxide are compared in Fig. 8. The gaseous, liquid, cubic, and monoclinic phases all exhibit modes which agree in position rather closely with vibrations of vitreous As_2O_3 .⁴² In Table 11, each mode is labeled by its frequency (given in cm^{-1}), symmetry species, and polarization (polarized--p or depolarized--dp). The modes of arsenolite and As_4O_6 vapor included in Table 11 are alike in frequency, symmetry, and polarization.⁴⁰

The significance of recurring bands rests in their correlation with structural units that persist in several phases of the As_2O_3 system. One can infer nothing about an observed normal vibration in a particular phase by merely citing its proximity in frequency to a band in a different phase, the

Fig. 8.

Raman Spectra of All Five Phases
of As_2O_3 .

structural origin of which is understood, although some authors have concluded otherwise. Bertoluzza,⁴³ for one, argued that recurring frequencies in the Raman spectra of cubic, monoclinic, and vitreous As_2O_3 were definitive evidence of structural similarities. The A_1 "water molecular" mode⁴⁴ of the glass at 50 cm^{-1} and the 55 cm^{-1} B_g rigid-layer mode of claudetite are structurally unrelated and provide a counterexample. Moreover, the 470-cm^{-1} and 560-cm^{-1} features in the arsenolite spectrum cannot be identified with the 480-cm^{-1} and 570-cm^{-1} bands of the glass, inasmuch as the modes of the glass and these particular modes of arsenolite possess conflicting polarization properties. The behavior of autonomous structural units must be manifested in both the symmetry and frequency of those normal modes of the macroscopic system to which they give rise.

According to the above criteria, the spectrum of claudetite exhibits vibrational features which match those of the glass or the liquid in frequency and depolarization characteristics for seven of the nine bands listed in Table 10.

Table 11. Recurring Bands in the Five Phases of As_2O_3 . Frequencies are listed below in cm^{-1} . Polarization characteristics are indicated in parenthesis to the right of the symmetry species.

Glass ^a	Vapor ^b	Arsenolite	Claudetite	Liquid ^c
50 A_1 (p) As-O-As	...	...	55 B_g (dp)	...
125 A_1 (p) AsO ₃	...	...	118 B_g (dp)	125 (p)
250 E (dp) AsO ₃	253 F_2 (dp)	269 F_2 (dp)	252 B_g (dp)	220 (dp)
370 A_1 (p) As-O-As	381 A_1 (p)	371 A_1 (p)	360 A_g (p)	370 (p)
480 A_1 (p) AsO ₃	496 F_2 (dp)	470 F_2 (dp)	464 A_g (p)	480 (p)
525 E (dp) AsO ₃	...	...	504 B_g (dp)	525 (dp)
570 A'' (dp)	556 A_1 (p)	560 A_1 (p)	548 B_g (dp)	520 (p)
Intermolecular coupling				
625 B_2 (dp) As-O-As	...	...	636 B_g (dp)	625 (p)
800 (dp) As ₄ Linkage	814 (dp) ^d	782 F_2 (dp)	777 B_g (dp)	800 (dp)

^aEach band in the glass is associated with one of several structural units described in Ref. 42 and labeled here accordingly.

^bRef. 40.

^cFrom Ref. 42; see, in particular, Figs. 8 and 12.

^dSee Section C.1 in this report.

C. Salt Vapor Studies (G. N. Papatheodorou, G. H. Kucera, M. A. Capote* and S. R. Goates†)

The formation of complex, vapor-phase compounds of "acidic" gases ($A_2X_6 = Al_2Cl_6, Al_2Br_6, In_2Cl_6$, etc.) with transition metal, lanthanide, and actinide halides (MX_p) has been established in recent years.⁴⁵⁻⁵⁰ The thermodynamics and stoichiometries of the reactions

have been measured for systems involving Al_2Cl_6 and Fe_2Cl_6 ⁵⁰ by spectrophotometric and/or transpiration techniques. For the various cases studied, the volatility enhancement ratio:

$$R(t) = \frac{P_c}{P_s} \quad (36)$$

(P_c = apparent pressure of the gaseous complexes; P_s = vapor pressure of the MX_p inorganic salt) varies from 10 to 10^{10} and is temperature dependent. The large $R(t)$ values suggest that the gaseous complexes might be useful for chemical transport, crystal growth, purification, and separation of inorganic salts by vapor processes. Vapor complexes with lanthanide halides have also been considered as lasing materials for the construction of high-power gas lasers.

Furthermore, because of the dissociation of the A_2X_6 gases and reaction (35), one expects that the acidic gas-complex mixtures will exhibit enhanced thermal conductivities and may prove useful as heat-transfer media. Our studies are aimed at understanding the structures and the thermodynamics of the gaseous complexes and at finding new complexes that show increased volatility enhancement ratios relative to the uncomplexed species.

1. Raman Spectra of Arsenic Oxide (S. R. Goates and G. N. Papatheodorou)

Raman spectra of arsenic oxide vapors have been observed previously by three different groups⁴⁰⁻⁴² and thus were considered ideal for testing the capabilities of our high-temperature Raman system. Table 12 is a comparison of data from this work with that from other studies. The polarization characteristics of the spectra are shown in Fig. 9 and are denoted by p and dp in the table. Band I at 99 cm^{-1} reported by Beattie *et al.*⁴⁰ was not detected; this result is further confirmation of the observations described in Refs. 41 and 51. Bands II and III are in agreement with previous studies; however, as shown in Fig. 9, we were able to resolve the vibrational-rotational structure of these bands. Repeated polarization measurements have shown that band VII at 409 cm^{-1} is polarized rather than depolarized, as reported in Ref. 40. An additional band (IX) of weak intensity was found superimposed on band VIII. The extreme of this band and its approximate frequency were

* Undergraduate Student Participant from Harvey Mudd College, Claremont, California.

† Undergraduate Student Participant from Brigham Young University, Provo, Utah.

Table 12. Observed Frequencies (in cm^{-1}) and Assignments for As_4O_6 Gas

Band	Raman (This Work)	IR (Ref. 52)	Raman (Refs. 40-42)	Assignment (Refs. 41-51)	Assignment (This Work)
I	not observed		99 ^{a,b} , dp		
II	185 ^c , dp		185 ^d , dp	E	F_2 ; ν_{10}
III	252 ^e , dp		253 ^d , dp	F_2	E; ν_4
IV		356(369) ⁴³		F_2	F_2 ; ν_9
V	379, p		381 p	A_1	A_1 ; ν_2
VI		395(414) ⁴³			F_2 ; ν_8
VII	409, p		409, dp ^f	E	$F_2 \times F_2$ ^{g,h} ; $\nu_7-\nu_8$
VIII	(492) ^e , dp		494, dp	F_2	E; ν_3
IX	(505) ^e , p		not observed		$E \times E$; $2\nu_3$
X	551, p		556 p	A_1	A_1 ; ν_1
XI	747, p		not observed		$E \times E$; $\nu_3-\nu_4$
XII	814, dp	830	not observed	F_2	F_2 ; ν_7

^a Observed in solid arsenolite.

^b Observed only in Ref. 40.

^c Bands II and III show vibrational-rotational structure (see Fig. 9).

^d No fine structure was observed.

^e Frequencies estimated from a depolarization ratio spectrum.

^f Polarization measurements were reported only in Ref. 40.

^g The symmetry species of the combination or overtone are:

$$F_2 \times F_2 = A_1 + E + F_2 + F_1; E \times E = A_1 + E.$$

^h The high Raman intensity of this band is attributed to Fermi resonance with the ν_2 fundamental.

confirmed by depolarization ratio measurements. Two new weak bands XI and XII were also found at 747 cm^{-1} and 814 cm^{-1} .

The vapors of arsenic oxide are known to be composed of As_4O_6 dimers with a T_2 molecular symmetry. There are 24 vibrational modes, which are classified according to the representation:

$$\Gamma_{\text{vib}} = 2A_1(R) + 2E(R) + 2F_1(IA) + 4F_2(R;IR)$$

All active fundamentals have been assigned by Beattie *et al.*⁴⁰ and Brumbach *et al.*⁴¹ and very recently have been used to calculate force constants and potential distributions for the As_4O_6 molecule.⁵¹ Our data alter some of these assignments, showing five polarized bands of which only two are expected to be fundamentals. If the high intensity bands V and X are assigned to the symmetric species A_1 (ν_1 and ν_2), then bands VII, IX, and XI should be attributed to overtones or combination bands. The combination ν_3 and ν_4 gives the polarized

Fig. 9. Raman Spectra of Gaseous As_4O_6 at 875 K. $\lambda = 514.5$ nm; slits ~ 5 cm^{-1} ; $t = 3$ sec; scan rate 0.4 nm/min. Insert figure on the right resolves the vibrational rotational structure of the first two bands: slits ~ 2.5 cm^{-1} ; $t = 7.5$ sec; scan rate 0.05 nm/min

overtone at 747, and, since the cross product $E \times F_2 = F_1 + F_2$ does not contain an A_1 species, we conclude that the ν_3 and ν_4 modes possess the same symmetry, *i.e.*, both are either F_2 or E . The ν_7 Raman frequency is close to that found in the IR⁵² and is assigned to F_2 . The ν_8 and ν_9 , found in both the gaseous⁵² and solid⁴³ IR spectra, are assigned to F_2 , and thus, the remaining two depolarized fundamentals ν_3 and ν_4 should have E symmetry. Finally, band VII is assigned to a combination of ν_7 - ν_8 ($F_2 \times F_2$), and its relatively high intensity (Fig. 9) is attributed to Fermi resonance between the A_1 component of the combination and the adjacent $\nu_2(A_1)$ fundamental. It must be emphasized that our assignment of band VII to the ν_7 - ν_8 combination is not unique and other alternatives, such as a $2\nu_6$ overtone of an infrared active fundamental, could possibly be considered.

2. Raman Spectra of Aluminum Chloride (S. R. Goates and G. N. Papatheodorou)

Structural studies by Raman spectroscopy of the gaseous complexes formed according to reaction 35 require an accurately determined Raman spectrum of the "acidic gas" (*i.e.*, A_2X_6), which, in many cases, is the major gas component over the metal halide, MX_2 , in the Raman cell. As found experimentally in the cases of $\text{Pd}(\text{AlCl}_4)_2$ and $\text{Cu}(\text{AlCl}_4)_2$, the Raman spectrum of the complex is superimposed on the spectra of the species in the equilibrium

Thus, a detailed knowledge of the band frequencies and band intensities of these vapor species and their temperature dependence is necessary in order to determine the fundamentals of the gaseous complex.

The equilibrium constant of Eq. 37 is ~ 1 near 800 K. The molecular symmetries and classification of vibrational modes of the two molecules are

Al_2Cl_6 :

$$\text{D}_{2h}; \Gamma_{\text{vib}} = 4 \text{ A}_{1g}(\text{R}) + \text{B}_{1g}(\text{R}) + 2 \text{ B}_{2g}(\text{R}) + 2 \text{ B}_{3g}(\text{R}) \\ + \text{A}_{1u}(\text{IR}) + 3 \text{ B}_{1u}(\text{IR}) + 2 \text{ B}_{2u}(\text{IR}) + 3 \text{ B}_{3u}(\text{IR}) \quad (38)$$

AlCl_3 :

$$\text{D}_{3h}; \Gamma_{\text{vib}} = \text{A}_1'(\text{R}) + \text{A}_2''(\text{IR}) + 2 \text{ E}'(\text{R,IR}) \quad (39)$$

Raman spectra and normal coordinate analysis of Al_2Cl_6 have been reported previously.⁵³⁻⁵⁵ Monomeric AlCl_3 has been the subject of numerous investigations, and its Raman and IR frequencies have been recently established using matrix isolation techniques.^{53, 56-59} The Raman spectra of aluminum chloride vapors at 460 K obtained from this study are shown in Fig. 10, and a comparison with the results of other researchers is given in Table 13. Our study reveals nine additional bands, determines depolarization ratios (Table 13), and shows that a band reported previously at 336 cm^{-1} is a temperature-dependent, polarized doublet (Fig. 10).

Fig. 10. Raman Spectra of Gaseous Al_2Cl_6 . $\lambda = 514.5 \text{ nm}$; slits $\sim 5 \text{ cm}^{-1}$; $t = 1 \text{ sec}$; scan rate 0.3 nm/min

Nine Raman active fundamentals are expected for the Al_2Cl_6 molecule, and of these nine, only four are polarized. Thus, it appears that of the 13 polarized bands found experimentally, nine are not fundamentals. There are only three bands (III, IV, XVI) with depolarization ratios larger than $3/4$. However, in the polarized spectrum, two additional bands with frequencies near the frequencies of bands II and VI are present, suggesting that both the peaks at 97 cm^{-1} and 218 cm^{-1} arise from a superposition of polarized and depolarized bands of approximately the same frequency. Symmetry considerations show that the Raman active overtones and/or binary combinations of the $\text{D}_{2h}(\text{Al}_2\text{Cl}_6)$ molecule arise from fundamentals of the same symmetry. Furthermore, no binary combinations between Raman active and infrared active fundamentals are present in the Raman spectrum of a molecule with D_{2h} symmetry. On the basis of these rules and the above observations, we present an assignment of the Al_2Cl_6 Raman modes in Table 13. The effect of temperature on the spectra is also

Table 13. Observed Raman Frequencies (in cm^{-1}) for Al_2Cl_6 Gas

Band	This Work T = 500 K				Beattie and Honder ^a T = 500 K Frequency and Polarization	Maroni <i>et al.</i> T ~670 K Frequency, Polarization and Assignment ^{b,c}	This Work Assignment
	Frequency, ν	Rel. Intensity ($I_{\text{II}} = 100$)	Depolarization Ratio, ρ	Assignment			
I	48 ± 2	3 (sh)	p	$B_{1u} \times B_{1u}^d$	77 dp	A_u	(e)
II	97 ± 0.5	100	0.40; p	$A_g; B_{3g}$	99-p	115-p A_g	$\nu_4; \nu_9$
III	117 ± 1	47	0.85; dp	B_{2g}	112-p		ν_7
IV	167 ± 1	6	0.87; dp	B_{1g}	165-(?)	168 (?) B_{3g}	ν_5
V	218 ± 0.5	48	0.12; p	$A_g; B_{3g}$	217-p	217 (?) A_g	$\nu_3; \nu_8$
VI	280 ± 2	3	0.55; p	$B_{1u} \times B_{1u}$		285 (?) -	(e)
VII	316 ± 1	6 (sh)	~0; p	$A_g \times A_g$; or $B_{3g} \times B_{3g}$	336-p		$\nu_4 + \nu_3$ or $\nu_3 + \nu_6$
VIII	331 ± 0.5	82	~0.01; p	A_g		336 A_g	ν_2
IX	340.5 ± 0.5	85	~0.01; p				(f)
X	352 ± 2	6 (sh)	~0; p	$B_{1u} \times B_{1u}$		(g)	(e)
XI	440 ± 2	1	~0; p	$A_g \times A_g$		(420) B_{2u} ; 438 B_{3g}	$2\nu_3$
XII	495 ± 2	1 (sh)	~0; p	$B_{2g} \times B_{2g}$		(484) ^h B_{1u}	$\nu_6 - \nu_7$
XIII	510 ± 1	6	~0; p	$B_{1u} \times B_{1u}$	510-(?)	501 A_g	(e)
XIV	522 ± 1	6	~0; p	A_g			ν_1
XV	547 ± 2	3 (sh)	~0; p	$B_{1u} \times B_{1u}$			(e)
XVI	613 ± 1	5	0.81; dp	B_{2g}	612-dp	608 B_{1g}	ν_6
XVII	650 ± 1	0.3	~0; dp	$A_g \times A_g$		(625) ^h B_{3u}	$3\nu_2$

^aRef. 53.^bRef. 54.^cRef. 55.^di = u (infrared active) or i = g (Raman active).^eOvertone or combination band of the IR active modes.^fTemperature-dependent Raman intensity.^gA frequency at 385 cm^{-1} was attributed⁵⁴ to combination bands; it is possible, however, that it is due to the presence of AlCl_3 monomer at that temperature (T, ~670 K; ν_{monomer} , ~377 cm^{-1}).^hW. Klemperer, J. Chem. Phys. 24, 353 (1956).

shown in Fig. 10. Increasing temperature decreases the intensity of band IX relative to ν_2 and gives rise to a new band, $\nu_1 = 377 \text{ cm}^{-1}$, which is due to the symmetric stretch^{53,55} of the $\text{AlCl}_3(\text{D}_{3h})$ monomer. Band IX is a characteristic of the gas phase spectra and does not exist in the liquid⁵⁴⁻⁶¹. A first guess is that its origin could be attributed to vibrational-rotational interactions involving the $\nu_2(\text{A}_g)$ fundamental. However, the high moments of inertia⁶² for the approximately symmetric-top $\text{Al}_2\text{Cl}_6(\text{I}_y \approx \text{I}_z)$ molecule give rise to very small spacings between the rotational levels, and rotational branches are unlikely to appear in the spectra. Furthermore, according to Jahn's⁶³ rule, the symmetry (D_{2h}) of the molecule does not allow Coriolis splitting of the ν_2 fundamental.

Another possible explanation for the origin of band IX could be the existence of another, yet undetermined, gaseous species of aluminum chloride in equilibrium with both $\text{AlCl}_3(\text{g})$ and $\text{Al}_2\text{Cl}_6(\text{g})$. This species should have a small number of Raman active modes and a stretching mode of lower energy than that of planar AlCl_3 .

At temperatures above 850 K, the Raman spectra show two $\text{AlCl}_3(\text{D}_{3h})$ fundamentals at 377 cm^{-1} and 150 cm^{-1} and a band at 425 cm^{-1} . However, we found that the 425 cm^{-1} peak is due to SiCl_4 produced by the attack of aluminum chloride on the quartz cells. This peak was observed to increase with time and was the sole feature of a Raman spectrum obtained at $\sim 400 \text{ K}$ with a cell that had been heated previously for ~ 1 hour at 800 K .

3. Raman Spectra of Indium (I), (II), and (III) Chlorides (G. N. Papatheodorou)

Indium trichloride plays an important role^{64,65} in the chemical vapor transport and crystal growth of intermetallic compounds (e.g., InAs , InP , etc.), and preliminary experiments have shown that it forms gaseous complexes with metal chlorides (Eq. 35). The chemical transport of the intermetallic compounds is believed to occur through disproportionation reactions in which lower valences of indium chloride are present (i.e., InCl , InCl_2). In the gas phase, indium trichloride forms dimers, whereas the thermodynamic behavior of indium monochloride suggests monomeric InCl molecules. We prepared anhydrous InCl_3 by sublimation of hydrated InCl_3 which was then mixed with the appropriate amounts of indium metal at 300°C to form InCl_2 and InCl liquids.

The Raman spectrum of InCl_3 was easily obtained in the temperature range from 450 to 900°C and was found to be in complete agreement with the spectra reported previously.⁵³ At 450°C , a vapor of $\sim 0.2 \text{ atm}$ pressure was in equilibrium with solid InCl_3 . At 600°C , all the InCl_3 was in the gas phase, giving a calculated (as In_2Cl_6) pressure of $\sim 2.2 \text{ atm}$. A typical spectrum at 600°C is given in Fig. 11. The peak at $\sim 340 \text{ cm}^{-1}$ is due to the symmetric stretch of the $\text{InCl}_3(\text{C}_{3v})$ monomer formed from the dissociation

At temperatures near 900°C , the predominant band is at 340 cm^{-1} , which indicates that the dimer is a minor constituent in the vapor. At lower temperatures (down to 450°C), both monomers and dimers are present. A tentative assignment of the vibrational frequencies of both species has been given.^{53,66}

Fig. 11.

Raman Spectra of Indium Halide Vapors.
 $\lambda = 514.5$ nm, slits ~ 4 cm^{-1} ; $t = 2$ sec,
 scan rate 0.22 nm/min. A: InCl_3 vapors
 at $t = 875$ K; B: InCl_2 vapors at $t =$
 975 K; C: InCl vapors at $t = 975$ K

The Raman spectrum of InCl vapor over the black-red indium monochloride liquid is shown in Fig. 11. The Raman intensity was found to change drastically with the frequency of the exciting radiation. Using a constant laser power of 150 mW for all Ar^+ ion laser lines, we found that the intensity of the 300 cm^{-1} band increased by a factor of three as the frequency of the exciting line changed from 5145 to 457.9 nm. This behavior is characteristic of preresonance Raman scattering from the InCl molecules. The temperature-dependence ($600\text{--}800^\circ\text{C}$) studies of the spectrum show only slight changes in the band width, indicating that InCl molecules do not dissociate.

The vibrational-rotational Raman selection rules for the symmetric top InCl molecule are $\Delta J = 0 \pm 2$, and the Raman spectrum consists of S, Q and O branches, with displacements around the pure vibrational transition ($\Delta V = 1$). At 1000 K, the J value for maximum Raman intensity is about $J_{\text{max}} = 54$. Using the spectroscopic constants for InCl given by Hertzberg,⁶⁷ we have calculated and assigned the maxima of the S, Q, and O branches for the InCl Raman fundamental:

$$\Delta V = 1; V = 1; J = 54$$

$$\begin{cases} \nu_0 = 285 \text{ cm}^{-1} \text{ (shoulder)} \\ \nu_Q = 310 \text{ cm}^{-1} \text{ (306 cm}^{-1}) \\ \nu_S = 335 \text{ cm}^{-1} \text{ (332 cm}^{-1}) \end{cases}$$

These values are in very good agreement with the observed maxima (values in parentheses) of the bands in Fig. 11. The assignment is further confirmed by polarization measurements, which show that the Q branch is highly polarized whereas the S and O branches are depolarized.

Vapor density measurements over the pale yellow liquid InCl_2 have been interpreted^{68,69} as indicating the existence of mainly three species in equilibrium:

Figure 11 shows the Raman spectrum of the vapor(s) over liquid InCl_2 at 700°C . The high-intensity polarized band at $\sim 350 \text{ cm}^{-1}$ and the low-frequency $\sim 90 \text{ cm}^{-1}$ depolarized band are very close to the ν_1 and ν_4 fundamentals of the InCl_3 monomer, whereas the broad polarized band at $\sim 300 \text{ cm}^{-1}$ is near the ν_2 branch of InCl . Temperature-dependence studies of the spectra show that the relative intensities of the polarized bands in the spectra remain approximately constant. These observations are best interpreted as indicating that the spectrum of vapors over InCl_2 liquid is a superposition of the spectra of InCl and InCl_3 monomers. No bands that could be assigned to either $\text{InCl}_2(\text{g})$ or $\text{In}_2\text{Cl}_4(\text{g})$ were found in the spectra.

4. Resonance Raman Spectra of PdAl_2Cl_8 and CuAl_2Cl_8 (M. A. Capote and G. N. Papatheodorou)

PdAl_2Cl_8 . The thermodynamics of reaction 35 for the $\text{PdCl}_2(\text{s})\text{-Al}_2\text{Cl}_6(\text{g})$ system have been studied spectrophotometrically.⁴⁵ Both thermodynamic and electronic absorption spectra measurements have suggested a structure in which a square-planar PdCl_4^{2-} is bridged with two tetrachloroaluminates:

All the high-intensity Ar^+ laser lines were strongly absorbed by the $d \rightarrow d$ electronic transitions in the complex, and Raman signals from cells containing ~ 0.3 atm of PdAl_2Cl_8 were very weak. However, we were able to obtain the Raman spectrum of the complex using the red $6471 \text{ \AA}$ line of a Kr^+ ion laser.* The data are presented in Fig. 12. A cell containing approximately 1.2 atm Al_2Cl_6 and 0.3 atm of PdAl_2Cl_8 in equilibrium with PdCl_2 solid at $\sim 575 \text{ K}$ was

* We thank S. A. Solin (Univ. of Chicago) for allowing us the use of his Kr^+ ion laser.

Fig. 12. Raman Spectra of Vapors in the $\text{Al}_2\text{Cl}_6(\text{g})$ - $\text{PdCl}_2(\text{s})$ System. $\lambda = 647.1 \text{ nm}$; slits 5 cm^{-1} ; $t = 2 \text{ sec}$; scan rate 0.5 nm/min . Band a, c, d are the main bands due to the PdAl_2Cl_8 gaseous complex; $t = 575 \text{ K}$; partial pressures $P_{\text{Al}_2\text{Cl}_6} \sim 1.2$; $P_{\text{complex}} \sim 0.3 \text{ atm}$; no $\text{PdCl}_2(\text{s})$ excess

used. A superposition of the PdAl_2Cl_8 and Al_2Cl_6 spectra is obtained (Table 14), but the Al_2Cl_6 frequencies (ν_1) can be easily distinguished using our previous data (Table 13). All new bands (ν_1^c) were found to be strongly polarized and were attributed to PdAl_2Cl_8 . The intensities of these bands were comparable to the intensities of the Al_2Cl_6 bands, while the relative concentration of the two gases in the cell was $\sim 1 \text{ PdAl}_2\text{Cl}_8 : 4 \text{ Al}_2\text{Cl}_6$. These are indications that preresonance enhancement of the gaseous complex intensities takes place.

In Table 14, we also present for comparison the frequencies of the square planar PdCl_4^{2-} Raman active fundamentals. The proximity of the ν_1^c band to the stretching frequency of the PdCl_4^{2-} supports a square planar arrangement for Pd in the gaseous complex. The $4\text{--}6 \text{ cm}^{-1}$ shift for the ν_1^c band of the gaseous complex is attributed to the high ionic field effect that the counter-ion Al^{+3} has on the Pd-Cl bonding. Furthermore, estimation of Pd-Cl stretching frequencies for "hypothetical" octahedral and tetrahedral coordinations of the palladium ion gave values below 280 cm^{-1} and no correlation was possible with any of the gaseous complex frequencies.

For a D_{2h} molecular symmetry of the complex, the vibrational modes are classified as

$$\begin{aligned} \Gamma_{\text{vib}} = & 5A_{1g}(\text{R}) + 3B_{1g}(\text{R}) + 3B_{2g}(\text{R}) + B_{3g}(\text{R}) \\ & + 2A_u(\text{I.A.}) + 4B_{1u}(\text{IR}) + 4B_{2u}(\text{IR}) + 5B_{3u}(\text{IR}) \end{aligned}$$

From the expected five polarized bands, three are observed in the Raman spectra. The ν_2^c and ν_4^c bands are close to and have intensities similar to the ν_5 and ν_4 Al_2Cl_6 bands. The depolarized modes, $B_{1g}(\text{R})$, are expected to have weak Raman intensities and probably are overcome by the Al_2Cl_6 bands; they are not seen in the spectra.

Table 14. Observed Raman Frequencies (cm^{-1}) for the Gaseous Mixture PdAl_2Cl_8 - Al_2Cl_6 .
 $T = 575 \text{ K}$; $\lambda_0 = 6471 \text{ \AA}$

Band	Raman Shift	Assignments ^a	Raman Frequencies ^b of PdCl_4^{2-}		
			Aqueous HCl Sol.	K_2PdCl_4	Assignment
I	65 p sh	ν^c (?)			
II	84.5 ± 1 p	ν_4^c (A_{1g}); PdAl_2Cl_8			
III	96 ± 1 p	ν_4 (A_{1g}); Al_2Cl_6			
IV	167 ± 2 dp (sh)	ν_5 (B_{1g}); Al_2Cl_6	165		
V	176 ± 1 p	ν_2^c ; (A_{1g}); PdAl_2Cl_8		196	ν_4 (B_{2g})
VI	217 ± 1 p	ν_3 , (A_{1g}); Al_2Cl_6	278	269	ν_2 (B_{1g})
VII	298 ± 1.5 p	ν_1^c ; (A_{1g}); PdAl_2Cl_8	304	303	ν_1 (A_{1g})
VIII	331 ± 1.5 p	ν_2 ; (A_{1g}); Al_2Cl_8			
IX	338.5 ± 1.5 p	ν_1^c			
X	376 ± 1 p	ν_1^c ; (A_1); $\text{AlCl}_3(\text{D}_{3h})$			
XI	507 ± 2 p	(d) Al_2Cl_6			
XII	$516 \pm$ p	ν_1 (A_{1g}); Al_2Cl_6			
XIII	610 ± 2 dp	(B_{1g}); Al_2Cl_6			

^aThe assignment of the Al_2Cl_6 band is taken from Section B.2.

^bY. M. Bosworth and R. J. H. Clark, *Inorg. Chem.* 14, 170 (1975).

^cTemperature-dependent polarized band (see Section B.2).

^dCombination band.

CuAl_2Cl_8 . Recent thermodynamic and Raman spectroscopic studies of the $\text{CuCl}_2(\text{s})$ - $\text{Al}_2\text{Cl}_6(\text{g})$ system by Emmenegger *et al.*⁷⁰ have suggested a CuAl_2Cl_8 stoichiometry and a ring-type structure for the complex, where a trigonal coordination was assumed for the Cu(II). The authors, however, failed to note the presence of resonance Raman characteristics in their spectra, which were taken with only the 514.5-nm Ar^+ -laser line.

We have obtained a series of Raman spectra of the vapor species formed in the $\text{CuCl}_2(\text{s})$ - $\text{Al}_2\text{Cl}_6(\text{g})$ system using different exciting lines from both an Ar^+ and a Kr^+ ion laser. The temperature dependence of the spectra was also studied. All Raman cells were prepared by equilibrating $\text{CuCl}_2(\text{s})$ with $\text{Al}_2\text{Cl}_6(\text{g})$ at 300°C and then cooling and isolating the gaseous species from the solid CuCl_2 . Thus, no excess of $\text{CuCl}_2(\text{s})$ was present in the cell at temperatures above 300°C . The Raman spectra of the "binary" gas system are shown in Fig. 13. The bands due to the gaseous complex can be identified by comparison with those of $\text{Al}_2\text{Cl}_6(\text{g})$ and are listed in Table 15. The intensities of these bands relative to those of Al_2Cl_6 were found to increase rapidly with

Fig. 13. Raman Spectra of Vapors in the $\text{Al}_2\text{Cl}_6(\text{g})$ - $\text{CuCl}_2(\text{s})$ System. Slits $\sim 7 \text{ cm}^{-1}$; $t = 2 \text{ sec}$; scan rate 0.22 nm/min . Bands a, b, c, d, e and all high frequency bands are due to the CuAl_2Cl_8 gaseous complex; $t \approx 575$; partial pressures $P_{\text{Al}_2\text{Cl}_6} \sim 0.3 \text{ atm}$; $P_{\text{complex}} \sim 0.06 \text{ atm}$; no CuCl_2 excess.

increasing temperature and/or wave number of the exciting line. In the spectra taken with the 647.1 and 568.2-nm lines, bands IV to XIII were not detectable and bands I-V were of weak intensity. However, with the Ar^+ laser lines, all of the gaseous-complex bands become the predominant features of the spectra. These changes in intensities can be attributed to the resonance Raman effect that takes place when the frequency of the exciting line approaches an absorption band of the complex. The absorption spectra of $\text{CuAl}_2\text{Cl}_8(\text{g})$ were obtained in a way similar to that described in Section C-5 and are presented in Fig. 14. All the laser lines used to obtain the Raman spectra lie between the Cu(II) d-d band and the $\text{Cu} \rightarrow \text{Cl}$ charge transfer (CT) band. It was also found that increasing temperature shifts the CT band to the red and increases the laser line-CT band overlap. Thus, a change of the laser line from 647.1 to 457.9 nm and/or an increase in temperature brings the CT band and the Raman exciting line closer to each other.

Table 15 lists the Raman active stretching frequencies of different copper chloride molecules and all of the frequencies of the CuCl_4^{2-} tetrahedron.⁷¹ Polarized Raman active modes are expected to dominate the resonance Raman spectra, and thus, bands III, IV, and V are assigned to A_1 species. The remaining bands have frequencies that correspond to combinations of the ν_1^{C} and ν_3^{C} fundamentals. The strong band at 448 cm^{-1} is far from the Cu-Cl symmetric stretch of the molecules listed in Table 15. Its intensity, relative to the intensities of bands II and IV, is enhanced more rapidly with increasing overlap between the exciting line and the CT band. This is considered as indicating a preferential resonance coupling between this vibrational mode and the CT band. A detailed analysis of the data has not been completed yet.

Table 15. Observed Raman Frequencies (cm^{-1}) for Gaseous Complex(es)
Formed in the $\text{CuCl}_2(\text{s})\text{-Al}_2\text{Cl}_6$ System^{a,b}

Band	Raman Shift	Assignments	Raman Active Frequencies in Different Copper Chlorides		
I	84.5 ± 1	ν_4^c ; (c)	104	ν_2 (E_g)	CuCl_4^- (d)
II	155 ± 1.5	$\nu_3^c - \nu_1^c$	135	ν_4 (F_{2g})	CuCl_4^{2-}
III	174.5 ± 1.5	ν_2^c ; (c)	252	ν_3 (F_{2g})	CuCl_4^{2-}
IV	291.5 ± 1.5	ν_1^c ; (c)	295	ν_1 (A_1)	CuCl_4^{2-}
V	448 ± 1	ν_3^c ; (c)	318	ν_1 (A)	CuCl_2 (e)
VI	738 ± 2	$\nu_1^c + \nu_3^c$	(388)	ν_1 (A)	CuCl^- (f)
VII	787 ± 2	---	(410)	ν_1 (A)	CuCl_3^- (f)
VIII	893 ± 2	$2\nu_3^c$	415	ν_1 (A)	CuCl (g)
IX	951 ± 3	---	416	ν_1 (terminal stretch)	Cu_2Cl_4 (h)
X	1032 ± 3	$2\nu_1^c + \nu_3^c$			
XII	1182 ± 4	$\nu_1^c + 2\nu_3^c$			
XIII	1326 ± 4	$3\nu_3^c$			

^aFrequencies due to Al_2Cl_6 are not listed.

^bA few weak intensity bands were also observed with the 4880 line at frequencies below 80 cm^{-1} .

^cThese were the only frequencies present in the spectra taken with the 6471 and 5862 lines.

^dRef. 71.

^eWe have measured the Raman spectra of CuCl_2 at 1000 K and observed a strong polarized band at this frequency.

^fEstimated by scaling to the PbCl^- and HgCl_3^- molecules.

^gRef. 30.

^hJ. R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, N. Y., 1971, p. 141.

Fig. 14. Electronic Absorption Spectra of Copper (II) Chloride-Aluminum Chloride Gaseous Complex

5. Spectra and Thermodynamics of the Cobalt Bromide-Aluminum Bromide Gaseous Complexes (G. H. Kucera and G. N. Papatheodorou)

Spectroscopic and thermodynamic data for the formation of the deep green gaseous complexes of cobalt (II) bromide with aluminum bromide are reported. The stoichiometry and thermodynamic quantities of the reaction

were obtained by measuring the electronic absorption spectra of the gaseous complex(es) over solid CoBr_2 in an atmosphere of $\text{Al}_2\text{Br}_6(\text{g})$. The purpose of this study is to examine the gas complexing capability of aluminum bromide to form gaseous complexes and to compare the thermodynamics, structure, and volatility enhancement ratios of the bromoaluminate complexes with those of the chloroaluminate complexes.⁴⁴

a. Experimental

A Cary 17H spectrophotometer was used for the light absorption studies. A high-temperature split furnace (maximum $t \approx 1200^\circ\text{C}$) was designed and installed in the cell compartment of the spectrophotometer.

An X-Y rotatable positioner was used for aligning the furnace in the compartment. A cut-away view of the furnace and support is shown in Fig. 15. Inside the furnace core, a cylindrical Inconel metal split block was placed for positioning cylindrical optical cells. Double quartz windows were mounted on lavite supports at the two ends of the furnace.

Fig. 15.

Cut-away View of Furnace and Support. A, insulating material; B, Inconel block; C, lavite; D, quartz windows; G, furnace support; F, x-y-rotational positioner; b, light beam; r.b., reference light beam; LL', MM', RR', kanthal heating wire

The three heating elements of the furnace are connected to three variacs so that the input to these heaters can be separately varied as a function of temperature. However, all power supplies are actuated by the same proportional controller. The setup allows a 2° to 5° gradient along the optical cell such that the middle of the cell is slightly cooler than the ends. This is desirable for avoiding condensation of nonvolatile salts on the cell windows.

Anhydrous aluminum bromide was purified by slow sublimation in silica tubes under vacuum. A similar procedure was used for the purification of anhydrous CoBr_2 .

b. Molar Absorptivity Measurements

Four experiments were designed for the determination of the apparent molar absorptivity, $\epsilon(\lambda)$, of the gaseous cobalt (II) complexes. The data are presented in Fig. 16. The molar absorptivity was found, within experimental error, to be independent of Al_2Br_6 gas pressure. This implies⁴⁵⁻⁴⁷ that species with fixed m and n values are present or that two or more species

Fig. 16. Electronic Absorption Spectra of Cobalt Chloride-Aluminum Chloride Gaseous Complex(es). Temperatures - A, 900 K; B, 800 K; C, 750 K; D, 700 K; E, 650 K

with different m values but equal "atomic absorptivities" are present. The $\epsilon(\lambda)$ values lie between those that one might expect for octahedral and tetrahedral geometries of Co (II) in bromide environments. The relative intensities of the absorption bands and their temperature dependence are very similar to those observed for $\text{CoAl}_2\text{Cl}_8(\text{g})$.⁴⁷ The substitution of chlorine by bromine creates a less effective ligand field around Co (II); thus, the cobalt (II) bromoaluminate bands are shifted to higher wave lengths relative to the bands of CoAl_2Cl_8 . This indicates that the structures of the Co (II) complexes in the Al_2Cl_8 and Al_2Br_6 are similar. No unambiguous conclusions, however, can be deduced about the geometric arrangement of Co (II) in these complexes.

c. Partial Pressures and Thermodynamics of the Complexes

The pressures of the cobalt gaseous complexes over solid CoBr_2 were determined from the relation $P_c = A_{\max}/\epsilon_{\max} RT$, where $A_{\max}$ is the measured absorbance at wave length $\lambda_{\max} = 697\text{--}702$ and $\epsilon_{\max}$ is the average absorptivity of the complexes (Fig. 16) at $\lambda_{\max}$. Measurements of P_c as a function of time showed that equilibrium was reached in a period of less than 0.5 hr. Seven different experiments with different pressures, P' , of $\text{Al}_2\text{Br}_6(\text{g})$ were performed. The pressures P' were calculated from the amount of Al_2Br_6 placed into the cell and by taking into account the dissociation constant for the reaction:

The dissociation constant, k , was calculated using the JANAF tables:

$$\ln k = 15.341 - \frac{11,598}{T} - \frac{497,106}{T^2} \quad (43)$$

Figure 17 shows that at fixed temperature P_c is proportional to P' . This implies⁴⁵⁻⁴⁷ that there is only one Al_2Br_6 molecule per gaseous complex and that the general formula of the complex is $(\text{CoBr}_2)_m \text{Al}_2\text{Br}_6$. Furthermore, the previously mentioned requirement for equal "atomic absorptivities" implies that all complexes have the same value of m . The present measurements cannot

Fig. 17.

Plots of P_c [pressure of the complex(es)] vs. P' (pressure of Al_2Br_6) at Different Temperatures. Slopes have been determined by a least squares fitting of the data

establish a value of m , but we shall assume that it is the same as in the case of CoAl_2Cl_6 .⁴⁷ With the values $n = 1$ and $m = 1$, reaction 41 becomes

with

$$K = \frac{P_c}{P' - P}$$

The variation of $\ln K$ vs. $1/T$ at temperature below 800 K was found to follow the second law:

$$R = \ln K = 9.4 + 9.9/T$$

and the thermodynamic quantities of reaction⁴⁴ are

$$\Delta H^\circ = 9.9 \text{ kcal/mol}$$

$$\Delta S^\circ = 9.4 \text{ e.u.}$$

These values are similar to the values found⁴⁴ for the $\text{CoCl}_2\text{-Al}_2\text{Cl}_6$ gas complex ($\Delta H = 10.0 \pm 2 \text{ kcal/mol}$; $\Delta S = 9.8 \pm 0.3 \text{ e.u.}$).

Volatility Enhancement Ratios. From a practical point of view, it should be useful to calculate and compare the volatility enhancement ratios $R(T)$ of the cobalt halides in different environments of "acidic gases". In terms of the thermodynamic quantities of reaction 35, Eq. 36 becomes:

$$R(T) = \frac{P'}{P_s(1 + k^{-1})} = \frac{P'}{P_s} \left(1 + e^{\Delta H/RT - \Delta S/R} \right)^{-1} \quad (45)$$

Equation 45 shows that increasing the temperature and/or pressure of Al_2X_6 increases the volatility enhancement ratio. Also, because of dissociation,⁴² the pressure of the dimer depends on the equilibrium constant, k :⁴³

$$P' = P_0 + \frac{k}{8} \left[1 - \sqrt{\frac{16 P_0}{k} + 1} \right] \quad (45a)$$

Combining Eqs. 45 and 45a and taking into account the consumption of Al_2X_6 due to reaction 35, we have calculated and plotted in Fig. 18 the temperature dependence of P_c and of the logarithm of $R(T)$ for the cobalt halides in Al_2Cl_6 , Al_2Br_6 , Ga_2Cl_6 and Fe_2Cl_6 atmospheres.⁷³ A constant pressure, $P_0 = 1 \text{ atm}$, was used at all temperatures. Clearly, the P_c passes through a maximum which depends on both the thermodynamic quantities of reactions 35 and 42. Calculations of P_c at different P_0 pressures were made and show that with increasing pressure the maximum P_c increases sharply and its position shifts to higher temperatures. The $\ln [R(T)]$ plots in Fig. 18 indicate that at lower temperatures Al_2Br_6 is a better gas-complexing agent than Al_2Cl_6 for the respective cobalt halides. At higher temperatures, however, the enhancement due to the aluminum chloride is greater than that due to aluminum bromide. Iron (III) chloride appears to be superior to both at higher temperatures, but the calculated values of $R(T)$ do not include a correction for the dissociation reaction: $\text{FeCl}_3 \rightleftharpoons \text{FeCl}_2 + 1/2 \text{ Cl}_2$; thus, the resultant curve is correct only in the presence of an overpressure of Cl_2 .

Fig. 18.

Apparent Partial Pressures and Volatility Enhancement Ratios of CoCl_2 and CoBr_2 in Different A_2X_6 Atmospheres. At each temperature, the "ideal gas" pressure of Al_2Cl_6 was $P_0 = 1 \text{ atm}$

The low reactivity of Al_2Br_6 with fused silica at temperatures up to 1000 K and its high $R(T)$ values make it attractive for detailed spectrophotometric studies of gaseous complexes. Furthermore, the critical constants $T_k = 763 \text{ K}$ and $P_k = 28.5 \text{ atm}$ ⁷² of Al_2Br_6 permit pressures of nearly 30 atm at temperatures near 800 K, where practically no attack on fused silica occurs. Under these conditions, aluminum bromide can be considered as a potential candidate for the construction of gas lasers by complexing and carrying in the gas phase considerable amounts of lanthanide bromides. Presently, we are developing experimental techniques to study spectrophotometrically such bromide gas complexes at elevated pressures and temperatures.

III. THERMODYNAMIC PROPERTIES OF ALLOYS (M. Blander)

Alloys of alkali and alkaline earth metals are important in a variety of advanced high-energy battery concepts. The paucity of thermodynamic data on such systems has hampered the search for optimum electrode materials. In addition, some lithium alloys (*e.g.*, Li-Pb) are candidates for blanket materials in controlled thermonuclear reactors. The objectives of our study are to obtain data on such alloy systems in a systematic manner and to utilize our experimental data to develop theories and techniques that will permit one to make predictions for systems of practical importance with a minimum of information.

A. Electromotive Force Measurements and Interpretation of the Activity Coefficients of Dilute Solutions of Lithium in Molten Aluminum-Tin Alloy (M. L. Saboungi)

We report on electromotive force measurements of dilute solutions of Li in molten Al-Sn alloys. Dilute solutions of Li in either pure liquid Al or in pure liquid Sn followed the Nernst law very precisely. For all compositions of the solvent, Al-Sn, the activity coefficients of Li have been measured and interpreted in terms of a generalized quasi-lattice theory.^{74,75,76} An additional term to the equations for the energetics of the metallic interactions is shown to be necessary⁷⁷ to provide a complete description of the thermodynamics of the system.

1. Experimental Procedure

The experimental arrangement of the cells and the procedure followed are similar to those previously used in the study of Li-Mg alloys.⁷⁸ In this investigation, the cell can be schematized as follows:

A significant improvement in the performance of the present design arose because of the choice of the reference electrode. The negative electrode consisted of a premelted two-phase binary system with an overall composition of 60.5 at. % Li and 39.5 at. % Bi held in a small tantalum cup which was submerged in the electrolyte. At the temperature of our measurements, $T = 949$ K, this composition provides a Li-Bi solution saturated with the compound $\text{Li}_3\text{Bi(s)}$. The electromotive force of this secondary reference electrode relative to pure Li has proven to be very stable with respect to small changes of Li compositions.⁷⁹ In addition, the solubility of metallic Li in the electrolyte is negligible, probably less than 10^{-2} mol %, ^{80,81} because of its low activity in the reference electrode.

The cells were operated starting with different solvents which were either pure aluminum, pure tin or an appropriate mixture of Al-Sn. The composition in the bulk alloy was changed by adding successive weighed quantities of Li, Sn or Al. For each point, the equilibration of the cell with respect to temperature and voltage was rapidly attained (usually less than 2 hr for large additions and 10 min for small additions which led to an increment of less than 1 mol %). The emfs measured were steady and stable within several

tenths of a millivolt for periods of observation up to a day. After temperature cycling, the emfs generally returned to the original value, thus demonstrating the reversibility of the cell. Finally, all the operations were carried out inside a glove-box filled with purified helium.

2. Results

a. Dilute Solutions of Li in Al and in Sn

Checks of the Nernst law for dilute solutions of Li-M ($M \equiv \text{Al}$ or $M \equiv \text{Sn}$) were carried out at a constant temperature, $T = 949 \text{ K}$. The emfs, E , of the alloys vary with composition according to the relation

$$E = E_{\text{Li}(M)}^{\circ} - \frac{RT}{F} \ln a_{\text{Li}} \quad (47)$$

where R is the gas constant; F , the Faraday constant; a_{Li} , the activity of lithium in the alloys; and $E_{\text{Li}(M)}^{\circ}$, the limiting potential of Li in pure liquid M versus the Li_3Bi reference electrode.

Figure 19 shows the results obtained at 949 K in two separate runs of the cell:

$$\text{Bi saturated with } \text{Li}_3\text{Bi(s)}/\text{LiCl-LiF/Li-Al} \quad (48)$$

The emfs are plotted as a function of atom fraction of Li in the binary alloys, together with the calculated Nernst slope: $2.3026 RT/F = 188.30 \text{ mV}$. A least-squares fit of the data led to a slope of $188.07 \pm 0.59 \text{ mV}$, which is in excellent agreement with the theoretical value, and to a value of $E_{\text{Li}(\text{Al})}^{\circ} = -536.39 \pm 1.54 \text{ mV}$. At 949 K, our present value of $E_{\text{Li}(\text{Al})}^{\circ}$ combined with the potential of the reference electrode versus pure lithium, 646.41 mV, as reported previously, provides a limiting excess chemical potential of Li in pure liquid Al: $\mu_{\text{Li}(\text{Al})}^{\text{xs}} = -2.54 \text{ kcal mol}^{-1}$ (or $-10.63 \text{ kJ mol}^{-1}$). Our value is in good agreement with the approximate value of $-2.6 \text{ kcal mol}^{-1}$ (or $-10.9 \text{ kJ mol}^{-1}$) obtained by extrapolating the data of Yatsenko and Saltykova⁸² from higher concentrations ($\geq 5 \text{ mol } \% \text{ of Li}$) and at 1023 K.

For the dilute solutions of Li in Sn, the data obtained versus the Li_3Bi reference electrode fit well along the Nernst slope of 188.30 mV with a value of $E_{\text{Li}(\text{Sn})}^{\circ} = 116 \pm 1 \text{ mV}$. The limiting excess chemical potential of Li in pure liquid tin is consequently: $\mu_{\text{Li}(\text{Sn})}^{\text{xs}} = -12.22 \text{ kcal mol}^{-1}$ (or $-51.14 \text{ kJ mol}^{-1}$). This value is consistent with the value of $-12.36 \text{ kcal mol}^{-1}$ (or $-51.71 \text{ kJ mol}^{-1}$) obtained by extrapolating the data of Foster *et al.*⁸³ from higher concentrations of Li ($\geq 10 \text{ mol } \%$).

The fit of the Nernst law equation in the Li atom fraction demonstrates that both dilute solutions of Li-Al and Li-Sn follow Henry's law and therefore the activity coefficient of Li is constant in this concentration range.

Fig. 19. Plot of Emf vs. the Logarithm of the Atom Fraction of Li in Li-Al Alloys at 949 K

b. Dilute Solutions of Li in the Al-Sn Alloy

The potentials of the cell (46) were measured at 949 K for different compositions of the alloy Al-Sn. In all these runs, the atom fraction of Li did not exceed 2.01×10^{-2} , which is within the range of concentrations where the Nernst law is obeyed.

Two separate series of measurements were carried out by adding small weighed amounts of Sn to a Li-Al alloy of a given composition ($X_{Li} = 1.63 \times 10^{-3}$ or $X_{Li} = 2.01 \times 10^{-2}$, respectively, with X_i referring to the atom fraction of the i th component in the solution). The experimental values obtained for the electromotive forces, E , at different compositions of the alloy are listed in Table 16. By choosing as standard state the solution of Li at infinite dilution in Al, the activity coefficients of Li, $\gamma_{Li}^{(Al)}$, can be calculated from the following equation:

$$\ln \gamma_{Li}^{(Al)} = \ln \frac{\gamma_{Li}}{\gamma_{Li}^{(Al)}} = \frac{-F[E - E_{Li}^{(Al)}]}{RT} - \ln X_{Li} \quad (49)$$

Table 16. Emf of Cell (46) for Dilute Solutions of Li and Sn in Al ($T = 949 \text{ K}$)^a

I			II		
$10^4 X_{\text{Al}}^b$	$10^2 X_{\text{Li}}$	$-E, ^c \text{ mV}$	$10^4 X_{\text{Al}}$	$10^3 X_{\text{Li}}$	$E, \text{ mV}$
9799	2.010	217.27	9984	1.630	-12.09
9756	2.003	210.43	9948	1.624	- 7.42
9716	1.995	204.19	9892	1.615	1.77
9657	1.982	194.78	9832	1.605	10.25
9603	1.971	187.31	9765	1.594	19.94
9540	1.958	177.37	9718	1.586	26.58
			9674	1.579	32.66
			9610	1.569	41.68
			9549	1.559	49.18
			9450	1.543	62.51

^aI refers to the set of measurements performed starting with the binary alloy Li-Al at a given composition ($X_{\text{Li}} = 0.0201$); II refers to the set of measurements performed starting with the binary alloy Li-Al at a given composition ($X_{\text{Li}} = 0.00163$). In both cases, weighed amounts of Sn were added to the initial alloy.

^b X_{Al} and X_{Li} represent the atom fractions of Al and Li, respectively, in the Li-Al-Sn alloy.

^cE represents the emf values obtained in cell (46).

where γ_{Li} represents the activity coefficient of Li referred to pure liquid lithium and $\gamma_{\text{Li}}(\text{Al})$, the activity coefficient of lithium at infinite dilution in Al.* The values of $\ln \gamma_{\text{Li}}^{(\text{Al})}$ are plotted versus X_{Sn} in the inset of Fig. 20.

At higher concentrations of Sn, two separate runs were performed. In the first series of measurements, successive additions of Al were made to a solution of Li-Sn ($X_{\text{Li}} = 0.0150$); in the second series, successive additions of Al were made to a solution of Li-Al-Sn ($X_{\text{Li}} = 0.0145$ and $X_{\text{Al}} = 0.3968$). Values of E , X_{Li} and X_{Sn} are reported in Table 17. In Fig. 20 values of $\ln \gamma_{\text{Li}}^{(\text{Al})}$ calculated from Eq. 49 are plotted versus the mole fraction of tin.

3. Interpretation

As the molar volumes of liquid Li, Al, and Sn do not differ greatly, the system under consideration can probably be best considered as a substitutional alloy.

* In order to convert these activity coefficients to activity coefficients with pure liquid lithium as the standard state, one should add to the r.h.s. of Eq. 49 the natural logarithm of $\gamma_{\text{Li}}(\text{Al})$ $\left[\ln \gamma_{\text{Li}}(\text{Al}) = \frac{-2540 \text{ cal}}{RT} = 1.347 \right]$.

Fig. 20.

Activity Coefficients of Dilute Solutions of Li in the Binary Solvent Al-Sn. I. Calculated with Eq. 60. II. Calculated with Eq. 61. III. Calculated with Eq. 56 using Wagner's approximation. IV. Calculated with Eqs. 56 and 57

a. Dilute Solutions of Li and Sn in Al

In this concentration range, formation of complexes or groupings between the interacting species Li and Sn in solution are postulated:

The K_i 's are defined as equilibrium constants and are true constants in solutions dilute enough to obey Henry's law. They are analogous to the interaction coefficients of Wagner.⁸⁴ Following the same method as in molten

Table 17. Emf of Cell (46) for Different Compositions of the Binary Solvent Al-Sn ($T = 949$ K)

A ^a			B ^b		
$10^4 X_{Al}$ ^c	$10^2 X_{Li}$ ^c	E , ^d mV	$10^4 X_{Al}$	$10^2 X_{Li}$	E , mV
214.8	1.472	227.63	4276	1.374	154.30
452.6	1.436	225.80	4550	1.307	151.75
999.7	1.354	221.81	4776	1.253	149.80
1499	1.279	217.47	5170	1.159	144.95
1983	1.206	213.75	5578	1.061	139.01
2569	1.112	209.15	6137	0.926	128.75
3167	1.028	203.70	6509	0.838	125.26
3780	0.936	197.75	6868	0.751	119.75
4352	0.850	191.35	7386	0.627	110.84
4879	0.770	185.75	7769	0.535	102.70
5370	0.697	179.20	8127	0.449	95.64
5822	0.628	173.38	8584	0.340	85.50
6182	0.574	168.28	8948	0.252	72.25

^aA refers to the set of measurements performed starting with a binary Li-Sn alloy to which successive weighed amounts of Al were added.

^bB refers to the set of measurements performed starting with an initial alloy of Li-Al-Sn ($X_{Al} = 0.3968$ and $X_{Li} = 0.0145$) to which successive weighed amounts of Al were added.

^c X_{Al} and X_{Li} represent the atom fractions of Al and Li, respectively, in the Li-Al-Sn alloy.

^dE represents the emf values obtained in cell (46).

salts,⁸⁵ one obtains by a least-squares fit of the data for dilute Li and Sn in Al: $K_1 = 17.39 \pm 0.15$, $K_2 = 7.13 \pm 0.28$, and $K_{12} = 10.00 \pm 0.15$. The uncertainties in these constants are probably about four times larger than the stated precision. The presence of a significant concentration of polynuclear species with more than two Li atoms would increase the uncertainty in K_{12} . In addition, the presence of such species, other than Li_2Sn , cannot be ascertained with measurements at only two concentrations of Li. The specific bond free energy ΔA_i associated with the i th equilibrium is related to the corresponding K_i by:

$$K_i = Z[\exp(-\Delta A_i/RT) - 1] \quad (53)$$

where Z is the coordination number. ΔA_1^0 is defined as:

$$\Delta A_1^0 = \lim (\Delta A_1)_{X_{Li}, X_{Sn}} = 0 \quad (54)$$

For $Z = 10$, using these values of K_1 and the more complex equations for K_2 and K_{12} , we deduce values of the specific "bond" free energies of $\Delta A_1^0 = -1.90 \text{ kcal mol}^{-1}$ (or $-7.95 \text{ kJ mol}^{-1}$), $\Delta A_2^0 = -1.83 \text{ kcal mol}^{-1}$ (or $-7.66 \text{ kJ mol}^{-1}$) and $\Delta A_{12}^0 = -2.10 \text{ kcal mol}^{-1}$ (or $-8.79 \text{ kJ mol}^{-1}$). The fact that the ΔA_i^0 are negative indicates that there is a preferential distribution of Sn about Li and of Li about Sn.

b. Dilute Solutions of Li in the Solvent Al-Sn

Equilibria (50) - (52) can be rewritten in a more general form:

where the brackets $[\text{Sn}_{i-1} \text{Al}_{Z-i+1}]$ and $[\text{Sn}_i \text{Al}_{Z-i}]$ define the distribution of Sn and Al in the coordination shell of Li while $[\text{Sn}, \text{Al}]$ means that the atom preceding it (Al or Sn) is an atom in the bulk alloy and occupies a position which is not near a Li atom. We have shown⁷⁷ that the activity coefficient of Li is given by:

$$\gamma_{Li}^{(Al)} = \sum_{i=0}^Z \left[\frac{Z!}{i!(Z-i)!} X_{Sn}^i (1 - X_{Sn})^{Z-i} \beta_0 \dots \beta_i \right]^{-1} \quad (56)$$

where the quantity $\beta_0 = \exp[\mu_{Sn}^{XS}(X_{Sn})/RT]$, $\mu_{Sn}^{XS}(X_{Sn})$ being the excess chemical potential of Sn in the binary Al-Sn alloy, and β_i ($i = 1, \dots, Z$) = $\exp(-\Delta A_i/RT)$, ΔA_i representing the changes in the specific "bond" free energy accompanying equilibrium (55). We have suggested⁷⁷ an approximation relating ΔA_i to ΔA_1^0 , to the number i , and to the deviations from ideality of the solvent:

$$\Delta A_i = \Delta A_1^0 + (i-1)h + Z^{-1} \left[\left(\mu_{Al}^{XS}(X_{Sn}) - \mu_{Al}^{XS}(X_{Sn} = 0) \right) - \left(\mu_{Sn}^{XS}(X_{Sn}) - \mu_{Sn}^{XS}(X_{Sn} = 0) \right) \right] \quad (57)$$

where h is a constant defined as the free energy difference for consecutive values of i .

Considering the following limiting cases, one can find equations derived earlier by other investigators:

1. If the quantity $h = 0$, the specific bond free energies are all equal: $\Delta A_i = \Delta'$ ($i=1, \dots, Z$). Equations 56 and 57 lead to the equation derived by Alcock and Richardson.⁸⁶

2. If the solvent, in this case Al-Sn, behaves as an ideal solution, ΔA_i as defined in Eq. 57 becomes concentration independent, and $\beta_0 = 1$. Equations 56 and 57 are then identical to those derived by Mathieu and co-workers^{87,88} and Wagner⁸⁹ for interstitial alloys.

3. If the solvent, Al-Sn, behaves as a regular solution, Eq. 57 can be written in a simple form:

$$\Delta A_1 = \Delta A_1^0 + (i - 1)h + \lambda Z^{-1} X_{Sn} \quad (58)$$

where λ would be the interaction coefficient in the "regular" solvent.

The variations of $\ln \gamma_{Li}^{(Al)}$ with the tin atom fraction are plotted in Fig. 20, together with the calculated values of $\ln \gamma_{Li}^{(Al)}$ according to different models, for $Z = 10$.

Curves I and II are computed using Alcock and Richardson equations⁸⁶ with the following modification: the atom fractions X are replaced by volume fractions $\bar{V}$ defined as follows:

$$\bar{V}_{Al} = \frac{X_{Al} V_{Al}}{X_{Al} V_{Al} + X_{Sn} V_{Sn}} \text{ and } \bar{V}_{Sn} = 1 - \bar{V}_{Al} \quad (59)$$

where V_{Al} and V_{Sn} are the molar volumes of Al and Sn. The Alcock-Richardson equations⁸⁶ can be rewritten as:

$$\ln \gamma_{Li}^{(Al)} = \bar{V}_{Sn} \ln \left(\frac{\gamma_{Li}(Sn)}{\gamma_{Li}(Al)} \right) - \frac{\Delta G^{xs}(Al-Sn)}{RT} \quad (60)$$

and

$$\gamma_{Li}^{(Al)} = \left[\bar{V}_{Al} (\gamma_{Al})^{1/Z} + \bar{V}_{Sn} \left(\frac{\gamma_{Sn} \gamma_{Li}(Al)}{\gamma_{Li}(Sn)} \right)^{1/Z} \right]^{-Z} \quad (61)$$

The differences between the experimentally derived curve and curves I and II are much larger than the combined uncertainties. The differences are even greater for the unmodified equations of Alcock and Richardson. Curves III and IV are computed using Eq. 56, but different approximations for ΔA_1 . Curve III represents the calculations according to the limiting case (2), where the deviations from ideality of the Al-Sn are not considered, whereas curve IV represents the calculations according to Eq. 57. The differences between experimental data and curve III are more important at the tin-rich end than at the aluminum-rich end. This is obviously due to the fact that the limiting slope is determined for low values of X_{Sn} . This constrains the curve to follow the experimental points initially.

The correspondence between the measurements and curve IV is surprisingly good; curve IV exhibits the same asymmetry as the experimental data. This excellent agreement leads us to conclude that Eq. 57 gives an accurate approximation for ΔA_1 for this case.

Within the context of the quasi-lattice model, the good fit of the measurements with the calculations implies that the distribution of the species can be tentatively estimated from the theory. The relative fraction of lithium atoms present in the i th species, $N_i^*(Li)$, were calculated as a function of the atom fraction of Sn in the Li-Al-Sn alloy. The results obtained for $i = 0, 1, 5, 9$, and 10 are plotted versus X_{Sn} in Fig. 21.

Fig. 21.

Relative Fraction of Species LiSn as a
Fraction of Composition of the Al-Sn
Binary Alloy Solvent Based on the Quasi-
Lattice Model for $Z = 10$

Despite the fact that the curves in Fig. 21 are model dependent, they probably provide a reasonable picture of the distributions of species in the real solution. Similar curves could be obtained for values of Z other than 10.

B. Electromotive Force Measurements in Molten Li-Pb Alloys (M. L. Saboungi and J. J. Marr)

Lithium-lead alloys exhibit attractive features from both the theoretical and applied point of view.

Recently, a neutron diffraction pattern of liquid lithium-lead alloys was measured.⁹⁰ The data, which are among the first on lithium alloys, indicated a short-range order interpreted in terms of a salt-like character in the bonding between lithium and lead ions. The activity coefficients of lithium can be used to test such a hypothesis according to Wagner.⁸⁶

Solid and liquid lithium-lead alloys are currently being considered as potential candidates for fusion reactor blanket materials for several reasons; some are the $(n, 2n)$ reaction afforded by the lead, the apparent chemical stability towards austenitic alloys, and a lower tritium inventory per unit volume than that of liquid lithium blankets.⁹¹

1. Experimental Procedure

The experimental arrangement of the cell and the procedure followed are identical to those described above (Section III.A.1).

At each temperature ($T = 770, 812, 869, \text{ and } 932 \text{ K}$), the cells were operated starting with either pure lead or pure lithium and making successive carefully weighed additions of either lithium or lead up to the composition of the liquidus (Fig. 22). The thermal reversibility of each cell was tested over a temperature range of more than 30°C . After temperature cycling, the emf's returned to their initial values within less than a millivolt.

Fig. 22. Measured Phase Diagram of the Li-Pb System Exhibiting Temperatures where Emfs were Measured

2. Results

a. Dilute Solutions of Li in Molten Lead

Checks of the Nernst law for dilute solutions of Li in Pb were carried out at four temperatures ($T = 770, 812, 869, \text{ and } 932 \text{ K}$). Using Eq. 47 where $M \equiv \text{Pb}$, the emfs were obtained as a function of the alloy composition.

Figure 23 shows a typical plot of the emfs obtained at $T = 770 \text{ K}$ for two separate runs. A standard least-squares fit of the data gave a slope of 152.40 ± 0.55 , which is in excellent agreement with the theoretical value $2.3026 (RT/F) = 152.78$, and a value of $E_{\text{Li(Pb)}}^\circ = -216.73 \text{ mV}$. At 770 K , with pure liquid lithium as a standard state (the emf of the reference electrode

Fig. 23.

Nernst Law Plot of the Emfs of Dilute Solutions of Li in Pb, Plotted vs. the Logarithm of the Atom Fraction of Li at 770 K

versus pure lithium is found to be 708.20 mV), the limiting excess chemical potential of Li in pure liquid Pb is $\mu_{\text{Li(Pb)}}^{\text{xs}} = -11.098 \text{ kcal mol}^{-1}$. Our determination of $\mu_{\text{Li(Pb)}}^{\text{xs}}$ is in reasonable consonance with the extrapolated value⁹² from higher concentrations ($X_{\text{Li}} \geq 0.03$): $\mu_{\text{Li(Pb)}}^{\text{xs}} \simeq -11.20 \text{ kcal mol}^{-1}$.

b. Concentrated Solutions of Li in Molten Lead

At higher concentrations of lithium, strong negative deviations from ideality were observed. The variations of $\ln \gamma_{\text{Li}}$ with atom fraction of Pb are plotted in Fig. 24 for $T = 932 \text{ K}$. S-shaped curves such as the one plotted in Fig. 24 are obtained at all temperatures, with an inflection point at about $X_{\text{Li}} \sim 0.2$. As noted by Wagner⁸⁴, curves with this "unusual" shape have been observed for mixtures such as Mg-Pb. One possible way of interpreting this peculiarity would be to correlate it with the existence of intermediate phases which tend toward a salt-like bonding.⁸⁴ The structure of Li_4Pb , which has an equal number of valence electrons from Li and Pb, appears to be particularly stable, and Li_4Pb may be the compound with salt-like character. Our data can be used to derive the activities of Pb at different temperatures and for different compositions from the Gibbs-Duhem equation. The excess entropy of mixing can also be deduced. A preliminary estimate of $\Delta S_{\text{Li}}^{\text{xs}}$ leads to values much greater than earlier measurements.⁹² Our high entropies are in consonance with measurements on alkali-metal alloys.⁹³

Fig. 24.

Plot of $\ln \gamma_{Li}$ vs. the Mole Fraction of Pb in the Binary Li-Pb Alloy at 932 K

Measurements are planned to check the data collected on the system Li_3Bi versus pure liquid lithium at several temperatures. These emf values will be used to refer the activities of Li in the alloys to pure lithium as standard state, rather than to the two-phase binary system $Li_3Bi + Bi$ of the reference electrode.

C. Computation of Phase Diagrams (M. L. Saboungi and C. C. Hsu)

In the search for a binary or multicomponent alloy that will perform optimally as negative electrodes in high-temperature batteries, a knowledge of the phase diagram as well as of the thermodynamics of the system is important. In this last decade, a numerical method⁹⁴ based on thermodynamic relations has been developed to compute binary and ternary phase diagrams taking into account the existence of limited solubilities of one component in the solution (*i.e.*, solid solutions), the binary compounds and their phase field in ternary systems, and the coexistence of two solid or liquid phases (*i.e.*, miscibility gaps). The coefficients defining the reactions occurring in the subsidiary binaries are consequently used to construct isothermal sections of the corresponding ternary phase diagram.

In most cases, the ternary phase diagram has not been experimentally determined. In addition to the fact that such computations provide a rather good thermodynamically self-consistent representation of ternary phase diagrams, one can often deduce valuable thermodynamic information on the free energy of formation of compounds. We will report here on the calculated phase diagrams of five binary systems Li-Mg, Li-Al, Li-Ca, Mg-Al and Ca-Mg.

1. Thermodynamics of Binary Systems

In this section, we will briefly review the equations that Kaufman and Nesor⁹⁴ used as a basis for their calculations, and discuss the limitations of such a treatment. The phase diagram is computed from the consideration of all possible reactions.

a. Solution Phases

In dealing with solution phases, the important feature is the definition of the excess Gibbs free energy. For a system comprising components 1 and 2, the excess Gibbs free energy of solution phases can be described by:

$$\Delta G^E = X_1 X_2 [X_1 h(T) + X_2 g(T)] \quad (62)$$

where X_i is the atom fraction of i , and $h(T)$ and $g(T)$ are temperature-dependent functions. The excess partial Gibbs free energies of components 1 and 2 are given as:

$$\Delta \bar{G}_1^E = X_2^2 \{g(T) + (2X_2 - 1)[h(T) - g(T)]\} \quad (63)$$

and

$$\Delta \bar{G}_2^E = X_1^2 \{g(T) + 2X_1[h(T) - g(T)]\} \quad (64)$$

The functions $g(T)$ and $h(T)$ are approximated by:

$$g(T) = g_0 + g_1 T \quad (65)$$

where g_0 and g_1 are constants. For a wider temperature range inclusive of 0 K, the following form is used:

$$g(T) = g_2 + g_3 T^2 + g_4 T^3 \quad (66)$$

where g_2 , g_3 and g_4 are constants. Similar equations hold for $h(T)$.

b. Compound Phase

In the present cases, all compounds will be considered as line compounds. The free energy of the compound "K" of fixed stoichiometry X_1', X_2' and structure α can be written as:

$$G^\alpha = X_1' G_1^\theta + X_2' G_2^\theta + X_1' X_2' [(X_2' X_1')^{-1} \Delta G_L^E(X') - C^\alpha] \quad (67)$$

where G_i^θ is the Gibbs free energy of the i th component in the θ form; X_i' , the composition of the compound; $\Delta G_f^L(X')$, the excess Gibbs free energy of the liquid phase at the composition X' ; and C^α , the compound parameter. The base phase θ is chosen as the most stable phase at the temperature of interest. Definition of the compound parameter describes the free energy of formation of the compound:

$$\Delta G_f = G^\alpha - X_1' G_1^\theta - X_2' G_2^\theta \quad (68)$$

The quantities G_1^θ and G_2^θ refer to the free energies of the stable forms of the components (1) and (2) at the corresponding temperature. The parameter C^α is usually expressed as a function of temperature:

$$C^\alpha = C_1 + C_2 T \quad (69)$$

c. Miscibility-Gap Phase

Again, the excess Gibbs free energy is used to calculate the limits of a miscibility gap between two solid phases or two liquid phases. The inflection in the curves (when it exists) representing the free energies of mixing at different temperatures defines the miscibility gap.

2. Calculations

Figures 25-29 show both the experimental and computed phase diagrams of five binary systems.

Fig. 25. Phase Diagram of the Li-Mg System

a. Measured

b. Calculated

Fig. 26. Phase Diagram of the Li-Al System

a. Measured

b. Calculated

Fig. 27. Phase Diagram of the Li-Ca System

a. Measured

b. Calculated

Fig. 28. Phase Diagram of the Mg-Al System

a. Measured

b. Calculated

Fig. 29. Phase Diagram of the Ca-Mg System

a. The Li-Mg System

The phase diagram of the Li-Mg was computed by considering three reactions occurring between the liquid phase, a bcc solid phase, and an hcp solid phase. The thermodynamics of the liquid solution were calculated from emf data obtained at ANL.⁷⁸ Figure 25 represents the observed⁹⁵ (Fig. 25a) and calculated (Fig. 25b) phase diagrams; the agreement between the two diagrams is excellent. As an example, the coordinates of the measured eutectic are $T_E = 861$ K and $X_{Li} = 0.21$, whereas those of the calculated eutectic are at $T_E = 865$ K and $X_{Li} = 0.23$. In addition, at the same temperatures, the intercepts of the hcp and the bcc phases with the liquid phases are exactly the same for the experimental and the computed phase diagrams.

b. The Li-Al System

In this study, we used as a basis for our computation the phase diagram recently investigated⁹⁶ by DTA methods (Fig. 26a). The new details are the peritectic formation of Al_4Li_9 at 608 K and the confirmation of the presence of Al_2Li_3 rather than $AlLi_2$. In the calculational procedure, the data on the liquid were taken from emf measurements.^{77,82} To a first approximation, the compounds are considered to be line compounds.

The computed phase diagram represented by Fig. 26b is probably more self consistent thermodynamically than the experimental phase diagram in the region of the α -aluminum solid solutions. In addition, the phase boundary between the α and $\alpha + \beta$ phases is more completely defined. One can also deduce the free energies of formation of the compounds. For example, the free energy of formation of the compound LiAl from pure liquid Li and Al at the melting point is:

$$\Delta G_f = G_{Li_{0.5}Al_{0.5}} - 0.5 G_{Li}(liq) - 0.5 G_{Al}(liq)$$

$$\Delta G_f = -4.56 \text{ kcal mol}^{-1}$$

c. The Li-Ca System

The phase diagram of this system is poorly known, especially at the calcium-rich end. Indeed, the data collected to define the calcium branch of the liquidus are even contradictory (Fig. 27a).

The phase diagram was constructed (Fig. 27b) taking into consideration the Ca transition occurring at 710 K from the bcc to the fcc phase. The compound Li_2Ca is included and its Gibbs free energy of formation calculated at 500 K is:

$$\Delta G_f = G_{Li_{0.667}Ca_{0.333}} - 0.667 G_{Li}(liq) - 0.333 G_{Ca}(liq)$$

$$\Delta G_f = -0.645 \text{ kcal mol}^{-1}$$

d. The Mg-Al System

The experimental and calculated phase diagrams of Mg-Al are represented in Figs. 28a and 28b, respectively. The data for the solid and liquid alloys are taken from Hultgren *et al.*⁹⁵ Within the limits of some simplifications, the calculated phase diagram confirms the fact that the thermodynamic data and the measured phase diagram are self-consistent. The calculated joins between the liquid and the Al(fcc) solid phase on the one hand and the Mg(hcp) phase on the other hand are close to the experimental joins.

I. Experiment: $T = 723 \text{ K}$ $X_{\text{Mg}} = 0.19$ and $X_{\text{Mg}} = 0.38$

Calculation: $T = 735 \text{ K}$ $X_{\text{Mg}} = 0.19$ and $X_{\text{Mg}} = 0.35$

II. Experiment: $T = 710 \text{ K}$ $X_{\text{Mg}} = 0.70$ and $X_{\text{Mg}} = 0.88$

Calculation: $T = 708 \text{ K}$ $X_{\text{Mg}} = 0.70$ and $X_{\text{Mg}} = 0.88$

e. The Ca-Mg System

The data on the Ca-Mg (solid and liquid alloys) were taken from Hultgren.⁹⁵ The asymmetry of the data (the deviations from ideality on the Mg side are more negative by a factor of 2 than those observed on the Ca side) reflects the asymmetry of the phase diagram (Fig. 29a). The calculated phase diagram reproduced the same asymmetry (Fig. 29b). The Gibbs free energy of formation of the compound Mg_2Ca is calculated at 1000 K:

$$\Delta G_f = G_{\text{Mg}_{0.667}\text{Ca}_{0.333}} - 0.667 G_{\text{Mg}} - 0.333 G_{\text{Ca}}$$

$$\Delta G_f = -3.390 \text{ kcal mol}^{-1}$$

3. Conclusion

The calculations performed on the binary systems

- (1) have served to check the consistency of available phase diagrams and thermodynamic data;
- (2) provided additional information on the thermodynamics of systems;
- (3) helped to fully define the phase diagrams in a thermodynamically self-consistent way in regions inaccessible to measurements or which are known with very poor precision; and
- (4) defined all the thermodynamic coefficients necessary for computing the phase diagram of the corresponding ternary system.

Computations are presently under way to calculate isothermal sections of the phase diagram of the Li-Mg-Al, Li-Mg-Ca and Ca-Mg-Al ternary systems.

IV. METEORITIC STUDIES (M. Blander and C. C. Hsu)

In order to fully determine the chemistry of the solar nebula (or of any other complex gas), a general quantitative calculation of reactions in multicomponent gases must be performed. We have adapted an existing computer program for the calculation of complex equilibria in multicomponent multiphase systems⁹⁸ from which one can calculate equilibrium compositions of a gas phase and the condensation of pure solids from the gas. Our initial aim was to modify the program to take kinetic constraints into account in order to have the capability of including nonequilibrium products that are known to exist in meteorites (as well as in effluents from combustion and metallurgical processes). The ultimate aim is to compare and correlate the properties of nebular condensates with the measured properties of chondritic meteorites.

We have performed calculations of condensation from a cooling gas of solar composition for total equilibrium and with the imposition of predicted nucleation constraints upon the condensation equilibria.⁹⁹ The nucleation constraints alter the chemistry of the condensation products in a major way. The results of the calculation lead to quantitative predictions of the products for which thermodynamic data are available. In order to obtain reasonable results, one must impose a hierarchy of kinetic constraints which are effective when temperatures are low enough. We report illustrative calculations in a system of solar composition composed of H_2 , O, C, Mg, Si, and Fe.

A. Equilibrium

The composition of the gas is determined by the mole ratios of the elements considered in a solar gas: $H_2/O/C/Mg/Si/Fe = 1.3 \times 10^{10}/2.36 \times 10^7/1.35 \times 10^7/1.05 \times 10^6/1.0 \times 10^6/8.90 \times 10^5$. Calculations were performed at total pressures of 10^{-6} , 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} atmosphere between 500 and 2500 K. The major vapor species deduced from the calculations are H_2 , H_2O , Mg, SiO and Fe. If a gas of the given composition is cooled from a high temperature, a sequence of condensates will form. Table 18, part a, gives the temperatures of first formation of the solid condensates Fe(s), Mg_2SiO_4 (s) and $MgSiO_3$ (s). At high pressures, metallic iron is the first condensate to be formed; it is followed by forsterite (Mg_2SiO_4), which is then mostly converted to enstatite ($MgSiO_3$). At lower pressures, forsterite precedes iron. The results of our computer calculations of nebular condensates permit a quantitative calculation of the fraction of any of the elements condensed at any given temperature. In curves such as those labeled Mg_2SiO_4 and "no constraints" of Fig. 30 are plotted the fraction of Mg condensed as Mg_2SiO_4 (s) and $MgSiO_3$ (s) at equilibrium. A condensation curve was also obtained for Fe(s).

B. Constrained Equilibria

From nucleation theory, one predicts that metallic iron will be difficult to nucleate and will not condense unless supersaturations are very large. If we impose this kinetic constraint on the condensation process, iron does not condense and can supersaturate in the vapor so as to alter the chemistry in a predictable manner. The results of our calculations for this case are given in Table 18, part b, where it can be seen that FeO(s) will form if iron condensation is blocked. The FeO will be converted to Fe_3O_4 at somewhat lower temperatures. Thus, even though FeO is not the stable phase, it can form

Table 18. Condensation Temperatures (K)

(a) With no constraints

<u>Pressure, atm</u> Condensed Compound or Element	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Fe(s)	1577	1466	1370	1285	1210
Mg ₂ SiO ₄ (s)	1533	1452	1379	1313	1253
MgSiO ₃ (s)	1444	1375	1314	1258	1207

(b) With constraint on metallic iron

<u>Pressure, atm</u> Condensed Compound	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Mg ₂ SiO ₄ (s)	1452	1379	1313	1253
MgSiO ₃ (s)	1375	1314	1258	1207
FeO(s)	1231	1165	1108	1056

Fig. 30. Fraction of Mg Condensed in Different Species as a Function of Temperature at $p = 10^{-4}$ atm H_2

because the formation of the stable phase is blocked. If the possibility of forming solid solutions of Fe_2SiO_4 in Mg_2SiO_4 is taken into account, then a fraction of the iron will end up as Fe_2SiO_4 . In Fig. 31 is plotted the calculated mole fractions of Fe_2SiO_4 in these (olivine) solid solutions. As can be seen, if the kinetics of the solid-solid reaction of the silicates to form Fe_2SiO_4 is fast enough, a significant fraction of the iron can condense to form such olivines by reactions with the forsterite (Mg_2SiO_4) already formed.

Fig. 31.

Activity of Fayalite in Olivine as a Function of Temperature at 10^{-2} , 10^{-4} and 10^{-6} Atmosphere with Constraints on Iron Condensation Only (labeled no Fe) and Constraints on Fe, FeO, MgSiO_3 and SiO_2 Condensation

Thus far only one constraint has been imposed. Other constraints are necessary. For example, as has been shown experimentally,¹⁰⁰ silica and enstatite are very hard to nucleate and, at temperatures that are low enough, they will not form. If constraints are imposed on these two minerals, the chemistry of the other condensates changes. For example, if enstatite and silica are not formed, then, as shown in Fig. 30, Mg_2SiO_4 will continue to condense. Because Mg_2SiO_4 has a lower Si/Mg ratio than the nebula, this leaves more SiO in the vapor than in the unconstrained case and the activity of $\text{Fe}(\text{SiO}_4)_{1/2}$ (fayalite) will be higher since it forms from the reaction

This increase in activity is illustrated in Fig. 31. Consequently, the constraint on MgSiO_3 and SiO_2 tends to increase the amount of fayalite in the olivine.

C. Discussion

The computer program permits us to make quantitative calculations for constrained equilibria. However, we must use external information in order to know which constraints are significant at a given temperature and pressure. For example, we can conclude from nucleation theory that, at low pressures (10^{-6} atm), the nucleation of iron can be completely blocked and metallic iron cannot form. At high pressures (10^{-2} atm), the blockage is small and the condensate will be close to equilibrium. Thus, the lower the pressure, the greater the tendency to have the iron condense in an oxidized form.

In addition to this influence of the constraints on iron condensation, constraints on the formation of SiO_2 and MgSiO_3 increase the activity of fayalite in the olivine condensate. For example, experiments indicate that it is difficult to nucleate silica or enstatite below 1350 K.¹⁰⁰ Consequently, if we examine the data in Table 18(a), we would deduce that curves such as that labeled "no MgSiO_3 " of Fig. 30 should apply at a pressure, p , of 10^{-2} atm, whereas curves such as that labeled "no constraint" apply at $p \leq 10^{-4}$ atm. An intermediate case will apply at $p = 10^{-3}$ atm. As shown in Fig. 31, the concentration of Fe_2SiO_4 is expected to be greater with constraints on SiO_2 and MgSiO_3 , so that, at 10^{-4} and 10^{-6} atm, the curves labeled "no Fe, FeO, MgSiO_3 , SiO_2 " apply.

A third hierarchical constraint that must be considered can arise when the kinetics of the reaction of the nebula with Mg_2SiO_4 to form the solid solution $(\text{Mg,Fe})_2\text{SiO}_4$ become too slow. When this occurs, this solid solution can form only by a direct condensation by reactions such as

At temperatures where x can be fairly large most of the Mg has already been condensed from the nebula. Consequently, little high-iron olivine can form by direct condensation, and the iron will then condense at lower temperatures as FeO or, under some conditions where iron has been partially depleted, it will condense as Fe_3O_4 .

From a comparison of these calculations and the properties of meteorites, we deduce the following:

- a. Enstatite chondrites which contain metallic iron and little iron in an oxide form were formed at high pressures ($\sim 10^{-2}$ atm),¹⁰¹ where the kinetic constraints discussed were not very large.
- b. Ordinary chondrites that contain both metallic iron and fayalitic olivines formed at pressures of $\sim 10^{-3}$ atm, where there was at least a partial nucleation constraint on metallic iron, as well as on

the formation of silica and enstatite. The constraint on the reaction of the nebula with Mg_2SiO_4 to form fayalitic olivine was relatively small, down to fairly low temperatures (~ 1250 K). Metallic iron nucleated before FeO or Fe_3O_4 formed.

- c. Carbonaceous chondrites formed at low pressures ($\leq 10^{-4}$ atm), where nucleation constraints on iron were large enough so that little if any metallic iron formed. The temperatures at which fayalitic olivine tended to form were low so that only a small amount could form largely by direct condensation. The amount was limited by the residual SiO and Mg content of the nebula. The remaining iron vapor forms FeO or Fe_3O_4 when it can no longer form fayalite.

These calculations will permit us to make quantitative estimates of the relative proportions of the different condensation products for direct comparison with meteoritic data. In addition, the computer program permits us to include a larger number of elements to obtain a much more complete calculation of the chemistry of nebular condensates.

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