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January—June 1972

by

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ABSTRACT

Studies in several diverse areas of physical and inorganic chemistry are continuing. Accurate pressure-composition isotherms for the Li-H system at temperatures of interest to fusion-reactor technologists are reported. Working estimates of Sieverts' constants for deuterium and tritium dissolved in liquid lithium are calculated. Limits of superheat were measured for a variety of hydrocarbons including the normal alkanes, branched alkanes, cyclic hydrocarbons, normal unsaturated hydrocarbons, and some mixtures of these compounds. A promising approach to the quantitative estimation of limits of superheat of liquids from their equations of state is described. Vapor-phase chemical equilibria of metal halide systems typical of those used in the purification and recovery of certain metals have been studied by laser-Raman spectroscopy. A nonempirical pair potential for argon is developed and used to accurately calculate thermodynamic and transport properties in the gas phase.

SUMMARY

Physicochemical and Thermodynamic Studies of Lithium-Containing Systems

Pressure-composition isotherms at 705, 799, and 899°C are reported for the Li-LiH system. Sieverts' law constants at these temperatures were determined from a thermodynamic analysis of the data obtained for each isotherm. Extrapolation of these results using existing thermodynamic data for the Li-LiD system and an empirical relationship which equates physicochemical properties of isotopically related species has permitted us to estimate Sieverts' constants for dilute solutions of deuterium and tritium in lithium. These numbers are important in estimating the concentrations and partial pressures of the isotopes of hydrogen in lithium-blanketed D-T fusion reactors.

Nucleation Studies

An understanding of bubble-nucleation phenomena is important to reactor technology in such areas as the superheating and boiling of liquid sodium coolant and the release of dissolved fission products from coolant or fuels. Our study of bubble nucleation in both pure liquids and liquid mixtures is continuing on both the experimental and the theoretical levels. Equations were devised for the rate of homogeneous nucleation in the processes of condensation and boiling for cases in which the gas phase is not ideal.

Laser-Raman Studies of Molten Salts and Salt Vapors

Raman spectra of gaseous BiCl_3 from 450 to 800°C have confirmed the existence of a bismuth subhalide (probably BiCl) at elevated temperatures. Attempts to control the concentration of this subhalide by adjusting the oxidizing environment have been highly successful. Results of a Raman study of solid and molten NaNH_2 showed that (1) the NH_2^{1-} ion has a bent structure with C_{2v} symmetry in both phases and (2) there is no intermolecular hydrogen bonding between NH_2^{1-} ions in either phase. Bands observed in the 300-700 cm^{-1} region for both phases were assigned to the hindered internal rotational modes of the NH_2^{1-} ion. Raman spectra of pure molten SnCl_2 and a series of SnCl_2 -KCl melts indicate the presence of a complex equilibrium involving polymeric aggregates of SnCl_2 molecules, similar in structure to solid SnCl_2 , and a single monomeric species of the type $\text{SnCl}_n^{(2-n)}$ which is most probably pyramidal SnCl_3^{1-} .

Phase Equilibria in the Lithium-Sulfur System

Work on the lithium-sulfur phase diagram has been completed. A steep-sided miscibility gap extending from about 0.2 to 37.0 at.% lithium at the monotectic temperature of 364.8°C and having a critical temperature above 600°C is the dominant feature of the phase diagram. The only intermediate phase found is Li_2S , which melts at 1372°C.

Theoretical Studies

A nonempirical pair potential for argon has been developed. It is based on the sum of a computer-generated Hartree-Fock repulsion between two ground-state argon atoms and a dispersive attraction which has been

corrected for overlap at intermediate interatomic separations. The accuracy of this potential has been tested by comparisons between calculated and experimental values of the second virial coefficients of the gas, the shear viscosities of the gas, and the vibrational energy levels of the diatomic molecule. The agreement with the best available experimental data is excellent in all cases.

A refined treatment of the specific repulsive forces acting between noble gas solute atoms and liquid metal solvents is being developed by the use of pseudopotential theory. This treatment is being incorporated into a model for noble-gas-liquid-metal solutions, for which detailed calculations are in progress.

Thermodynamic Properties of the Orthopyroxenes and Clinopyroxenes Based on the Ideal Two-Site Model

An analysis of the thermodynamic properties of orthorhombic and monoclinic pyroxenes ($MSiO_3$) has been made in terms of the ideal two-site model of Mueller. All available data on ion-exchange equilibria in the pyroxene-olivine assemblage can be fit to equations derived from the model using only two well-defined free-energy parameters, one of which can be deduced from Mössbauer data. The attempts to utilize compositional data on orthopyroxene-olivine or orthopyroxene-clinopyroxene mineral pairs as "thermometers" on volcanic and metamorphic rocks or in meteorites is shown to be questionable.

I. PHYSICOCHEMICAL AND THERMODYNAMIC STUDIES OF LITHIUM-CONTAINING SYSTEMS

(E. Veleckis, E. Van Deventer, V. A. Maroni)

A. Activity Measurements in the Lithium-Lithium Hydride System (E. Veleckis, E. Van Deventer)

Accurate knowledge of the thermodynamics and phase relations for the lithium-hydrogen, -deuterium, and -tritium systems is essential to the development of lithium-blanketed fusion reactors. Yet, as we have discussed previously,¹ published data for these systems are very sparse. Recently,² we thermodynamically analyzed existing data for the Li-LiH system in an attempt to relate hydrogen pressure, temperature, and composition in the form of a single, semi-empirical equation. Although this equation correctly represented the gross features of the phase diagram (e.g., the miscibility gap), it is not adequate for quantitative representation of isotherms mainly because of the large scatter and internal inconsistencies in the original data. Because of these inadequacies in the existing data, we are conducting an experimental program to produce more consistent sets of pressure-composition isotherms for the systems Li-LiH, Li-LiD, and Li-LiT which would be amenable to meaningful thermodynamic interpretation. Currently the data are being obtained for the system Li-LiH.

Hydridation experiments are being carried out in a modified Sieverts' apparatus. The procedure of a typical experiment is as follows. Approximately 2 g of pure lithium is sealed *in vacuo* in a small Armco iron capsule (2 in. long, 0.5-in. dia, 0.015-in. wall) and placed in a double-wall quartz tube. Double-wall construction is necessary because of an appreciable permeability of hydrogen through quartz. Diffusion losses are minimized by maintaining the hydrogen pressure in the annular space of the tube at the same value as that of the inner chamber containing the sample. The tube is then connected to the apparatus, evacuated, and heated to a preselected temperature. Hydrogen is added to the sample gradually in twenty to thirty portions. The sizes of these portions are varied in such a way as to aid in the delineation of the isotherm. Thus, at the very low and the very high hydrogen concentrations, where the isotherms are steep, small additions (~ 2 millimoles H_2) are used whereas, in the extensive plateau portions, the additions are made quite large (~ 20 millimoles H_2).

For each addition, the amount of hydrogen is measured in a thermostated, calibrated bulb ($\sim 500\text{ cm}^3$). The contents of the bulb are then quantitatively transferred into an equilibration section by flooding the bulb with mercury. The latter section consists of a small, partially thermostated manifold, two high-precision, low-volume pressure gauges, and the double-wall tube containing the sample. The effective volume of this section is determined, just prior to each experiment, by a calibration with pure helium.

According to Heumann and Salmon,³ the rate of reaction of hydrogen with lithium in open crucibles is very rapid compared with the rate of diffusion of hydrogen through iron. For the sealed iron capsules (same wall thickness as in our work), they found that the rate of hydrogen uptake was very nearly equal to that expected for hydrogen diffusion through iron. They allowed 8-12 hr for each equilibration. The amount of lithium used in the present work is about 50 times larger and the time required to reach equilibrium is 12 to 48 hr, depending on the amount of hydrogen added, temperature, and equilibrium hydrogen pressure.

When the equilibrium is established, hydrogen pressure and sample temperature are recorded. Then, successive portions of hydrogen are added by the same procedure until the equilibrium hydrogen pressure reaches one atmosphere. The concentration of hydrogen in lithium after each hydrogen addition can be calculated from the weight of lithium, total hydrogen added, the amounts of hydrogen remaining in the effective volume and in the vapor space inside the capsule, and the amount of hydrogen dissolved in iron.

To date, three isothermal hydriding experiments at 705, 799, and 899°C are complete. The data are shown in Fig. I-1. Each isotherm consists of two rising portions, the first corresponding to a solution of LiH in liquid lithium and the second to a solution of lithium in liquid LiH, and a connecting plateau which defines the region of coexistence (miscibility gap) of the two solutions. The plateau pressures and the boundaries of the miscibility gap are shown in Table I-1.

Fig. I-1. Pressure-Composition Isotherms for the Li-LiH System at 705, 799, and 899°C

TABLE I-1. Plateau Pressures, Miscibility Gap Limits, and Sieverts' Constants for Three Isotherms in the System Li-LiH

Temp., °C	Plateau Pressure, Torr	Miscibility Gap, mol % LiH		Sieverts' Constant, Torr ^{1/2} (mol fr.) ⁻¹
		Low Limit	High Limit	
705	37.9	25.0	98.0	32.6
799	172.1	35.0	96.3	51.3
899	661.0	48.5	89.7	78.0

Isotherms similar to those shown in Fig. I-1 can be represented by the following semi-empirical equation²

$$\ln \sqrt{P} - \ln \frac{N_{\text{LiH}}}{1-N_{\text{LiH}}} = \sum_{i=0}^k B_i N_{\text{LiH}}^i \quad (1)$$

where P is the hydrogen pressure, N_{LiH} is the mole fraction of LiH, and B_i 's are constants to be determined from the data. At the extreme limits of the concentration range, $N_{\text{LiH}} \rightarrow 0$ and $N_{\text{LiH}} \rightarrow 1$, Eq. 1 becomes

$$N_{\text{LiH}} \rightarrow 0 \quad \ln \left(\frac{\sqrt{P}}{N_{\text{LiH}}} \right) = \lim_{N_{\text{H}} \rightarrow 0} \ln \left(\frac{\sqrt{P}}{N_{\text{H}}} \right) = \ln K \quad (2)$$

and

$$N_{\text{LiH}} \rightarrow 1 \quad \ln \sqrt{P} (1-N_{\text{LiH}}) = \ln K' \quad (3)$$

Equation 2 is a statement of Sieverts' law for the very dilute solutions of hydrogen in lithium. Since the dilute region is of special importance to the controlled thermonuclear reactor (CTR) programs, the calculated Sieverts' constants are listed in column 5 of Table I-1.

Equation 3 states that near the composition $N_{\text{LiH}} = 1$, $1/\sqrt{P}$ becomes a linear function of N_{LiH} . The hydride-rich portions of the 705 and 799°C isotherms (data are insufficient for the 899°C isotherm) are plotted as $1/\sqrt{P}$ vs. N_{LiH} in Fig. I-2. In similar plots, using the original data, the extrapolated curves intersected the abscissa at approximately 100.2 mol % LiH for 705°C and 100.6 mol % LiH for 799°C. This small discrepancy is attributed to an error accumulated during numerous hydrogen additions. The N 's in Eq. 1 were multiplied by a normalization factor, s , of such a magnitude as to produce the best least-squares fit of the experimental data with the curve crossing the abscissa at exactly 100 mol % LiH ($s = 0.9976$ for 705° and 0.9943 for 799°C). The data shown in Figs. I-1 and I-2 are normalized. This procedure also permits a precise determination of the end of the plateau region, i.e., the saturated solubility of lithium in liquid LiH.

The data shown in Figs. I-1 and I-2 are thermodynamically consistent and show considerably less scatter than those of all previous investigations. Additional isotherms are presently being obtained. A complete thermodynamic

Fig. I-2. Hydride-Rich Portions of the 705, 799, and 899°C Isotherms for the Li-LiH System

analysis of the Li-LiH system, based on our data, will be presented at the conclusion of the experimental work. Measurements will also be made with deuterium and tritium.

B. Estimates of Sieverts' Constants for Solutions of Deuterium and Tritium in Liquid Lithium (V. A. Maroni)

The results presented above have provided working estimates for the Sieverts' law constants for hydrogen in lithium in the 700 to 900°C range. Sieverts' constants for deuterium and tritium solutions in lithium are expected to differ from those for hydrogen in lithium due to isotopic effects. In light of this we have attempted to make some estimates for the Sieverts' constants for deuterium and tritium dissolved in liquid lithium by taking into account some earlier work on the Li-LiD and Li-LiT systems and applying an empirical relationship which equates thermodynamic quantities of isotopically related species.

Heumann and Salmon³ have measured pressure-composition isotherms in the Li-LiD and Li-LiT systems. Their results at 700°C, shown in Fig. I-3, indicate a significant isotope effect on the partial pressure at a given mole fraction. For instance the deuterium pressure over lithium is consistently a factor of two higher than the hydrogen pressure at concentrations in the single-phase region (<20 mol % LiH in Li). The results for the Li-LiT system at 700°C are inconsistent with those for the Li-LiH and Li-LiD systems, in that the pressure-composition curve for tritium in lithium at 700°C should lie parallel to and slightly above that for deuterium in lithium on the log-log plot in Fig. I-3. As a result of this apparent discrepancy for the Li-LiT results, it is not possible to determine the tritium-to-hydrogen partial-pressure ratio at 700°C from the data of Heuman and Salmon.³

Swain *et al.*⁴ have derived the following equation

$$\frac{Q_H}{Q_T} = \alpha \left(\frac{Q_H}{Q_D} \right)^{1.442} \quad (4)$$

Fig. I-3. Pressure-Composition Data for Solutions of Hydrogen, Deuterium, and Tritium in Liquid Lithium at 700°C (Heumann and Salmon)

which yields the isotopic effect on the quantity Q for tritium to the known values of Q for deuterium and hydrogen where Q is restricted to be such quantities as equilibrium constants, rate constants, partial pressures, etc. which are proportional to the partition function of the system. The value of α has been found to vary from 0.907 to 1.157 in tests of a variety of appropriate experimental data over a wide temperature range. Using Eq. 4 with $\alpha = 1.0$ and assuming $P_D/P_H \approx 2.0$ as indicated in Fig. I-3 ($Q = P =$ partial pressure), we estimate that $P_T/P_H \approx 2.7$ for H in Li and T in Li solutions having the same mole fraction of H and T and the same temperature. Using these values for the P_D/P_H and P_T/P_H ratios and Veleckis' and Van Deventer's results for the Li-LiH system given above, we have calculated Sieverts' constants for the dilute (in hydrogen isotope) regions of the Li-LiD and Li-LiT systems. In this approximation, we have assumed that the isotopic partial-pressure ratios are independent of temperature. The data given in Table I-2 (for 700, 800, 900, and 1000°C) represent the best estimates of values for these Sieverts' constants that can be extracted from existing data at this time. Experiments are in progress in our laboratory to confirm or refine their accuracy.

TABLE I-2. Estimated Sieverts' Constants, K_S , for Dilute Solutions of Hydrogen, Deuterium, and Tritium in Lithium

Temp., °C	K_S , Torr ^{1/2} /(Atom Fraction H, D, or T)		
	H in Li	D in Li	T in Li
1000	111	157	182
900	78	110	128
800	52	74	85
700	32	45	52

II. NUCLEATION STUDIES

An understanding of bubble-nucleation phenomena is important to reactor technology in such areas as the superheating and boiling of liquid sodium coolant and the release of dissolved fission products from coolant or fuels. Our experimental study of bubble nucleation in both pure liquids and liquid mixtures is continuing. An approach to predicting the limit of superheat through the mechanical stability condition is also explored. Equations were also devised for the rate of homogeneous nucleation in the processes of condensation and boiling for cases in which the gas is not ideal.

A. Measurement of the Limit of Superheat of Liquids (J. G. Eberhart, W. Krensner, E. Hathaway)

In our last report,⁵ an apparatus was described for superheating liquid hydrocarbon droplets in a glycerin medium to determine the temperature of explosive boiling which corresponds to the homogeneous limit of superheat of the liquid at 1 atm pressure. The results of our measurements on a number of pure hydrocarbons and on mixtures of n-octane in n-pentane were also presented.

Since then the study of pure liquids has been extended to include a wider variety of hydrocarbons. In Table II-1, our measured limit of superheat, T_h , is listed for hydrocarbons of various molecular structures including normal alkanes, branched alkanes, cyclic hydrocarbons, and normal unsaturated hydrocarbons. For comparison, Table II-1 also shows the normal

TABLE II-1. The Homogeneous Limit of Superheat of Liquid Hydrocarbons

	T_b , °C	T_h , °C	T_c , °C	$T_h - T_b$, °C	$\frac{T_h}{T_c}$	$\frac{T_h}{T_c}$
Normal Alkanes						
n-butane	0	105	152	105	0.641	0.890
n-pentane	36	147	197	111	0.659	0.896
n-hexane	69	182	234	113	0.674	0.899
n-heptane	98	213	267	115	0.688	0.901
n-octane	126	240	296	114	0.701	0.902
n-nonane	151	265	321	114	0.713	0.906
Branched Alkanes						
2,2-dimethylpropane	9	113	161	104	0.652	0.891
2,3-dimethylbutane	58	173	227	115	0.663	0.893
2,2,4-trimethylpentane	99	215	271	116	0.658	0.898
Cyclic Hydrocarbons						
cyclopentane	49	184	239	135	0.628	0.894
cyclopentene	44	178	233	134	0.627	0.892
cyclohexane	81	220	280	139	0.640	0.891
methylcyclohexane	101	237	299	136	0.654	0.892
Normal Alkenes and Alkynes						
1-pentene	30	144	192	114	0.653	0.898
1-octene	121	237	293	116	0.696	0.901
1-hexyne	71	192	-	121	-	-

boiling temperature, T_b , the critical temperature, T_c , and the extent of superheat, $T_s \sim T_b$. For the hydrocarbons studied to date, the extent of superheat at 1 atm pressure varies from 104 to 139°C. When all temperatures are expressed on the absolute scale, it is found that the reduced limit of superheat, T_s/T_c , falls within the range 0.89 to 0.91. Variation in T_s/T_c can be correlated with the reduced boiling temperature, T_b/T_c , as shown in Fig. II-1. This relationship between T_s/T_c and T_b/T_c can be used to estimate the limit of superheat of other hydrocarbons at 1 atm, but the relationship has not been tested for compounds other than hydrocarbons.

Because of the difficulty of finding suitable liquid media for the superheating of liquids other than hydrocarbons, experiments have also been carried out in Pyrex and fused-silica capillary tubes. These U-shaped tubes are cleaned, completely filled with the liquid to be studied, and heated only at the bottom of the U until the explosive vaporization occurs. This technique has been applied to methanol and water. The explosive vaporization temperatures determined to date for methanol, which has a boiling point of 65°C, range from 80 to 184°C. Water, with a boiling point of 100°C, explosively vaporizes over the range of 130 to 258°C. The best estimate of the homogeneous limit of superheat is the maximum temperature observed for the explosive vaporization of the liquid, i.e., 184°C for methanol and 258°C for water. The lower temperatures also observed probably are the result of incomplete wetting of the capillary and the heterogeneous nucleation of boiling.

Further experimentation on liquid mixtures has also been in progress since our last report. Using the apparatus for droplet heating in a glycerin medium, the limit of superheat has been determined for hydrocarbon mixtures of cyclohexane in n-pentane, n-dodecane in n-pentane, and n-cetane in n-pentane. The measured limits of superheat for these systems, in addition to the n-octane in n-pentane mixtures described in the last report,⁵ are presented in Figs. II-2 through II-5. The figures are arranged in order of increasing difference in volatility of the two components. Both the cyclohexane in n-pentane and the n-octane in n-pentane show a positive deviation from linearity in the mole fraction, as well as a skewing toward the more volatile component (Figs. II-2 and II-3). For n-dodecane in n-pentane, there is also a positive deviation from linearity with an apparent symmetry about a mole fraction of 1/2 (Fig. II-4). The n-cetane in n-pentane system has a negative deviation from linearity if one considers the mean value of the many measurements made at each composition. For this system, a wide range was observed in the limit of superheat and the range increased with increasing n-cetane mole fraction (Fig. II-5). This phenomenon was first observed by Blander *et al.*⁶ in the 0 to 25 mol % n-cetane range. The observations of our study in the 25 to 60 mol % range are consistent with their results. This effect can be explained through nucleation theory and the time required for diffusion of the more volatile component into the bubble nuclei.⁶ If the maximum observed limits of superheat are employed, then the mole-fraction dependence appears to be linear.

B. Calculation of the Limit of Superheat of Liquids from the Mechanical Stability Condition and the Equation of State (J. G. Eberhart and H. C. Schnyders)

A variety of experimental studies have demonstrated that a liquid may be "stretched" isothermally into states having pressures below the

Fig. II-1. Reduced Limit of Superheat versus Reduced Boiling Temperature for a Variety of Liquid Hydrocarbons

Fig. II-2. Limit of Superheat versus Mole Fraction for Mixtures of Cyclohexane in n-Pentane

Fig. II-3. Limit of Superheat versus Mole Fraction for Mixtures of n-Octane in n-Pentane

Fig. II-4. Limit of Superheat versus Mole Fraction for Mixtures of n-Dodecane in n-Pentane

Fig. II-5. Limit of Superheat versus Mole Fraction for Mixtures of n-Cetane in n-Pentane

saturation pressure (even to negative pressures) or heated isobarically to temperatures above the boiling temperature. In either type of experiment, the liquid ultimately achieves a lower pressure limit or an upper temperature limit at which it vaporizes explosively. Investigators of this phenomenon have suggested two approaches to predicting the limiting pressure or temperature of superheat. One approach is that of nucleation theory,⁷⁻¹⁰ which has been used successfully in the quantitative interpretation of limit-of-superheat measurements.^{6,11-16} The second approach is that of the mechanical stability condition of classical thermodynamics, which has been suggested by a number of investigators^{14,17-19} but has not been explored, to our knowledge, with any equation of state other than that of van der Waals. We have revived the stability approach using improved empirical and theoretical equations of state which yield estimates of the limit of superheat which are in quantitative agreement with experimental values.

The mechanical stability condition of classical thermodynamics is based on the Clausius inequality^{20,21} and shows that metastable liquids or vapors can exist provided $(\partial P/\partial V)_T < 0$, where P , V , and T are pressure, molar volume, and absolute temperature, respectively. States for which $(\partial P/\partial V)_T > 0$ are unstable, and the spinodal curve, along which $(\partial P/\partial V)_T = 0$ (by definition), delineates the boundary of the metastable regions of a substance. The spinodal curve along which $(\partial^2 P/\partial V^2)_T > 0$ is the limit of superheat for the liquid while the curve along which $(\partial^2 P/\partial V^2)_T < 0$ is the limit of supercooling for the vapor.

The most complete superheating data presently available for testing these ideas are those of Skripov *et al.*,^{14,15} who have measured the pressure dependence of the limit of superheat for the liquids n-pentane, n-hexane, n-heptane, diethylether, and benzene. One of the interesting features which Skripov and Ermakov¹⁴ pointed out about their measurements of the pressure dependence of the limit of superheat is that if the data for all five liquids are plotted in reduced form, then the experimental results are nearly superimposed on each other. This is shown in Fig. II-6 where we have plotted the reduced limit of superheat, $\theta_L = T_L/T_C$, against the reduced ambient pressure, $\pi = P/P_C$. Although small, systematic differences can be seen among these liquids of differing molecular geometry, the near coincidence of the data suggests a simple way to estimate the limit of superheat for other liquids as well as the possibility that a two-parameter equation of state could provide a spinodal curve which adequately represents the data.

The two most familiar two-parameter equations of state are those of van der Waals (vdW) and Berthelot (Ber) which are

$$\left(P + \frac{a}{T^n V^2}\right) (V - b) = RT \quad (5)$$

where R , a , and b are constants, or in reduced form

$$\left(\pi + \frac{3}{\theta^n \phi^2}\right) \left(\phi - \frac{1}{3}\right) = \frac{8}{3} \theta \quad (6)$$

where $\phi = V/V_C$. In Eqs. 5 and 6, $n = 0$ gives the vdW equation while $n = 1$ gives the Ber equation. The two equations are combined in this form, which we will call the modified Berthelot equation of state (MBer), because an intermediate value of n will be considered later. Figure II-6 shows the reduced spinodal curves, calculated from $(\partial\pi/\partial\phi)_\theta = 0$, for $n = 0$ (curve 1) and $n = 1$ (curve 5). By comparing curves 1 and 5 with the experimental data in Fig. II-6, it is clear that the vdW equation gives results which

Fig. II-6. Reduced Limit of Superheat versus Reduced Pressure for n-Pentane, n-Hexane, n-Heptane, Diethylether, and Benzene^{14,15} Compared with Spinodal Curves Derived from the Following Equations of State: (1) van der Waals ($n = 0$), (2) Augmented van der Waals ($c = 3$), (3) Modified Berthelot with $n = 1/2$, (4) Modified van der Waals for Regular Tetrahedra ($c = 6.704$), (5) Berthelot ($n = 1$)

are too low in temperature, while the Ber equation is high. As an empirical representation of the data, it was found that a value of $n = 1/2$ gives a good fit to the superheating data. Curve 3 in Fig. II-6 shows the spinodal based on the modified Berthelot (MBer) equation with $n = 1/2$. It is useful in predicting the limit of superheat of other liquids within the approximation that all liquids have the same reduced spinodal curve, independent of molecular geometry.

The reduced limit of superheat at zero pressure, θ_L^0 , represents the reduced temperature below which it is possible to achieve negative pressures for a liquid. Equation 6 yields a particularly simple result for zero pressure, namely

$$\theta_L^0 = (27/32)^{1/(n+1)} \quad (7)$$

The zero-pressure value of θ_L is also a convenient point of comparison for the spinodal curves of various equations of state. For the values of $n = 0$ (vdW), $n = 1/2$ (MBer), and $n = 1$ (Ber) considered here, θ_L^0 is 0.844, 0.893, and 0.919, respectively.

From a theoretical point of view, it is interesting that the experimental data in reduced form fall between the spinodal curves derived from the classical van der Waals equation of state and the Berthelot equation of state (see Fig. II-6). Clearly, the only distinction between these two equations of state is the assumed value of the exponent n in Eq. 5. Let us rearrange this equation into a convenient form for discussion

$$Z = \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{RT^{n+1}V} \quad (8)$$

where Z is the compressibility factor. The first term on the right-hand side (RHS) of Eq. 8 represents the effects of volume exclusion due to the infinite repulsive force which acts between hard spheres at contact, and the second term on the RHS represents the effect of the constant average attractive potential in which the hard spheres move. Van der Waals assumed this average attractive potential was inversely proportional to the molar volume, V , with a constant of proportionality, a , which is independent of temperature. Berthelot chose to correct the defects in the van der Waals model by merely assigning an arbitrary temperature dependence to a , namely, $a_B = a/T$. This choice is not justified theoretically and is more or less a camouflage for a primary defect in the van der Waals model at high densities, namely, the inaccurate description of volume exclusion effects given by the first term on the RHS of Eq. 8.

The term $V/(V-b)$ in Eq. 8 is an oversimplification of excluded volume effects at high densities where the overlap of exclusion spheres of volume b (equal to four times the rigid-sphere volume per sphere for a pair of rigid spheres) becomes significant. In the spirit of the augmented van der Waals (AvdW) theory of Longuet-Higgins and Widom²² and Alder and Hecht,²³ we replace this term in Eq. 8 by the far more accurate compressibility factor, Z_0 , for the rigid-sphere fluid given by scaled-particle theory,²⁴

$$Z_0 = \left(\frac{PV}{RT} \right)_0 = \frac{1+y+y^2}{(1-y)^3} \quad (9)$$

where $y = N_D v_h / V$, N_D is Avogadro's number, and v_h is the rigid-sphere volume. For our present purposes, we shall continue to assume with van der Waals that a is a constant or $n = 0$. The reduced spinodal curve corresponding to the AvdW equation of state is represented by curve 2 in Fig. II-6. Agreement with the experimental data in reduced form is decidedly improved over the results of classical van der Waals theory (curve 1).

Recently, scaled-particle theory has been extended to fluids of particles with arbitrary rigid convex shape.²⁵ Since it seems likely that all of the molecules for which experimental data are given in Fig. II-6 are better represented by something other than a sphere, we decided to test the effect of molecular shape on the spinodal curve. We now replace Eq. 9 by the more general equation of state for arbitrary rigid convex shapes,²⁵

$$Z_0 = \frac{PV}{RT} = \frac{1}{1-y} + \frac{c^2 y^2}{3(1-y)^3} + \frac{c y}{(1-y)^2} \quad (10)$$

where the geometrical shape parameter, c , is given by

$$c = \bar{RS}/v_h \quad (11)$$

and $\bar{R}$ is a mean radius of curvature for the rigid convex shape,^{26,27} S is its surface area, and v_h is its volume. The resulting family of equations of state

$$Z = \frac{PV}{RT} = \frac{1}{1-y} + \frac{c^2 y^2}{3(1-y)^3} + \frac{c y}{(1-y)^2} - \frac{a y}{N_D v_h RT} \quad (12)$$

we choose to call the modified van der Waals (MvdW) equations of state. There is a corresponding family of reduced spinodal curves, two of which are displayed in Fig. II-6 as curves 2 and 4. The parameter c has a minimum value of 3 for the shape of maximum symmetry, the rigid sphere. The spinodal (curve 2) corresponding to the AvdW equation of state is identical to that derived from Eq. 12 with $c = 3$. Curve 4 corresponds to the MvdW equation of state with $c = 6.704$, i.e., the geometrical shape parameter for a rigid, regular tetrahedron.

Qualitatively, at least, the remaining discrepancy between the experimental data and the AvdW spinodal (curve 2) of Fig. II-6 is explained by the "departure" of the basically cylindrical molecular shapes of these compounds from spherical symmetry as is manifested by increasing values of c . In fact, if the data are examined closely, the fairly systematic ordering of increasing reduced limits of superheat with increasing length of the molecule can be seen at any fixed reduced pressure. Such a trend can be explained by MvdW theory for rigid cylinders of radius R and length L . As the ratio of L to R , τ , increases (corresponding to increasing length of saturated hydrocarbons), c increases and the spinodal shifts to high reduced temperatures. This is the apparent trend in the experimental data as one goes from *n*-pentane to *n*-heptane. This trend suggests that estimates of c be made for each molecule from molecular-structure data and compared with the corresponding MvdW spinodal with each fluid individually. A further illustration of the shift of the MvdW spinodal with c is given in Fig. II-7, where the reduced limit of superheat at zero pressure, θ_L^0 , is plotted as a function of $3/c$, which varies from one to zero as c varies from its minimum value of 3 to infinity. As c approaches infinity, θ_L^0 approaches a limit of 0.928.

Fig. II-7. Reduced Limit of Superheat at Zero Pressure as a Function of the Molecular Shape Parameter c .

For the purpose of exploring the rigid-cylinder approximation, we will consider only the normal alkanes. It is assumed that the rigid cylinder, whose length-to-radius ratio, τ , increases systematically as the length of a normal hydrocarbon increases, is a fair approximation to the structure of these molecules. The angle between adjacent carbon-carbon bonds in these molecules is close to 109.5° . Assuming the usual chain structure for the molecule, which we approximate by a zig-zag configuration of carbon atoms in a plane, one finds for a cylinder whose surfaces contain the nuclear centers of all the carbon atoms

$$\tau = 2(n - 1) \tan \phi \quad (13)$$

$$c = (1 + \tau)(\pi + \tau)/2\tau \quad (14)$$

where n is the number of carbon atoms in the normal alkane molecule and ϕ is one half the angle between adjacent carbon-carbon bonds in the molecule. This geometrical assumption is called the nuclear center cylindrical envelope for the molecule. Another possible assumption is based on choosing the boundaries of the cylinder to be tangent to the outer edges of the carbon

atoms which are assigned a radius of one half of the carbon-carbon bond distance in the molecule. This cylinder is referred to as the molecular envelope and c is found by substituting

$$\tau = [2(n-1) \sin \phi + 2] / (\cos \phi + 1) \quad (15)$$

into Eq. 14. For both of these choices the hydrogen atoms are ignored.

In Fig. II-8, we show our limit-of-superheat calculations with these two envelopes for a number of normal alkanes as a function of ambient pressure and compare them with the data of Skripov *et al.*^{14,15} and the unpublished results of Eberhart and Kremsner (see the preceding section). In Fig. II-9, we further compare the calculated reduced limit of superheat at 1 atm pressure for the two envelopes with the observed values of Eberhart and Kremsner.

We regard the c values corresponding to the cylindrical nuclear envelopes of the molecules as the preferred choice for three reasons. First, the curvature of the line corresponding to the nuclear-envelope model is in better agreement with that found for the data in Fig. II-9. Second, nucleation theory suggests that, if our experiments were repeated with the smallest observable droplets (about five orders of magnitude smaller in volume), a limit of superheat would be obtained which is about 1 or 2 degrees higher in temperature than those we have reported. Furthermore the experimental values have all been the average of many observations,

Fig. II-8

Pressure Dependence of the Limit of Superheat for the Normal Alkanes (open points - Skripov *et al.*; filled points - Eberhart and Kremsner). ANL Neg. No. 308-2914

Fig. II-9. Reduced Limit of Superheat versus Number of Carbon Atoms per Molecule for Normal Alkanes

rather than the experimental maximum or a mean value plus one or two standard deviations. Thus we expect our experimental results to be several degrees below the limit of superheat. Third, preliminary calculations of the vapor pressure for the MvdW model indicate better agreement with the nuclear envelope ϕ -values. Finally, we note that the calculated limits of superheat agree with experimental data to within a few degrees for all the substances for which data are available.

We intend to explore some interesting extensions of the ideas presented herein. Experimental or theoretical equations of state may provide reasonable estimates of the limit of superheat for liquids of special interest (water, sodium, etc.). The possibility of using spinodal curves to interpret vapor supersaturation measurements will also be investigated. Finally, in multicomponent systems, it is hoped that relatively straightforward extensions of stability theory will provide a means for interpreting the concentration dependence which has been observed in the measurements reported in the previous section.

C. Homogeneous Nucleation Involving Nonideal Gases (M. Blander, J. L. Katz*)

Equations were derived for the rate of homogeneous nucleation in the processes of condensation and boiling for cases in which the gas phase is not ideal. The calculations were considerably simplified by the use of the formalism discussed by Hill²⁸ and Mayer²⁹ where all deviations from ideal behavior can be rigorously ascribed to the presence of "mathematical" polymers. Utilizing a method of calculation used by Katz *et al.*,³⁰ we derive the equation for J , the rate of nucleation per unit volume in condensation

$$J = \frac{p_1}{dkT} \left[\frac{2\sigma m}{\pi} \right]^{1/2} \left[4^{3/2} \alpha_i n_i \exp \left\{ \frac{-16\pi (\sigma)^3 (m)^2}{3 (kT)^2} \left[\frac{1}{\ln (p_1/p_{1\infty})} \right]^2 \right\} \right] \quad (16)$$

* Professor Katz is a member of the Chemical Engineering Department, Clarkson College, Potsdam, New York.

where p_1 is the partial pressure of monomer in the supersaturated vapor, d the liquid density in the critical-sized droplet, σ the surface tension, m the mass of a monomer molecule, i the number of molecules in a polymer, α_i the condensation coefficient of an i 'mer, n_i the number density of an i 'mer, and $p_{1\infty}$ the partial pressure of monomer in the vapor in equilibrium with the liquid phase. This equation is valid for any type of gas non-ideality. Both the prefactor and the exponential differ from classical nucleation theory derived with the assumption of ideality of the gas phase. The differences in the prefactor are negligibly small. However the factor $\ln(p_1/p_{1\infty})$ leads to significant differences from classical theory, especially for large deviations from ideal gas behavior.

For boiling, the calculated rate of nucleation is

$$J = N_0 \left(\frac{2\sigma}{\pi m B} \right)^{1/2} \frac{\sum i^{3/2} \alpha_i n_{ic}}{\sum i n_{ic}} \exp \left[\frac{-16\pi \sigma^3}{3kT(p_c - p_0)^2} \right] \quad (17)$$

where N_0 is the number density of the liquid, p_c is the gas pressure inside a critical-sized bubble, p_0 is the external pressure on the liquid, n_{ic} is the number density of i 'mers in a critical size bubble, and B is given by

$$B = \left\{ 1 - \frac{1}{3} \left[1 - \frac{p_0}{p_c} \right] \sum i^2 N_{ic} / \left[\sum i N_{ic} \right]^2 \right\} \quad (18)$$

where N_{ic} is the mole fraction of i 'mer in the critical-sized bubble. The exponential factor is identical with that of classical theory, as has been shown by Moore.³¹ The pre-exponential factor differs from classical theory and the form differs from Moore's calculations which were based solely on thermodynamic reasoning. However, only for mixtures and other cases where the exponential factor is not a very strong function of temperature are the differences between classical theory and Eq. 17 significant.

III. LASER-RAMAN STUDIES OF MOLTEN SALTS AND SALT VAPORS (V. A. Maroni, E. J. Hathaway, P. T. Cunningham)

A. Laser-Raman Spectra of Gaseous Bismuth Trichloride from 450 to 800°C

Our program of laser-Raman spectroscopy has been extended to include studies of molten-salt vapors. These studies are aimed at an understanding of gas-phase transport phenomena in systems involving a volatile metal salt and a relatively involatile metal. In the case of metal-metal halide systems, some evidence exists³² which implies that transport of metals in the presence of a gaseous metal halide proceeds through formation of a subhalide in a reaction of the following type

where M and M' are metal atoms and X is a halogen atom.

The equilibrium in this reaction is usually displaced further and further to the right by increasing the temperature. Since reactions of this type can and in fact do form the basis of methods for recovery and purification of metals (e.g., purification of aluminum using $AlCl_3$), it is of interest to identify and characterize the species present in metal halide vapors.

The applicability of laser-Raman spectroscopy to the study of structures of gaseous inorganic species at elevated temperatures (to 1000°C) has been demonstrated.³³⁻³⁷ Several studies have provided information on thermodynamic quantities,³³ chemical equilibria,^{35,37} and force constants^{33,36} for both pure materials and mixtures. In a number of cases, however, strong resonance fluorescence has obscured the vibrational Raman spectra of the species present.^{34,35} The source of this resonance fluorescence can be either the material under investigation³⁵ or a species (e.g., a subhalide) formed through disproportionation of the sample material. An example of the latter case is the resonance fluorescence of $BiCl$ which overlaps the gas-phase Raman scattering of $BiCl_3$.

Ozin *et al.*³⁴ observed the Raman spectrum of $BiCl_3$ vapors near the boiling point ($\approx 450^\circ C$) using 4880 and 5145 Å exciting radiation, but upon raising the temperature to $750^\circ C$, they found that the Raman spectrum was barely visible in the presence of an intense resonance fluorescence spectrum. Based on the spacings observed in the fluorescence spectrum and the known spectroscopic constants for $BiCl$, they attributed the fluorescence to $BiCl$ but did not rule out $BiCl_2$ or $BiCl_3$ as the fluorescing species.

We have examined the Raman spectrum of pure unsaturated gaseous $BiCl_3$ from 450 to $800^\circ C$ and our results are substantially in agreement with those of Ozin *et al.*³⁴ However, we find that the higher frequency Raman bands of $BiCl_3$ are partially obscured by resonance fluorescence even at $450^\circ C$ and about 1 atm pressure and are almost totally obscured by fluorescence at $600^\circ C$.

Laser-Raman studies of a variety of metal-halide vapors in progress in our laboratory have shown that, in some cases, it is possible to suppress the formation of compounds of lower oxidation states of the metal by

addition of a small amount of an appropriate oxidizing material. In the case of BiCl_3 , addition of varying amounts of HgCl_2 significantly reduces the formation of the bismuth subhalides, and an unobscured Raman spectrum of BiCl_3 can be observed up to temperatures above 800°C . The addition of 5 mol % HgCl_2 to the BiCl_3 completely suppresses the resonance fluorescence due to subhalide formation up to 600°C , 10 mol % suppresses it to just under 700°C , and 50 mol % suppresses it to well over 800°C . This is illustrated in Fig. III-1 where curve a shows the Raman spectrum of an equimolar mixture of BiCl_3 and HgCl_2 at 800°C and about 2 atm total pressure obtained using the $4880 \text{ \AA}$ line of an argon ion laser for excitation. The ν_1 mode of HgCl_2 (the only Raman-active mode of HgCl_2), which we find at 355 cm^{-1} in pure HgCl_2 vapors, appears as a weak shoulder on the high-frequency side of the 341 cm^{-1} band of BiCl_3 . Curve c in Fig. III-1 is a portion of the resonance fluorescence spectrum for a pure BiCl_3 sample at 800°C and ≈ 1 atm, which we show here to indicate the degree to which the resonance fluorescence obscures portions of the BiCl_3 Raman spectrum at this

Fig. III-1. Raman Spectra of 50 mol % HgCl_2 in BiCl_3 (curves a and b) and Pure BiCl_3 (curve c) at 800°C . Spectral Slit Width $\approx 6 \text{ cm}^{-1}$, Time Constant = 3 sec, Scan Rate = $8 \text{ cm}^{-1}/\text{min}$, Sensitivity = 0.1 mV Full Scale for Curves a and b and 2.0 mV Full Scale for Curve c, $\perp$ and $\parallel$ Indicate Direction of Polarization of the Laser Beam with Respect to the Direction of Observation. ANL Neg. No. 308-2863

temperature.* (The band heads in curve c of Fig. III-1 are the first two on the Stokes side of the exciting line.) From a comparison of curves a and c in Fig. III-1, it is clear that the resonance fluorescence cannot be due to BiCl_3 , and that the lower oxidation states of bismuth producing this fluorescence are indeed suppressed by the addition of HgCl_2 .

The observed Raman bands in curve a of Fig. III-1 and their states of polarization, as indicated in curve b of Fig. III-1, are consistent with a pyramidal BiCl_3 species having C_{3v} point symmetry. The following assignments can be made: $\nu_1 (A_1) = 341 \text{ cm}^{-1}$, $\nu_2 (A_1) = 125 \text{ cm}^{-1}$, $\nu_3 (E) = 323 \text{ cm}^{-1}$, and $\nu_4 (E) = 105 \text{ cm}^{-1}$. These results are in excellent agreement with the data of Ozin *et al.*³⁴ for gaseous BiCl_3 at 460°C .

The results of our experiments with BiCl_3 , and preliminary results with other metal halide systems (e.g., PbCl_2 , BiBr_3) where we have observed resonance fluorescence due to a subhalide, suggest that the technique of controlling the concentration of subhalides by adjustment of the oxidizing environment of the sample may be applicable to a wide variety of metal halide systems. We are also using this technique to examine some thermodynamic properties (e.g., free energies of formation) that have been estimated for species at higher temperatures.

B. Raman Spectra of Solid and Molten Sodamide: Evidence for Hindered Rotation of the Amide Ion

In keeping with our continued interest in species which are important to AEC programs involving liquid metals and molten salts, we have completed our structural studies of solid and molten NaNH_2 aimed at characterizing the NH_2^{1-} ion. Raman spectra of solid NaNH_2 at 25°C and of the liquid at 220°C have been reported previously.³⁸ The observed frequencies are listed in Table III-1. The polarized bands at 3218 and 1550 cm^{-1} and the depolarized

TABLE III-1. Raman Data for Solid (25°C) and Molten (220°C) Sodamide

Frequencies, cm^{-1} ^a	
Liquid	Solid
3267 dp	3267
3218 p	3218
1550 p	1531
789 dp ^b	522
506 dp ^b	468
283 dp ^b	349 sh

^ap = polarized, dp = depolarized, sh = shoulder.

^bValues obtained from computer curve resolution analysis; see Fig. III-2 and text.

*Note the twentyfold sensitivity increase for curve a over that of curve c as indicated in the figure caption.

band at 3267 cm^{-1} for the liquid are assigned to $\nu_1(A_1)$, $\nu_2(A_1)$, and $\nu_3(B_2)$ for the NH_2^{1-} ion with a bent structure having C_{2v} point symmetry. Of the corresponding bands in the solid, only $\nu_2(A_1)$ is shifted ($\approx 19\text{ cm}^{-1}$) from the frequency observed in the liquid. The sharpness of the fundamental modes of the NH_2^{1-} ion in both the solid and liquid is in marked contrast to Raman spectral results for water,³⁹⁻⁴¹ where aggregates of H_2O molecules linked by hydrogen bonds cause extensive broadening of the fundamentals in both phases. We take this as evidence that there is little, if any, hydrogen bonding among NH_2^{1-} ions in either solid or liquid NaNH_2 . This view is supported by crystal structure data for NaNH_2 ,⁴² which indicate that the shortest H-H distance for hydrogens of neighboring NH_2^{1-} ions is $\approx 2.3\text{ \AA}$ and is not unexpected in view of the charge on the ions.

In addition to the fundamental vibrations of the NH_2^{1-} ion, there are additional bands in the spectrum of the solid between 300 and 700 cm^{-1} , which persist to a certain extent in the spectrum of the liquid. Our study of the temperature dependence of these bands from 25 to 220°C showed that while the bands observed for the solid broadened with increasing temperature, the major part of the transition of the band envelope occurs at the melting point. In the infrared spectrum of solid NaNH_2 reported by Novak *et al.*,⁴³ two bands are observed between 400 and 800 cm^{-1} , but their frequencies (602 and 573 cm^{-1}) are significantly different from those in Table III-1. We have not attempted to resolve this discrepancy for solid NaNH_2 , although various combinations of allowed and forbidden lattice modes may account for the differences in frequency.

In his extensive studies of the structure of water by Raman and infrared spectroscopy, Walrafen³⁹⁻⁴¹ reported a spectral contour in the 300 - 800 cm^{-1} region of liquid H_2O , which he assigned to "intermolecular librational motions" of pure water. Walrafen³⁹ further showed that this contour should contain three components corresponding to restricted rotation around each of the three principal axes of H_2O . He was, in fact, able to resolve the observed spectral contour for H_2O (from 300 to 800 cm^{-1}) into three Gaussian-shaped bands having average frequencies of 439 , 538 , and 717 cm^{-1} . In light of Walrafen's results, we have attempted to resolve the band envelope for liquid NaNH_2 in the 300 to 700 cm^{-1} region into its components using a computer program written specifically to resolve spectroscopic band contours into either Gaussian or Lorentzian components. The principal difficulty encountered in this analysis lay in subtracting the Rayleigh background from the Raman scattering. In order to do this with some consistency, a plot of $\log I$ vs. ν (I = measured intensity at a frequency ν in cm^{-1} from the exciting line) was made for frequencies close to the exciting line ($\nu < 100\text{ cm}^{-1}$). This plot yielded a straight line up to the frequency where the Raman scattering began to occur. Extrapolation of the linear portion of the $\log I$ vs. ν plot provided a Rayleigh scattering background* and permitted measurement of the Raman scattering intensity in the frequency region where the two types of scattering overlapped.

The result of a computer resolution of the Raman band contours thus obtained is shown in Fig. III-2. The experimental data (indicated by small

*The application of $\log I$ vs. ν plots in describing Rayleigh scattering for simple liquids has been demonstrated. See for example: J. P. McTague, P. A. Fleury, and D. B. DuPré, *Phys. Rev.* **188**, 303 (1969).

Fig. III-2. Computer-Resolved Spectrum of Molten Sodamide from 100 to 1200 cm^{-1} . $\square$ = experimental intensity data, — = resolved bands and computed total intensity, X = difference between observed and computed total intensity. (Intensity values are in arbitrary units.) ANL Neg. No. 308-2837

rectangular boxes in Fig. III-2) are fit reasonably well by the summed intensities of the three Gaussian bands determined by the computer analysis. The differences between observed and calculated total intensities (indicated by the X's in Fig. III-2) are generally small, being only a few percent of the average observed intensity. As expected, these differences are greatest in the low-frequency region where uncertainties due to the extrapolation procedure become important. Addition of a fourth Gaussian band to the envelope did not give a significant improvement in the fit between observed and calculated results.

The computer-determined values for the peak frequencies of the three resolved bands in Fig. III-2 are listed in Table III-1. Since these bands have appreciable intensity in the liquid relative to the NH_2^{1-} fundamental vibrations, it is very unlikely that they arise from impurities or NaNH_2 lattice modes. Comparison with the results obtained by Walrafen for H_2O offers strong evidence that these bands are, in fact, due to hindered rotation of the NH_2^{1-} ion in both the solid and the liquid. The differences in band shape, peak frequency, and relative intensity of these bands between the solid and liquid can be ascribed to changes in the shape and depth of the potential functions which restrict rotation about each principal axis. Furthermore, it is not clear from this study whether the correlation of the bands in the solid and liquid below 800 cm^{-1} is as given in Table III-1 because of the major spectral transformation which occurs at the melting point. There is also a possibility that one or more of these bands in the solid arise from lattice vibrations.

For the NH_2^{1-} ion with C_{2v} point symmetry, the three expected rotational modes R_z , R_y , and R_x belong to the species A_2 , B_1 , and B_2 , respectively. Here x , y , and z are the principal axes of rotation with z being the axis on which the nitrogen atom lies, x the axis perpendicular to the plane of the molecule, and y the axis in the plane of the molecule. If the site symmetry of the NH_2^{1-} ion in the liquid is not lowered from C_{2v} by local perturbations, the hindered rotations corresponding to R_z (A_2), R_y (B_1), and R_x (B_2) should belong to the symmetry species A_2 , B_1 , and B_2 , and consequently, all three should be depolarized in the spectrum of the liquid. This is, in fact, the case. Spectra of the liquid obtained with the exciting radiation polarized perpendicular to the direction of observation gave results that were virtually identical to those for parallel polarization, with no indication that any portion of the envelope is polarized.

Based on the assignments of the "librational modes" of H_2O made by Walrafen,³⁹ the bands at 283, 506, and 789 cm^{-1} in liquid NaNH_2 would be expected to result from the hindered rotations R_z (A_2), R_x (B_2), and R_y (B_1), respectively, if the relative ordering of frequencies were the same. These assignments are not unequivocal, however, and more work needs to be done in this regard. A Raman study of molten NaNH_2 , together with infrared measurements on molten NaNH_2 and NaNH_2 , would add much to our knowledge of the structure and interactions in these liquids.

C. Studies of Divalent Metal Halide Melts

The structures of species in divalent metal halide-alkali halide melts are of interest because of their importance in understanding the thermodynamics of systems which contain a divalent cation, a monovalent cation, and a halide anion. In a previous paper,⁴⁴ we summarized the results of Raman spectroscopic studies of structures in a number of divalent metal halide systems. This summary pointed out that in most cases the observed Raman data for $\text{MX}_2\text{-AX}$ melts (M = divalent metal, A = alkali metal, and X = halogen) have been interpreted in terms of a complex equilibrium involving a polymeric species, $[\text{MX}_2]_p$, and one or more monomeric species of the type $\text{MX}_n^{(2-n)}$, with the latter species increasing in concentration as the mole fraction of AX was increased.

Recently, Clarke and Solomons⁴⁵ investigated the Raman spectra of $\text{SnCl}_2\text{-KCl}$ melts. They interpreted their data in terms of the existence of polymeric chains of bent SnCl_2 molecules in pure molten SnCl_2 with an average coordination of three chloride ions per stannous ion of the Sn(II) . On increasing the mole fraction of KCl , their results indicated a gradual depolymerization of the SnCl_2 chains leading to the formation of pyramidal SnCl_3^{1-} ions. We have conducted a reinvestigation of the $\text{SnCl}_2\text{-KCl}$ system and have made some experimental observations that are somewhat different from those of Clarke and Solomons.⁴⁵

The Raman spectrum of molten SnCl_2 at 250°C (curve a in Fig. III-3) contains a broad band centered near 220 cm^{-1} and a somewhat sharper band at about 110 cm^{-1} , which is partially obscured by the Rayleigh scattering. Raman spectra of $\text{SnCl}_2\text{-KCl}$ melts have essentially the same features as the spectrum of SnCl_2 except that a shoulder is observed on the high frequency side of the 220 cm^{-1} band. This shoulder increases in intensity with increasing mole fraction of KCl as shown by the spectra in Fig. III-3 for

Fig. III-3

Raman Spectra of Molten SnCl_2 and Some SnCl_2 - KCl Melts Recorded with the Exciting Radiation Polarized Perpendicular ($\perp$) to the Direction of Observation (ratio of the number of moles of chloride ion to number of moles of stannous ion is represented by r ; spectral slit width 8 cm^{-1} ; time constant = 5 sec; scan rate = $20\text{ cm}^{-1}/\text{min}$). ANL Neg. No. 308-2865

melts with $r = 2.5, 3.0$, and 4.5 ($r = \text{moles of Cl}^-/\text{mole of Sn}^{2+}$), which (except for curve d) were recorded near the melting point of the indicated sample. The reduction in SnCl_2 vapor pressure, which results from the addition of KCl ,⁴⁶ permitted us to record spectra at 100-degree intervals from 250 to 550°C for the samples with $r = 2.5$ and 3.0. For the higher melting sample with $r = 4.5$, spectra were recorded at 610 and 680°C. In all cases, the observed bands were slightly broader at the higher temperatures, but the spectral changes as a function of temperature were generally insignificant.

Since at most only three genuine features are apparent in any of the spectra in Fig. III-3, an attempt was made to extrapolate these spectra to a horizontal base line and then to resolve the resulting spectral contours into their component bands, using the technique described above for the NaNH_2 spectral resolution.

A typical result of the curve-resolution analyses described above is shown in Fig. III-4 for the sample with $r = 3.0$ at 250°C. The open squares are the I vs. ν values determined from the extrapolated spectral contours,

Fig. III-4. Resolution Analysis of the Raman Spectrum of a $\text{SnCl}_2\text{-KCl}$ Sample with $r = 3.0$ at 250°C into Gaussian Components ($\square$ = experimental intensities (I_{obs}), — = computed total intensity curve (I_{calc}) and individual Gaussian bands, and $X = I_{\text{obs}} - I_{\text{calc}}$; intensity scale is in arbitrary units). ANL Neg. No. 308-2864

the solid lines are the computed total intensity curve and individual band envelopes, and the X's are the differences between I_{obs} and I_{calc} . The results of these analyses, given in Table III-2, were obtained for the spectra in Fig. III-3, and consequently represent the experimental condition where the incident exciting radiation is polarized perpendicular ($\perp$) to the direction of observation. Curve-resolution analyses on spectra recorded with the incident exciting radiation polarized parallel ($\parallel$) to the direction of observation indicated the polarization characteristics for each band, as given in Table III-2.

Incorporation of a fourth band in each curve-resolution analysis failed to give a significantly better fit between observed and calculated total intensities than that represented by the data in Table III-2. Consequently, while we do recognize that other weak bands may indeed be present, we feel the results of this study do not warrant the identification of any bands in addition to those listed in Table III-2.

TABLE III-2. Computer-Resolved Frequencies (ν) and Intensities (I) for the Raman Spectra in Fig. III-3^a

r = 2.0 at 250°C		r = 2.5 at 250°C		r = 3.0 at 250°C		r = 3.0 at 550°C		r = 4.5 at 610°C	
ν	I	ν	I	ν	I	ν	I	ν	I
105 dp	79.9	113 dp	89.1	116 dp	92.2	113 dp	89.3	113 dp	101
220 p	72.9	231 p	91.1	228 p	88.3	227 p	60.2	220 p	65.5
280 p	5.6	279 p	25.7	280 p	35.8	278 p	25.9	270 p	36.6
S.E. ^b = ± 1.40		S.E. = ± 2.18		S.E. = ± 1.70		S.E. = ± 2.00		S.E. = ± 2.62	

^ar = moles of Cl^- per mole of Sn^{2+} , p = polarized, dp = depolarized, ν is in cm^{-1} .

^bS.E. = standard error in the intensities.

Inspection of the data in Table III-2 shows that within the overall experimental error of the computation (most of which is undoubtedly due to the extrapolation procedure), all of the observed spectra reported in Fig. III-3 can be interpreted in terms of three principal bands at $275 \pm 5 \text{ cm}^{-1}$, $225 \pm 6 \text{ cm}^{-1}$, and $110 \pm 6 \text{ cm}^{-1}$ (henceforth referred to as 275, 225, and 110 cm^{-1}). The uncertainties in the peak positions (about $\pm 6 \text{ cm}^{-1}$) are considered to be small in view of the fact that the widths of the three bands at one half the peak height ranged from 40 to 100 cm^{-1} .

Comparisons of the relative intensities of these bands for each spectrum in Fig. III-3 (based on the results in Table III-2) are given in Table III-3. In each case, the relative intensity was computed with respect to the intensity of the 110 cm^{-1} band. It appears from the results in Table III-3 for samples at 250°C that within experimental error, the bands at 225 and 110 cm^{-1} do not change in relative intensity with change in the mole fraction of KCl. Their ratio at the higher temperatures of 550 and 610°C is also relatively constant with respect to mole fraction of KCl. Assuming that the temperature dependence of relative intensities of the 225 and 110 cm^{-1} bands is due solely to effects of temperature on the

TABLE III-3. Relative Intensities of the Computer-Resolved Bands for the Raman Spectra in Fig. III-3

$\text{Cl}^{-1}/\text{Sn}^{+2}$ mole ratio	Temperature, $^\circ\text{C}$	Relative Intensity		
		$110 \pm 6 \text{ cm}^{-1}$	$225 \pm 6 \text{ cm}^{-1}$	$275 \pm 5 \text{ cm}^{-1}$
2.0	250	1.0	0.9 ₁	0.07 ₀
2.5	250	1.0	1.0 ₂	0.2 ₉
3.0	250	1.0	0.9 ₆	0.3 ₉
3.0	550	1.0	0.6 ₇	0.2 ₉
4.5	610	1.0	0.6 ₅	0.3 ₆

respective normal modes, these two bands must arise from the same species. With regard to the 275 cm^{-1} band, the data in Table III-3 indicate that the species associated with this band increases in concentration with increasing mole fraction of KCl.

The results of this study for SnCl_2 and the $\text{SnCl}_2\text{-KCl}$ melts can be interpreted in terms of a complex equilibrium involving polymeric aggregates of SnCl_2 molecules and a monomeric species $\text{SnCl}_n^{(2-n)}$. The expression describing this equilibrium might take the following form:

The structure of the units $[\text{SnCl}_2]_p$, $[\text{SnCl}_2]_{p-1}$, etc., probably resembles that of the lattice network in solid SnCl_2 ,⁴⁷ i.e., chains of bent SnCl_2 molecules with one chlorine atom on each molecule forming a bridge to the tin atom of an adjacent molecule. The Raman data of Clarke and Solomons⁴⁵ for solid SnCl_2 at 30°C show bands at 195 and 90 cm^{-1} , which presumably arise from this chain structure. Accordingly, we assign the bands at 225 and 110 cm^{-1} to the polymeric aggregates in both pure molten SnCl_2 and the $\text{SnCl}_2\text{-KCl}$ melts. The band at 275 cm^{-1} , which increases in intensity with increasing mole fraction of KCl, is assigned to the monomeric species $\text{SnCl}_n^{(2-n)}$.

For the most part, our results are in reasonably good agreement with those of Clarke and Solomons,⁴⁵ but there are some differences. For pure molten SnCl_2 , we find the 110 cm^{-1} band to be depolarized whereas they find it to be polarized. Also, for the melt with $r = 3.0$ (i.e., $\text{SnCl}_2\cdot\text{KCl}$), they report five bands (268 cm^{-1} p, 220 cm^{-1} dp, 212 cm^{-1} p, 110 cm^{-1} p, and 105 cm^{-1} dp), but, as indicated above, we only find conclusive evidence for three bands. In view of the fact that in their paper they do not mention the use of curve-resolution methods, it is not clear how they could have resolved bands in this system separated by 5 to 8 cm^{-1} (e.g., 212 from 220 cm^{-1} and 105 from 110 cm^{-1}) when the band widths at one half the peak height exceed 40 cm^{-1} . Clarke and Solomons assigned these additional bands in the sample with $r = 3.0$ to $\text{SnCl}_n^{(2-n)}$ and presented an argument which suggested that this species was, in fact, pyramidal SnCl_3^{1-} .

We agree with Clarke and Solomons that pyramidal SnCl_3^{1-} is the most likely structure for the monomeric species involved in Eq. 16. However, the results of our study do not permit a conclusive determination of the structure of this species, since we do not observe any of the additional bands expected for various plausible structures* of $\text{SnCl}_n^{(2-n)}$. Undoubtedly the polarized band at 275 cm^{-1} arises from the totally symmetric Sn-Cl stretching mode of this species. In previous studies of divalent metal halide melts,⁴⁴ the totally symmetric stretching modes of the monomeric species were always found to be considerably more intense than both the nontotally symmetric stretching modes and the bending modes. This might be the case for $\text{SnCl}_n^{(2-n)}$ as well and explains our inability to resolve these other bands in the presence of the more intense Raman scattering due to $[\text{SnCl}_2]_p$, $[\text{SnCl}_2]_{p-1}$, etc.

* See Table I of Ref. 44.

There is some evidence from other studies to support the existence of pyramidal SnCl_3^{1-} . For example, the crystal structure of $\text{K}_2\text{SnCl}_4 \cdot \text{H}_2\text{O}$ was found to contain discrete pyramidal SnCl_3^{1-} units.⁴⁸ Also, Raman spectra of ether extracts from aqueous solutions of stannous chloride in hydrochloric acid⁴⁹ were consistent with the existence of this structure. Results of these and other studies of a similar nature have been reviewed by Rundle and Olsen⁵⁰ as evidence that for the most part Sn(II) systems are characterized by a pyramidal structure with an average coordination of three ligands to each Sn(II) ion and with the Sn(II) $5s^2$ electrons occupying a fourth coordination site. Furthermore evidence from electrochemical,⁵¹ thermal,⁴⁶ and tensimetric⁴⁶ studies indicate (but do not confirm) that KSnCl_3 is a stable compound in SnCl_2 - KCl melts; hence it is not unreasonable to assume that pyramidal SnCl_3^{1-} does exist in the SnCl_2 - KCl system.

IV. PHASE EQUILIBRIA IN THE LITHIUM-SULFUR SYSTEM (P. T. Cunningham and S. A. Johnson)

Work has been completed on the lithium-sulfur phase diagram, for which preliminary data and experimental details were previously reported.⁵² The phase diagram was determined using ordinary heating and cooling curves, differential thermal analysis (DTA), and chemical analysis of quenched samples.

All of the experimental results are summarized in Fig. IV-1. The thermal analysis results, which are presented in Table IV-1, show that five thermal effects were observed. The few measurements made on the lithium-rich side of Li_2S indicate that Li_2S does not affect the melting point of pure lithium (180.5°C) within the accuracy of these measurements ($\pm 1^\circ\text{C}$) and that there are no other thermal invariants present in this composition range below 860°C . The melting point of Li_2S was observed to be $1372_{-5}^{+10}^\circ\text{C}$. This value is considerably higher than the previously reported literature value.⁵³

On the sulfur-rich side of Li_2S , thermal effects were observed at $104.0 \pm 3.7^\circ\text{C}$, $115.5 \pm 1.0^\circ\text{C}$, and $364.8 \pm 4.0^\circ\text{C}$. These temperatures are weighted averages where the weighting is admittedly somewhat subjective. The indicated uncertainties show the variance of the data. The effects observed at 104 and 115.5°C are associated with the transformation from α (orthorhombic) sulfur to β (monoclinic) sulfur and the melting of β sulfur, respectively. The accepted value for the $\alpha \rightarrow \beta$ transition is 95.5°C ,⁵⁴ but in none of our experiments, even with pure sulfur, was the effect observed at this temperature. The fact that the $\alpha \rightarrow \beta$ transition is observed about 10° above the equilibrium temperature is typical and in good agreement with the temperature for the appearance of the β form in thin films of α sulfur.⁵⁵ Pure sulfur was observed to melt at 118.0°C in our experiments, in fair agreement with the accepted value of 118.9°C .⁵⁴ With lithium present, this transition was observed at 115.5°C , which is significantly lower than 118.9°C and is presumably the temperature of a eutectic reaction [$\text{L}_1 + \text{Li}_2\text{S}(\text{s}) + \beta$ sulfur]. The thermal effect at 364.8°C is attributed to a monotectic reaction [$\text{L}_2 + \text{Li}_2\text{S}(\text{s}) + \text{L}_1$].

The results of the chemical analyses are summarized in Table IV-2. They show that at the monotectic temperature the miscibility gap extends from about 0.2 to 37.0 at. % lithium.

Thermal effects associated with liquidus crossings were not observed. Attempts to establish the location of the upper liquidus by determination of the equilibrium sulfur vapor pressure as a function of temperature for compositions greater than 37 at. % lithium gave very scattered results. The time necessary for equilibration between the vapor and the condensed phase was at least several days. It is significant that the vapor pressure of samples with less than 34 at. % lithium was not significantly different from that for pure sulfur within the experimental uncertainty ($\pm 10\%$).

X-ray powder patterns were taken on a large number of samples of various compositions and thermal histories. In all cases, the observed lines were accounted for by the appropriate terminal phase and Li_2S .

Fig. IV-1. Partial Phase Diagram of the Lithium-Sulfur System.
 O, thermal analysis; $\diamond$, DTA; $\square$, chemical analysis.
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TABLE IV-1. Summary of Thermal Data on the Lithium-Sulfur System

Over-all Composition, at. % Li in S	Method ^a	Container Material	Max. Temp., °C	Temperature of Thermal Effects Observed, °C ^a				
100 (Li)	DTA	Nb	475	180.3				
87.1	DTA	Nb	860	180.7				
66.7 (Li ₂ S)	DTA	Al	400	No effect observed				
66.7 (Li ₂ S)	TA	Quartz	1080	No effect observed				
66.7 (Li ₂ S)	Visual	Nb	1425	1372				
66.7 (Li ₂ S)	Visual	Vitreous graphite	1400	1372				
63.3	DTA	Al	400	109.3	114.6	359.1		
60.0	TA	Al	395	-	-	367.0		
52.2	DTA	Al	400	102.6	114.5	365.0		
47.5	DTA	Al	410	102.9	115.5	366.8		
41.9	DTA	Nb	405	106.3	116.4	369.2		
40.5	DTA	Nb	405	105.6	116.4	364.1		
37.3	DTA	Al	420	105.6	118.1	366.0		
36.4	DTA	Al	405	105.0	116.4	365.5		
34.3	DTA	Al	405	104.9	115.4	367.1		
30.0	DTA	Al	400	105.0	116.3	360.7		
28.2	DTA	Al	405	105.2	115.6	367.1		
23.7	DTA	Al	405	105.0	-	364.1		
23.1	TA	Al	390	-	-	365.9		
14.8	TA	glass	400	101.9	114.7	359.5		
13.0	TA	glass	410	101.0	115.0	365.0		
9.3	TA	glass	500	102.7	114.6	366.0		
9.0	DTA	Al	400	102.6	114.5	363.4		
8.6	DTA	Al	390	102.6	114.9	365.0		
5.0	TA	glass	400	-	-	361.0		
4.7	DTA	Al	400	102.6	114.9	363.0		
0.0 (S)	DTA	Al	395	102.6	118.0	-		
Weighted Average Values				104.0	115.5	180.5	364.8	1372

^aMethods used were heating and cooling curves (TA), where the reported temperatures are those of thermal arrests, and differential thermal analyses (DTA), where reported temperatures are those of the intersection.

TABLE IV-2. Summary of Chemical Analyses on Lithium-Sulfur Samples

Temperature Prior to Quenching (°C)	Component analyzed (see Fig. IV-1)					
	L ₁			L ₂		
	Sample Weight (g)	Lithium Weight (mg)	At. % Lithium	Sample Weight (g)	Lithium Weight (mg)	At. % Lithium
602	0.0995	0.054	0.25	0.0961	10.9	37.3
602	0.1340	0.084	0.29	0.1573	17.2	36.2
508	0.4032	0.15	0.17	0.2248	25.4	37.1
508	0.3087	0.099	0.15	0.1923	21.4	36.7
456	0.1771	0.082	0.21	0.1615	19.3	38.5
456	0.3421	0.15	0.20	0.1143	12.8	36.8
417	0.1735	0.012	0.032	0.1319	14.8	36.8
417	0.1448	0.0097	0.031	0.1910	20.7	36.0
396				0.4123	43.4	35.2
396				0.1717	16.8	33.4
377	0.3580	0.26	0.34	0.1684	19.0	37.0
375	0.1558	0.21	0.62	0.1523	17.0	36.7
375	0.2777	0.48	0.79	0.1981	22.0	36.6

The lithium-sulfur phase diagram is very much like that which we found for the lithium-selenium system.⁵⁶ Our study of the lithium-tellurium system is presently being completed.

V. THEORETICAL STUDIES
(H. M. Feder and H. C. Schnyders)

A. A Nonempirical Pair Potential for Argon

1. Development

Since the advent of quantum mechanics, prediction of the behavior of bulk matter from the properties of statistical assemblages of molecules with calculable properties has been an outstanding goal. With the development of high-speed computing machinery, the achievement of this goal in a typical case--the prediction of equations of state for solid, liquid, and gaseous argon--appears imminent. The connection between the bulk properties and the molecular properties in this case is made in terms of the intermolecular potentials, of which the pair potential is the most important.

The pair potential for argon may be expressed in the form of a perturbation series whose terms correspond to increasing powers of the perturbing potential, $\sum_{A \neq B} Z_A Z_B / r_{AB}$, where the Z's are the various electronic and nuclear charges in atoms A and B, and the r's are the distances between those charges. For neutral atoms, the first-order term can be shown to be always short-ranged and repulsive. It is calculable as a function of the internuclear distance, R, given optimized wave functions of the ground-state atoms. The second-order terms, also known as van der Waals, London, or dispersion terms, are always attractive and long-ranged. They have been shown to arise from the interactions between electronically excited states induced in each atom by the presence of the other.

In collaboration with Dr. A. C. Wahl of the Chemistry Division, the Hartree-Fock equations have been solved to yield the repulsive potential between two ground-state argon atoms in the range of R values of greatest interest in equation-of-state calculations. These results, obtained with optimized single-configuration wave functions, are shown in Table V-1. For convenience in subsequent statistical-mechanical calculations these results have been fitted by a four-constant equation:

$$V(R) = Ae^{-BR} - Ce^{-DR^2} \quad (17)$$

where

$$\begin{aligned} A &= 1.263,148,731 \times 10^8 \text{ eV} = 399.895,124,78 \text{ h} \\ B &= 3.668,263,874 \text{ \AA}^{-1} = 1.941,124,1894 a_0^{-1} \\ C &= 2.256,610,858 \times 10^6 \text{ eV} = 7.144,112,6347 \text{ h} \\ D &= 1.187,508,964 \text{ \AA}^{-2} = 0.332,523,5453 a_0^{-2} \end{aligned}$$

The fitted function is adequately accurate in the region of greatest interest, the well of the intermolecular potential, ~ 5.4 - 7.3 bohrs.

The dispersion term may itself be expressed as the sum of a series expansion, as follows

$$D(R) = - \frac{C_6 f_6(R)}{R^6} - \frac{C_8 f_8(R)}{R^8} - \frac{C_{10} f_{10}(R)}{R^{10}} \dots \quad (18)$$

TABLE V-1. Repulsive Potential between Two Ground-State Argon Atoms

R^a	$V(R)^b$ (Wahl)	$V(R)^b$ (Eq. 17)
3.8	0.19086	0.19161
4.0	0.13516	0.13483
4.2	0.09536	0.09490
4.6	0.04676	0.04669
4.7	0.03896	0.03902
5.0	0.02246	0.02262
5.4	0.01078	0.01077
5.8	0.00506	0.00506
6.1	0.00286	0.00285
6.4	0.00160	0.00160
6.7	0.00090	0.00090
7.0	0.00050	0.00050
7.3	0.00028	0.00028

^aBohr units, $a_0 = 0.529167 \text{ \AA}$.

^bHartree units, $h = 27.214 \text{ eV} = 3.1587 \times 10^5 \text{ K}$.

This series consists of terms dependent on the multipolar nature of the electronic excitations. Thus, the first three terms in Eq. 18 arise from induced excitations of the dipole-dipole, dipole-quadrupole, and dipole-octupole plus quadrupole-quadrupole varieties, respectively. The constants C_6 , C_8 , and C_{10} were chosen after a scrupulous review of the extensive literature. The values so chosen were $C_6 = 4.491 \times 10^5 (\text{K})(\text{\AA})^6$; $C_8 = 3.401 \times 10^6 (\text{K})(\text{\AA})^8$; and $C_{10} = 3.151 \times 10^7 (\text{K})(\text{\AA})^{10}$. Equation 18 frequently appears in the literature without the factors $f(R)$. This omission makes Eq. 18 applicable only at very long range; overlap of the atoms, in fact, reduces the dispersive interactions. Our estimate of the reduction factors is based on the analogous problem for two hydrogen atoms, which has been solved exactly. The resulting factors are approximated by

$$f_n(R) = [1 + 170 g_n \exp(-dR)]^{-1} \quad (19)$$

where $g_6 = 1$, $g_8 = 3.9$, $g_{10} = 11.8$, and $d = 2.34 \text{ \AA}^{-1}$.

In addition to the overlap effect, there is another correction to be made to the dispersion term; it arises because the electromagnetic interaction between atoms is retarded, i.e., propagates at a finite velocity. At very long distances--beyond the range of immediate interest--the effect of retardation is to convert the $1/R^6$ dependence of the dispersion potential to a $1/R^7$ dependence. In the range of interest its effect is to add a very small term which has been estimated to be

$$P(R) = \frac{0.8 C_6}{(137.15 a_0)^2 R^4} \quad (20)$$

The total intermolecular potential, $U_{FS}(R)$, to be tested is thus

$$U_{FS}(R) = V(R) + D(R) + P(R) \quad (21)$$

The absolute accuracy of the calculations of $V(R)$ is difficult to judge; the accuracy with which the fitting function reproduces the data is limited to $\pm 1^\circ\text{K}$ in the well region. In the same region the uncertainties in the values of C_6 , C_8 , and C_{10} contribute a net uncertainty of not more than 3°K . We judge the a priori overall accuracy of $U_{\text{FS}}(R)$ to be about 3°K at each point in the well region.

2. Vibrational Levels Test

One of the most direct and sensitive tests of a proposed pair potential is its ability to reproduce the experimental vibrational spectrum of the diatomic molecule it represents. A computer code^{57,58} for the solution of the radial Schrodinger equation for spherically symmetrical potentials has been adopted to calculate the vibrational eigenfunctions and eigenvalues for the potential $U_{\text{FS}}(R)$. The results of this computation are presented in Table V-2. The spectral observations of Tanaka and Yoshino⁵⁹

TABLE V-2. Vibrational Energies of Diatomic Argon

Vibr. Quantum Number, v	"Observed" Energy, ^a cm ⁻¹ b	Calculated, cm ⁻¹
0	14.7 $\pm$ 0.2	15.24
1	40.2 $\pm$ 0.4	41.51
2	60.3 $\pm$ 0.6	61.33
3	75.8 $\pm$ 0.9	78.02
4	86.1 $\pm$ 1.2	89.01
5	94.1?	95.92

^aReferences 59 and 60.

^b1 cm⁻¹ = 1.4390 K.

in the 780-1080 Å region have been inverted by Maitland and Smith⁶⁰ by the Rydberg-Klein-Rees method to obtain "observed" energy levels. A comparison of the "observed" and calculated energy levels verifies that our uncertainty estimate of 3°K is justified and may be conservative.

3. Second-Virial-Coefficient Test

Another sensitive test of an intermolecular pair potential is the calculation of the second virial coefficient of the equation of state of the gas, particularly at low temperatures. The classical second virial coefficient is related to the pair potential by the integral⁶¹

$$B_{\text{class}}(T) = -2\pi N_0 \int_0^\infty [e^{-\beta U(R)} - 1] R^2 dR \quad (22)$$

where N_0 is Avogadro's number, $\beta = (k_B T)^{-1}$, and k_B is Boltzmann's constant. This is the leading term in the Wigner-Kirkwood expansion for the second virial coefficient and its values, obtained by numerically evaluating Eq. 22 with $U_{\text{FS}}(R)$, are tabulated in the second column of Table V-3. The first quantum correction (or the second term in the Wigner-Kirkwood expansion),

TABLE V-3. Second Virial Coefficients of Argon Gas

T, °K	Calculated, cm ³ /mol			Experimental, cm ³ /mol
	B _{class}	B _Q	B	B
89.57	-229.90	+2.15	-227.75	-228.2
93.59	-211.64	+1.89	-209.75	-209.7
97.69	-195.33	+1.66	-193.67	-193.6
102.79	-177.71	+1.44	-176.27	-175.8
107.93	-162.37	+1.25	-161.12	-161.1
113.97	-146.85	+1.08	-145.77	-146.0
122.38	-128.76	+0.90	-127.86	-127.3
124.70	-124.36	+0.85	-123.51	-123.5
130.96	-113.54	+0.75	-112.79	-112.7
140.04	-100.14	+0.64	-99.50	-99.1
159.72	-77.79	+0.46	-77.33	-77.1
179.85	-61.26	+0.35	-60.91	-60.7
209.94	-43.73	+0.25	-43.48	-43.7
241.04	-31.09	+0.19	-30.90	-30.9
271.39	-22.04	+0.15	-21.89	-21.9
273.15	-21.59	+0.15	-21.45	-21.3
298.15	-15.85	+0.12	-15.73	-15.63
323.15	-11.15	+0.11	-11.04	-11.06
348.15	-7.23	+0.10	-7.13	-7.14
373.15	-3.92	+0.09	-3.83	-3.89
398.15	-1.09	+0.08	-1.01	-1.08
423.15	+1.35	+0.07	+1.42	+1.42

B_Q is proportional to the square of Planck's constant, h , and is given by⁶¹

$$B_Q = \frac{h^2 N_0 \beta^3}{48 \pi \mu} \int_0^\infty e^{-\beta U(R)} \left(\frac{dU}{dR} \right)^2 R^2 dR \quad (23)$$

where μ is the reduced mass of a pair of molecules. The sum of B_{class} and B_Q is the calculated second virial coefficient, B , which should be compared with the experimental results given in the last column of Table V-3.

The experimental data we consider to be the most accurate in their respective temperature ranges are those of Byrne, Jones, and Staveland⁶² at 90-273°K and of Michels, Wijker, and Wijker⁶³ at 25-150°C.

The accuracy of the experimental data is estimated to be 0.8% or 0.25 cm³/mol, whichever is larger. The average deviation between the calculated results and the data is about 0.16 cm³/mol, well within the experimental scatter and without systematic variation.

4. Shear Viscosity Test

Transport processes and atomic beam scattering are phenomena which are sensitive to details at the intermolecular potential. We have chosen to calculate gas viscosities since a large body of accurate data

over a wide temperature range has been recently published.^{64,65} According to the kinetic theory of gases,⁶⁶ the coefficient of shear viscosity is given by

$$\eta = \frac{26.693\sqrt{MT}}{\sigma^2\Omega^{(2,2)*}(T^*)} f_{\eta} \quad (24)$$

where η is in units of micropoise, M is the molecular weight, σ (Å) is the collision diameter where $U_{FS}(\sigma) = 0$, T^* is the reduced temperature (kT/ϵ) where $\epsilon = U_{FS}$ minimum, and f_{η} is a correction factor which is a function of the reduced collision integrals $\Omega^{(L,S)*}(T^*)$ in which the integrand contains the intermolecular pair potential. A summary of the results obtained for the potential $U_{FS}(R)$ is given in Table V-4.

TABLE V-4. Shear Viscosities of Argon Gas

T, °K	η_{calc} , micropoise	η_{exp} , micropoise ^a
134.4	107.9	108.9
200.9	158.2	160.1
252.3	193.8	196.1
300	224.9	228.1
500	336.0	341.6
800	470.0	474.4
1600	752.1	753.5

^aExperimental viscosity data taken from Refs. 64 and 65.

The agreement between calculated and experimental shear viscosities is better than 1.5% over the entire range of 1500°K. (The differences, however, appear systematic.) When one considers that empirical potentials with three or four adjustable constants frequently fail to give agreement this good with both virial coefficient and viscosity data, there is reason to believe that the U_{FS} potential may be reliably accurate. Two further tests of this potential are contemplated via beam scattering and thermal-conductivity data. Finally, to the extent that this potential is accurate, the opportunity presents itself to test methods which have been developed for predicting the equation of state for liquids. Until now these methods could not have been adequately tested because it would have been unclear whether the failure of the calculations were to be ascribed to inadequate potentials, to inadequate convergence of the terms, or to many-body effects.

B. Solutions in Liquid Metals

The specific repulsive forces acting between a solute atom and the surrounding solvent atoms affect the chemical potential of the solute in solution; a new approach to the description of these forces is now being incorporated into our model for solutions of noble gases in liquid metals.⁶⁷ Previously we had estimated this effect by calculating the reversible work done in compression of the pure solute gas from its standard density to the number density of the solvent. Recently, a pseudo-potential calculation of the interaction between all alkali-metal noble gas pairs has been

published.⁶⁸ These potentials provide a more accurate estimate of the repulsive forces contribution to the chemical potential in the following manner. One assumes that at a distance R from the solute atom, a number, N_s , of nearest-neighbor solvent atoms are located in a spherical shell. The number N_s is calculated on the assumption that the packing fraction of the solvent atoms in this layer is not significantly different from the packing fraction in the bulk liquid. If y be the latter packing fraction and a the effective hard-sphere diameter of the solvent atom, then

$$N_s = 8 y \left[\left(R + \frac{a}{2} \right)^3 - \left(R - \frac{a}{2} \right)^3 \right] / a^3 \quad (25)$$

Because repulsive forces are quite short ranged, their contribution, μ_{rep} , to the chemical potential is well approximated by considering only the nearest neighbors. Then

$$\mu_{\text{rep}} \approx N_s U_R(R) \quad (26)$$

where $U_R(R)$ is the repulsive part of the interatomic potential of the alkali metal-noble gas atom pair. These calculations are under way.

VI. THERMODYNAMIC PROPERTIES OF THE ORTHOPYROXENES AND CLINOPYROXENES
 BASED ON THE IDEAL TWO-SITE MODEL*
 (M. Blander)

Pyroxenes (MSiO_3) are important minerals in volcanic and metamorphic rocks as well as in meteorites. Pyroxenes have equal numbers of two types of sites (M1 and M2) which can be occupied by divalent cations. The divalent cations in orthorhombic pyroxenes (orthopyroxenes) are largely Mg^{++} and Fe^{++} , and in the monoclinic form they are largely Mg^{++} , Fe^{++} , and Ca^{++} .

All available thermodynamic data on Fe^{++} - Mg^{++} exchange equilibria between M1 and M2 sites in orthopyroxenes and between olivine and orthopyroxene phases have been reanalyzed and can be fit to the ideal two-site model of Mueller⁶⁹ with only two free-energy parameters. The standard free energy for exchange between M1 and M2 sites, ΔG° , which is consistent with all the data from 900 to 1300°C is 3.6 kcal/(gram formula weight), the same value that was deduced by Virgo and Hafner⁷⁰ from Mössbauer data for 600-1000°C. The analysis shows that the interpretation of data on coexisting olivine-orthopyroxene assemblages in meteorites and volcanic rocks in terms of rate of cooling is invalid.

The free-energy change, ΔG° , deduced for the reaction

is 1.65 kcal/gfw. From this, the standard free energy of formation of ferrosilite from wüstite and β cristobalite deduced at 900°C is -1.8 kcal/gfw.

As a consequence of the strong preference of Ca^{++} ions for M2 sites in clinopyroxenes, the $\text{Fe}^{++}/\text{Mg}^{++}$ ratios in clinopyroxenes in equilibrium with a given orthopyroxene are very sensitive to Ca^{++} content. This places in doubt the use of the Fe^{++} - Mg^{++} exchange equilibria between clino and orthopyroxenes as a "thermometer" and means that the Ca^{++} content of clinopyroxenes must be accurately known for meaningful thermodynamic analyses. An analysis of all available meteoritic data is consistent with the model.

The ideal two-site model is not consistent with measured activity coefficients in orthopyroxenes or in olivines indicating significant cancellation of activity coefficient ratios in the ion-exchange equilibria.

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