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**CHEMICAL ENGINEERING DIVISION
PHYSICAL INORGANIC CHEMISTRY
SEMIANNUAL REPORT**

January-June 1973

**M. Blander, P. T. Cunningham, H. M. Feder,
V. A. Maroni, H. C. Schnyders, E. Veleckis,
R. C. Vogel, and L. Burris**

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS
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ABSTRACT

Tensimetric and gravimetric measurements of the thermodynamic properties of the Li-H₂ system have been made and Sieverts' law constants for H₂ in molten lithium and free energies of formation of LiH were derived from the data. An experimental investigation of the Li-N₂ system was initiated. Scoping studies for the handling and recovery of tritium in fusion reactor reference models were made to better define potential problems. The limit of superheat for propane was measured and a theoretical calculation of the thermodynamic limit of superheat is given. Conditions for the attainment of the limit of superheat are discussed to define conditions where contact vapor explosions may occur. Raman spectra of LaCl₃-KCl melts confirm the presence of one symmetric complex ion. The conformal ionic solution (CIS) theory has been utilized to calculate liquidus temperatures in the Na, Tl || NO₃, Cl and the Li, K || NO₃, Cl systems, which are in good agreement with measurements. A limitation of the CIS theory for calculating miscibility gaps is discussed. Calculations of physical properties using nonempirical pair potentials for helium are in excellent agreement with measurements. A detailed study of calcium-aluminum-rich inclusions in the Allende meteorite indicate that they had been liquid. This places important constraints on their origin. The chemistry of atmospheric particulates was studied as a function of size and time. Chemical differences between different size fractions were large.

SUMMARY

Physicochemical and Thermodynamic Studies of Lithium-Containing Systems

Tensimetric Studies in the Lithium-Lithium Hydride System. Tensimetric measurements are described for the equilibria between H₂ and molten Li-LiH mixtures at temperatures ranging from 710 to 903°C. These measurements indicate a miscibility gap spanning a range of mole fractions of lithium hydride from 0.252 to 0.984 at 710°C and from 0.454 to 0.855 at 903°C. For the temperature range from 710 to 903°C, the Sieverts' law constants,

K_s , are given by

$$\log K_s [\text{Torr}^{1/2} (\text{at.fr.H})^{-1}] = 4.263 - 2685 T^{-1}$$

For the same temperature range, the standard free energy of formation, ΔG_f° , of molten LiH is given by

$$\Delta G_f^\circ (\text{cal mol}^{-1}) = 13.47 T - 16,545$$

The activity coefficients of both components derived from the data are greater than unity.

Gravimetric Studies of Hydrogen-Metal Systems. A gravimetric study of hydrogen dissolved in niobium was made to test the sensitivity and accuracy of the technique. The results obtained at 612 and 664°C indicate that the technique will be useful for measurements on lithium systems contained in niobium.

Physicochemical Studies of the Lithium-Nitrogen System. Nitrogen is a potentially troublesome contaminant in a lithium heat-transfer system, and thermodynamic data on this system are necessary to understand its chemistry. A literature survey indicates uncertainties and discrepancies in the solubility relations in the Li-Li₃N system. An experimental study of solubilities in this system has been initiated and pure Li₃N has been prepared for use in these solubility studies, as well as in other anticipated thermodynamic studies.

Scoping Studies of Fusion Reactor Subsystems. Some consideration has been given to problems related to tritium handling and recovery in fusion reactors. A scheme for processing the lithium blanket of a D-T-fueled fusion reactor by molten-salt extraction is presented and discussed. A computer program which provides a hydrogen-isotope map for fusion power plants has been written. This program has been used to analyze the significant tritium losses in two current conceptual fusion power plants.

Nucleation Studies

The limit of superheat of propane was measured in a glycol-water medium and found to be 52.9°C, which is somewhat lower than the value of 55.3°C calculated from homogeneous nucleation theory.

The thermodynamic stability limits for supersaturated vapors has been calculated for a Lennard-Jones potential and the usefulness of thermodynamic stability theory is discussed.

One mechanism for contact vapor explosions involves superheating of volatile materials close to the limit of superheat. This can be achieved if the volatile material wets the hot substrate. Hydrocarbons on water or on other hydrocarbons may reach such limits if no solids form at the interface. It is possible to reach such limits in a water-papermaking smelt system. Attainment of this limit in a molten UO₂-Na system is very unlikely.

Laser-Raman Spectroscopy of Molten Salts

Raman spectra of $\text{LaCl}_3\text{-KCl}$ melts with compositions in the range from 10 to 65 mol % LaCl_3 confirm the presence of at least one highly symmetric complex ion. The concentration maximum of this species is near 25 mol % LaCl_3 , indicating that the complex may be LaCl_6^{3-} .

Phase Equilibria

The conformal ionic solution (CIS) theory was used to calculate liquidus temperatures in the reciprocal systems $\text{Na, Tl} || \text{NO}_3, \text{Cl}$ and $\text{Li, K} || \text{NO}_3, \text{Cl}$ systems. The calculated phase diagrams are in excellent agreement with measurements. The $\text{Li, K} || \text{NO}_3, \text{Cl}$ system is an example of a rare type of system containing one ternary eutectic and one ternary peritectic.

Application of the conformal ionic solution (CIS) theory to calculation of liquid-liquid miscibility gaps in an idealized molten reciprocal system indicates the limitations of the theory. When the binary interaction parameters in the theory are not very small, problems in the calculations arise because the theory has not been derived to high enough order.

Theoretical Studies

A proposed nonempirical interatomic potential for helium has been tested against experimental data on the second virial coefficients of both ^3He and ^4He at 1.6-10°K, the isotopic diffusion of ^3He in ^4He gas at 1.7-900°K, and the viscosity of helium at 100-1800°K. In all these comparisons, agreements between calculated and experimental results are obtained which are at least as good as those obtained with fitted empirical potentials.

Meteoritic Studies

A detailed study of the mineralogy, textures, and assemblages of calcium-aluminum-rich inclusions in the Allende meteorite indicate that these apparently high-temperature condensates appear to have crystallized from a liquid and could not be an agglomeration of solid nebular condensates. This fact places important constraints on the origins of these important primordial materials.

Chemistry of Airborne Particulates

A program has been initiated to study the chemical and elemental composition of airborne particulate material as a function of particle size and time. Techniques have been developed for sample collection, handling, and analysis. Preliminary results clearly show variations in the chemistry of airborne particulates as a function of particle size and time. These results tend to support recent theories relating to the origin of these particulates. They also indicate that methods presently employed in assessing the potential health hazards and in establishing appropriate control standards may not be adequate.

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I. PHYSICOCHEMICAL AND THERMODYNAMIC STUDIES OF LITHIUM-CONTAINING SYSTEMS

The importance of lithium as a blanket and/or coolant material in thermonuclear reactors has been identified in previous reports.^{1,2} As a result of an extensive review¹ of the properties (physical, chemical, thermal, etc.) of lithium, we have initiated several experimental studies to provide needed basic chemical data in areas of interest to controlled thermonuclear research. Recent progress in these studies is summarized below.

A. Tensimetric Studies in the Lithium-Lithium Hydride System (E. Veleckis, E. Van Deventer)

In the present conceptual designs for D-T-fueled fusion reactors, liquid lithium appears to be uniquely suited to act as a breeder blanket fluid. The knowledge of the chemical activity of hydrogen isotopes in the blanket is necessary in order to evaluate conditions for the removal of H, D, and T or for recycling D and T. Because such information is lacking, we have determined the thermodynamic properties and phase relations for the system Li-LiH in the range 710-903°C, 1-760 Torr, and 0.5-99 mol % LiH by measuring the equilibrium hydrogen pressures over encapsulated lithium samples.

Description of the apparatus and procedure for the hydridation experiments, as well as six isotherms in which the square root of hydrogen pressure is plotted against the mole percent of LiH, have been presented in an earlier report.² Final tabular results are shown in Table 1.

If we assume that hydrogen in the condensed phases is present as a hydride, then the equilibrium reaction between gaseous hydrogen and liquid lithium can be written as follows:

where the underlined symbols indicate that both the lithium metal and its hydride are in the same solution. The equilibrium constant, K, for this reaction and the standard free energy of formation of liquid LiH, ΔG_f° , are given by

$$K = \frac{N_2 \gamma_2}{N_1 \gamma_1 \sqrt{P}} \quad (2)$$

and

$$\Delta G_f^\circ = -RT \ln K \quad (3)$$

where the subscripts 1 and 2 refer to Li and LiH, respectively, N's are the mole fractions, γ 's are the activity coefficients, P is the equilibrium hydrogen pressure, R is the gas constant, and T is the absolute temperature. Equation 2 can be rewritten in the form

$$\ln (\sqrt{P} \cdot N_1 / N_2) = -\ln K + \ln (\gamma_2 / \gamma_1) \quad (4)$$

TABLE 1. Pressure-Composition Data for Six Isotherms in the Li-LiH System

710°C		759°C		803°C		847°C		878°C		903°C	
100 N _{LiH} (Mol % LiH)	P _{H₂} (Torr)	100 N _{LiH} (Mol % LiH)	P _{H₂} (Torr)	100 N _{LiH} (Mol % LiH)	P _{H₂} (Torr)	100 N _{LiH} (Mol % LiH)	P _{H₂} (Torr)	100 N _{LiH} (Mol % LiH)	P _{H₂} (Torr)	100 N _{LiH} (Mol % LiH)	P _{H₂} (Torr)
2.153	0.53	4.632	4.17	1.686	0.97	1.596	1.38	1.163	1.04	2.595	6.37
3.698	1.49	6.749	8.64	3.104	3.23	2.858	4.30	3.111	7.10	4.528	18.17
6.390	4.26	9.598	16.53	4.927	8.08	4.688	11.57	5.033	18.08	6.375	34.73
8.286	6.84	13.37	29.83	7.485	17.93	7.212	26.58	7.003	34.01	8.581	60.98
10.42	10.80	17.88	47.53	10.42	33.00	10.05	49.21	9.030	54.60	11.37	101.8
12.41	14.58	22.32	67.79	13.71	53.22	13.34	81.85	11.17	79.49	14.71	160.1
14.20	18.08	25.44	79.09	17.40	77.90	17.59	129.5	13.44	110.4	17.96	224.3
16.11	22.16	28.10	85.66	22.83	117.5	22.32	184.3	15.83	144.8	21.21	292.6
18.74	27.40	30.84	86.77	26.72	142.6	27.67	244.7	18.77	191.3	25.52	378.6
20.96	31.90	34.97	87.29	32.19	166.8	31.74	284.2	22.11	254.7	30.36	474.3
23.57	35.52	50.15	87.94	37.64	169.7	35.24	310.7	25.98	316.2	36.63	571.3
27.54	36.45	69.85	88.53	47.25	171.6	39.02	323.2	30.37	380.9	42.67	628.2
33.27	37.10	89.50	88.54	61.99	172.1	42.87	329.4	35.31	439.1	49.86	653.6
39.38	37.75	92.26	88.71	76.67	173.1	48.76	329.9	40.81	486.1	57.78	657.8
50.13	37.38	92.81	88.78	91.31	173.3	64.76	331.1	43.70	499.0	68.74	658.3
60.95	38.38	95.46	89.03	95.16	168.5 ^a	76.26	332.3	46.92	500.1	75.95	662.0 ^a
71.67	39.24	96.59	89.41	96.04	190.4	92.61	332.0	66.21	502.2	81.28	662.3
82.39	39.14	97.38	104.5	96.36	204.8	92.76	329.4	85.96	504.1	86.46	670.8 ^a
87.39	38.84	97.64	115.2	96.79	232.6	93.21	343.8 ^a	89.30	504.0	87.14	685.4
90.88	39.26	97.97	141.0	97.12	263.8	93.88	363.2	89.96	513.7 ^a	87.96	705.2
92.68	38.87	98.18	166.6	97.73	368.6	94.55	392.2	91.06	541.6		
94.45	39.05	98.47	214.3	98.00	467.4	95.33	447.3	91.73	563.8		
96.22	39.88	98.67	266.4	98.17	563.0	95.81	494.5	92.45	600.6		
97.55	38.93	98.84	347.2	98.28	641.9	96.18	549.4	93.08	641.0		
98.92	74.18	98.96	433.3	98.36	708.0	96.47	603.4	93.52	680.3		
99.30	142.8	99.05	506.0			96.73	659.7	93.87	720.8		
99.47	256.3	99.13	576.9			96.92	715.0				
99.54	329.0	99.19	640.9								
99.58	393.9	99.25	702.2								
99.64	539.6										
99.69	669.8										
99.70	744.5										

^aReversed equilibration measurement. Equilibrium attained from the low-pressure side by removing small amounts of hydrogen from the sample.

According to Margules, the activity coefficients of a binary solution can be represented by power series in N . When the series are truncated at the cubic term, they are given by³

$$\ln \gamma_1 = \alpha N_2^2 + \beta N_2^3 \quad (5a)$$

and

$$\ln \gamma_2 = (\alpha + \frac{3}{2} \beta) N_1^2 - \beta N_1^3 \quad (5b)$$

Substitution of Eqs. 5a and 5b into Eq. 4 yields a second-order power series of $\ln (\sqrt{P} \cdot N_1/N_2)$ vs. N_2

$$\ln (\sqrt{P} \cdot N_1/N_2) = -\ln K + (\alpha + \frac{1}{2} \beta) - 2\alpha N_2 - \frac{3}{2} \beta N_2^2 \quad (6)$$

At the extreme limits of the composition range, $N_2 \rightarrow 0$ and $N_2 \rightarrow 1$, Eq. 6 becomes

$$\lim_{N_2 \rightarrow 0} \ln (\sqrt{P}/N_2) = -\ln K + (\alpha + \frac{1}{2} \beta) \quad (7)$$

and

$$\lim_{N_2 \rightarrow 1} \ln (\sqrt{P} \cdot N_1) = -\ln K - (\alpha + \beta) \quad (8)$$

Equation 7 is a statement of the Sieverts' law, $\sqrt{P} = K_S N_2$, where $K_S = [\exp (\alpha + \frac{1}{2} \beta)]/K$ is the Sieverts' law constant. Equation 8 states that near the composition $N_2 \rightarrow 1$, $1/\sqrt{P}$ becomes a linear function of N_1 .

Thermodynamic and phase information extracted from the data in Table 1 is presented in Table 2. The items in the latter table are discussed below.

1. Miscibility Gap Limits

The lower limits, N_2^l , represent the saturated solubility of LiH in lithium; the upper limits, N_2^u , represent the solubility of lithium in LiH. Both limits are plotted against $1/T$ in Fig. 1. The high-temperature end of the upper curve shows significant deviations from linearity, probably due to a large temperature coefficient of activity coefficients of lithium when dissolved in the LiH. The lower curve is linear, and may be represented by

$$(710-903^\circ\text{C}) \quad \log N_2^l = 0.9707 - 1553 T^{-1} \quad (9)$$

with an uncertainty (95% confidence level) of 2.4% in the predicted mean value of N_2^l .

An approximate extrapolation was made into the region below the monotectic temperature by connecting the monotectic point (22.4 mol % LiH, 685°C) with the single solubility value obtained for the solid LiH. The freezing points of mixtures of LiH and lithium obtained in the range from 624 to 679°C by the thermal-analysis method by Messer *et al.*⁴ are also shown in Fig. 1. In spite of the low precision of our point, it is clear that there is a discrepancy between the two sets of data. We believe that, because of the relative steepness of the freezing-point curve, the thermal values may not be reliable.

TABLE 2. Thermodynamic Properties for the System Li-LiH

Temperature (°C)	710	759	803	847	878	903
Miscibility gap limits: ^a N_2'	0.252	0.285	0.332	0.386	0.418	0.454
N_2''	0.984	0.971	0.957	0.923	0.888	0.855
Plateau pressure (Torr)	38.5	88.3	171.4	29.2	500.2	658.8
Activity coefficients: ^a α'	0.7739	0.7263	0.6872	0.6512	0.6275	0.6093
β'	2.244	2.132	2.041	1.957	1.901	1.859
γ_1'	1.084	1.122	1.169	1.230	1.283	1.334
α''	-6.099	-4.616	-3.400	-2.280	-1.542	-0.975
β''	10.290	8.392	6.836	5.402	4.458	3.732
γ_2''	1.002	1.006	1.013	1.032	1.059	1.091
Equilibrium constant, K (atm ^{-1/2})	5.398	3.611	2.597	1.917	1.569	1.345
ΔG_f° for LiH(1) (kcal/mol)	-3.294	-2.634	-2.041	-1.448	-1.030	-0.694
Sieverts' constant, K_s [Torr ^{1/2} (at.fr.H) ⁻¹]	34.0	45.8	58.6	73.4	85.1	95.4

^aFor N's and γ 's the superscripts ' and '' indicate the low and high limits of the miscibility gap; for α 's and β 's the same superscripts refer to the first and second rising portions of the isotherms. Subscripts 1 and 2 refer to Li and LiH, respectively.

Fig. 1. Temperature Dependence of the Miscibility Gap Boundaries for the Li-LiH System

2. Plateau Dissociation Pressures

A review of the literature on the plateau-pressure data for the Li-LiH system has been made elsewhere.⁵ The results obtained in this study and those in the recent work of Heumann and Salmon⁶ (700 to 804°C) are shown in Fig. 2. With the exception of their lowest temperature point (omitted from the least-squares analysis), the agreement between the two studies is remarkable. The data of older work appear to be less reliable and are excluded.

The combined data of Fig. 2 may be represented by

$$(700-903^{\circ}\text{C}) \quad \log P = 9.176 - 7464 T^{-1} \quad (10)$$

with a 1.5% uncertainty (95% confidence level) in the predicted mean value of P , where P is the plateau pressure in Torr.

Fig. 2. Temperature Dependence of the Plateau Pressures for the Li-LiH System

* Datum Point not Included in the Least-Squares Analysis

3. Activity Coefficients

Because of the width of the miscibility gap, it is difficult to generate a single set of activity coefficients that would satisfy the data for both terminal solutions and still maintain reasonable extrapolated values within the miscibility gap. As an alternative, we chose to disregard the miscibility-gap problems and to obtain precise activity coefficients separately for each terminal solution. Therefore, the data of the first and second rising portions of the isotherms were separately curve-fitted to the analytical form of Eq. 6. For each temperature, Table 2 lists α' , β' , α'' , and β'' , calculated from the coefficients in Eq. 6, and the activity coefficients γ_1' and γ_2'' , obtained from Eqs. 5a and 5b. The unlisted values of γ_2' and γ_1'' can also be calculated from the same equations. (The significance of the superscripts ' and '' is explained in the footnote under Table 2.)

4. Equilibrium Constant and Standard Free Energy of Formation of LiH(l)

The equilibrium constant, K , can be evaluated from Eq. 2 by choosing a singular point on an isotherm for which the values of N 's, γ 's, and P are readily available. Such singular points occur at either of the two miscibility-gap limits. Thus, at the lower limit,

$$K = \frac{N_2' \gamma_2'}{N_1' \gamma_1' \sqrt{P}(\text{plateau})} \quad (11)$$

Since the activity of component 2 remains constant across the gap, *i.e.*, $N_2' \gamma_2' = N_2'' \gamma_2''$, Eq. 11 is equivalent to

$$K = \frac{N_2'' \gamma_2''}{N_1' \gamma_1' \sqrt{P}(\text{plateau})} \quad (12)$$

where both γ 's, at their respective miscibility-gap limits, refer to the solvent rather than the solute. This choice for γ 's is convenient because their values are never far removed from unity and can be precisely determined from the data.

The equilibrium-constant data, plotted in Fig. 3, may be represented by the equation

$$(710-903^\circ\text{C}) \quad \log K (\text{atm}^{-1}) = 2.944 + 3615 T^{-1} \quad (13)$$

with a 0.6% error (95% confidence level) in the mean value of K . The corresponding expression for the standard free energy of formation of liquid LiH is (cf. Eq. 3)

$$(710-903^\circ\text{C}) \quad \Delta G_f^\circ (\text{cal/mol}) = 13.47 T - 16,545 \quad (14)$$

A comparison is made in Fig. 3 between K values obtained in this study and those derived from the JANAF tables.⁷ The agreement is good, considering that the JANAF values are based on calorimetric data alone.

Fig. 3. Temperature Dependence of the Equilibrium Constant for the Reaction $1/2 \text{H}_2(\text{g}) + \text{Li}(\text{l}) \rightleftharpoons \text{LiH}(\text{l})$

5. Sieverts' Constants

The data of the first rising portions of the isotherms can be reliably extrapolated into the dilute-solution region to yield the Sieverts' law constants, K_S , for hydrogen in lithium. They were calculated from Eq. 7 with $\alpha = \alpha'$, $\beta = \beta'$, K evaluated from Eq. 13, and $N_2 \cong N_H$, the atom fraction of hydrogen. The data may be fitted to a linear equation

$$(710-903^\circ\text{C}) \quad \log K_S [\text{Torr}^{1/2} (\text{at.fr.H})^{-1}] = 4.263 - 2685 T^{-1} \quad (15)$$

with a 0.9% uncertainty (95% confidence level) in K_S . A plot of $\log K_S$ vs. $1/T$ is shown in Fig. 4.

Fig. 4. Variation of Sieverts' Law Constant with Temperature for the Li-LiH System

The knowledge of the Sieverts' constants for the hydrogen isotopes is of particular importance in the Controlled Thermonuclear Research programs. Recently, we have initiated similar experiments for the Li-LiD system.

B. Gravimetric Studies of Hydrogen-Metal Systems (V. A. Maroni, R. M. Yonco)

Gravimetric studies of the lithium-lithium hydride system have continued. Our current efforts are directed toward investigation of lithium samples encapsulated in niobium or niobium-alloy ampoules. (All of our prior measurements of hydrogen solubility in lithium by tensimetric or gravimetric methods were made using iron capsules.) The purposes of these investigations are to determine the solubility of lithium hydride in lithium below the monotectic⁴ (~685°C) and to investigate interactions of container materials with solutions of hydrogen in lithium. Because the hydrogen permeability of niobium-base materials is much greater⁸ than that of iron over the temperature range of interest (400-700°C), we expect considerably shorter equilibration times than were required in previous experiments with iron capsules.

In preparation for studies of the solubility of hydrogen in niobium-encapsulated lithium samples, tests were made of the hydrogen-uptake characteristics of pure niobium at temperatures that will be of interest in our examinations of the solubility of lithium hydride in lithium. The gravimetric apparatus used in these tests was described in the preceding semiannual report.² A piece of high-purity seamless niobium tubing (Fansteel Metals Company, 99.8%) 3 in. long, 1/2-in. OD, and 20-mil wall thickness was suspended from the balance beam with narrow gauge platinum wire and heated to the desired temperature of the experiment. The apparent weight of the sample, $W(\text{He})$, was then determined at a number of helium pressures, $P(\text{He})$, between 1 and 121 Torr. [A plot of $P(\text{He})$ vs. $W(\text{He})$ gave a smooth curve.] Next the helium was pumped out of the balance, hydrogen was introduced to the sample, and the sample was allowed to reach a constant weight, $W(\text{H})$, at a number of hydrogen pressures between 1 and 121 Torr. Correction factors for the upward force on the sample due to thermomolecular effects were determined by replacing the niobium tube with a platinum tube of the same dimensions and recording the apparent weight of the platinum tube first in helium and then in hydrogen at a series of pressures between 1 and 121 Torr. (Platinum does not absorb or occlude a measurable amount of hydrogen at the temperatures and pressures used in our studies.⁹) The difference between the apparent weight of the platinum tube in hydrogen and its apparent weight in helium, ΔW , at a given pressure, P , was determined and a plot of ΔW vs. $\sqrt{P}$ was made. (This plot also yielded a smooth curve.)

The amount of hydrogen dissolved in the niobium was determined using Eq. 16:

$$\text{Weight of H in Nb} = W(\text{H}) - W(\text{He}) - \Delta W \quad (16)$$

where the values of $W(\text{H})$, $W(\text{He})$ and ΔW are taken for the same temperature and pressure. Data obtained at 664 and 612°C are compared with the results of Veleckis and Edwards¹⁰ in Fig. 5. The excellent agreement

Fig. 5. Pressure-Composition Data for the Niobium-Hydrogen System at 664 and 612°C

between our data and the curve determined from Eq. 7 of the paper by Veleckis and Edwards confirms the utility of the gravimetric method for determining hydrogen solubilities in metals, and indicates that the sensitivity of the technique will be sufficient to permit precise corrections for the hydrogen dissolved in a niobium ampoule containing lithium.

C. Physicochemical Studies of the Lithium-Nitrogen System

Previous considerations¹¹ regarding the problems of operating lithium-blanketed fusion reactors indicate that the compatibility of lithium with structural materials may be changed drastically by small amounts of dissolved impurities such as nitrogen, oxygen, and carbon. Of these impurities, nitrogen is one of the most common contaminants found in lithium--the only alkali metal known to form a stable nitride by direct combination of the elements.¹² It is also worthy of note that experiments with thermal-convection lithium loops¹³ fabricated using Nb-1% Zr (an alloy considered to have merit as a fusion-reactor structural material) indicated preferential movement of zirconium and nitrogen between heated and cooled regions. In light of these observations and in view of the present state of knowledge concerning the thermodynamics of the lithium-nitrogen system (as discussed below), we have initiated a series of studies of the physicochemical properties of this binary system.

1. Studies of the Solubility of Nitrogen in Liquid Lithium (E. Veleckis)

A literature survey has revealed three studies related to the solubility of Li_3N in lithium. Bolshakov *et al.*¹⁴ obtained a major portion of the Li- Li_3N phase diagram by thermal analysis. They reported a temperature horizontal (eutectic) at 185°C , a liquidus line that extended up to 100% Li_3N , and the melting point of Li_3N (815°C). Concurrently with the Russian work, Hoffman¹⁵ determined the solubility of Li_3N at 50-degree intervals from 250 to 450°C by sampling lithium melts saturated with solid Li_3N . More recently, Weatherford *et al.*¹⁶ made observations of the freezing-point lowering due to additions of Li_3N to lithium. They reported an apparent eutectic composition of 3.0×10^{-3} mol % Li_3N , corresponding to a freezing-point lowering of 0.16°C below the melting point of lithium, which they determined to be at 181.8°C . Since the most widely accepted value¹⁷ for the melting point of lithium is 180.6°C , the eutectic temperature can be taken to be 180.4°C . (The high value for the eutectic reported in the Russian work, 185°C , is probably in error.)

The data of the three studies are plotted in Fig. 6 as mol % Li_3N vs. $1000/T$. The figure shows some inconsistencies. For example, the trend in the lower-composition points of Bolshakov *et al.* would result in a higher (50x) Li_3N content in the eutectic than that reported by Weatherford *et al.* Hoffman's data, despite their large scatter, tend to support Weatherford's value. The curve in Fig. 6 gives preference to the thermal data¹⁴ at higher concentrations and to the sampling data^{15,16} in the more dilute region. We have included the curve in an attempt to make what might be a reasonable compromise in the existing data, particularly in view of the observation (based on our experience) that the thermal-analysis results of Bolshakov *et al.* in the 10 to 1 mol % Li_3N region are likely to be in error due to undercooling effects resulting from the rapid drop in solubility with temperature in this region. In any case,

Fig. 6. Comparison of Literature Data for the Solubility of Li_3N in Liquid Lithium

it is quite clear from the data in Fig. 6 that the current state of knowledge of the lithium-nitrogen system is inadequate in providing reliable information on the solubility of Li_3N in lithium. For this reason, we have initiated a study to redetermine the solubility of Li_3N in lithium in the temperature range 200–800°C. The study is intended to resolve discrepancies among the previous investigations and to generate more reliable data, especially in the dilute-solution ranges. The results of this study will be reported in forthcoming progress reports.

2. Preparation and Characterization of High-Purity Li_3N (R. M. Yonco, V. A. Maroni)

An important part of the program to examine the thermodynamics of the lithium-nitrogen system is the preparation and characterization of high-purity Li_3N . This material will be used in studies of the solubility, melting point, heat of formation, and heat capacity of Li_3N .

Li_3N is a difficult material to prepare and maintain in a high-purity form, because it is extremely reactive with air and moisture and is easily oxidized. A review of the literature on preparative methods indicated two general procedures for the synthesis of Li_3N : (1) direct reaction of the elements at temperatures between 25 and 800°C using up to 8 atm of nitrogen pressure^{12,18-20} and (2) reaction of lithium metal with liquid ammonia, accompanied by continuous removal of the evolved hydrogen.¹⁹

For the purposes of our anticipated needs, a method along the lines of procedure (1) above was selected. The apparatus developed for this method is shown in Fig. 7. Prior to each experiment the furnace

Fig. 7. Apparatus for the Preparation of Li_3N

tube and empty cups were baked out at 300°C under vacuum. All subsequent handling of the open furnace tube (loading, etc.) was done in a helium-atmosphere glovebox. In a typical experiment, lithium from a fresh ingot (Foote Mineral Co., 99.9+%) was melted in a tantalum crucible. Droplets of molten lithium were bottom-poured through a hole in the underside of the crucible by manipulating a tantalum plug which was inserted in the hole to prevent continuous flow of the lithium. The droplets were allowed to grow into spherules with a mean diameter of ~ 1 cm, at which point they were quenched on a tantalum plate. This procedure was carried out at the lowest possible temperature to minimize the amount of dissolved impurities in the lithium. The solid spherules formed in this way were completely free of surface oxide.

About 100 of these spherules were placed in a stainless steel cup, the cup was inserted in the furnace tube, and a second stainless steel cup containing some freshly poured sodium was placed above the lithium spherules as shown in Fig. 7. (The purpose of the sodium is to provide a getter for oxygen which may enter the furnace tube during a preparation run.) The lid was then bolted to the furnace tube, and the

entire assembly was removed from the glovebox and attached to the nitrogen supply system. After evacuating the furnace tube, the lithium was heated to the desired temperature, and ~ 8 atm of nitrogen (ultrahigh-purity grade, Liquid Air, Inc., containing <10 ppm $O_2 + H_2O$) was introduced. Preparations were carried out at several temperatures between 25 and $180^\circ C$. In all cases, the reaction proceeded rapidly and was nearly complete after 4 hr. However, to insure complete reaction, the nitrogen pressure was maintained at ~ 8 atm for at least 24 hr. Chemical analyses performed on several preparations typically showed the products to be 99+% lithium and nitrogen by weight, with Li/N atom ratios of 3.015 ± 0.005 . Oxygen levels (when the sodium getter was employed) were always below 0.2 wt %.

We are currently conducting experiments to determine the optimum temperature for carrying out this reaction. In the meantime, sufficient quantities of high-purity Li_3N have been prepared for the solubility and thermochemical studies.

D. Scoping Studies of Fusion Reactor Subsystems

The work* described in this section was initiated during the past year as part of two cooperative controlled-thermonuclear-research conceptual-design studies, one involving ANL and Los Alamos Scientific Laboratory (LASL), and the other involving ANL and the Princeton Plasma Physics Laboratory (PPL). The objectives of this work were to conceive and evaluate methods for the recovery and handling of tritium in conceptual fusion power plants and to begin developing models for the distribution, migration, and leakage of tritium in such plants.

1. Tritium Recovery from Liquid Lithium Blankets (V. A. Maroni)

A number of recent studies²¹⁻²⁵ have addressed the problems associated with tritium management in fusion power plants. A significant conclusion drawn from these studies (and numerous earlier ones) is that tritium losses resulting from its permeation through the heat-transfer circuits could present a serious obstacle to the demonstration of the environmental acceptability of thermonuclear power. This is particularly true for D-T-fueled reactor concepts with liquid-lithium blankets and niobium-alloy structures, because of the relatively high hydrogen permeability of niobium^{23,25} and the appreciable solubility of hydrogen in lithium.²

At least two avenues of approach appear to exist toward solution of this problem. One is to develop multilayered materials for use in construction of heat-exchanger walls. These laminated materials would be fabricated so that at least one of the layers consisted of a contiguous, relatively impermeable (to hydrogen) substance. The other avenue of approach is to devise a process which is, for all practical purposes, infinitely efficient in removing tritium from lithium. The latter approach should be favored because it reduces the driving force for permeation by minimizing the inventory of tritium in the lithium,

* Support for this work was provided by funds obtained through ANL's Engineering Division (ENG).

but in all probability both approaches will have to be employed.

It does not appear that methods which involve evaporation²⁶ (distillation), gas sparging,²⁴ or mechanically pumped permeable membranes²⁴ will sufficiently reduce the tritium concentration in lithium so as to bring the tritium partial pressure down to an acceptable level ($\leq 10^{-10}$ Torr). Schemes that employ a solid, hydrogen-gettering substance in intimate contact with the lithium look promising²⁴ from the standpoint of reducing the tritium concentrations in the lithium, but practical methods for regenerating the getter need to be developed.

A process familiar to fission reactor fuel processing, which may have application in fusion devices, involves removal of fuel materials from liquid metals by extraction with a molten salt.^{27,28} With regard to lithium-blanketed fusion reactors, it appears possible to extract lithium hydride (LiH) from lithium, using a lithium chloride-containing molten salt. In Fig. 8, we have plotted pressure-composition data for the LiH-LiCl and LiH-Li systems. The LiH-LiCl data (which have been liberally extrapolated over four orders of magnitude in composition) were determined as part of the lithium-hydrogen galvanic-cell program.²⁹ The data for LiH in Li were recently obtained in our ongoing study of the thermodynamics of the LiH-Li system. The curves in Fig. 8 imply a molar distribution coefficient for LiH between LiCl and Li of about six at 597°C. If the extrapolation is reasonably accurate and holds for the distribution of LiT between LiCl and Li, then it should be possible, in principle, to obtain a high tritium recovery rate and a very low steady-state inventory of tritium in the blanket by an extraction process. Figure 9 shows schematically how this process might be applied to a fusion reactor. The low-temperature lithium ($\sim 410^\circ\text{C}$) and the lithium halide salt are fed simultaneously into a centrifugal contactor where they are intimately mixed to effect an equilibrium separation of the LiT and then separated by centrifugal force. With adequate staging of the centrifugal sector, a complete separation of the lithium and the salt should be possible, because, at the temperatures of interest (400-600°C), the specific-gravity ratio of the salt to the liquid metal is more than three. The salt phase (containing most of the LiT) is then circulated to a processor and the tritium is either removed electrochemically (by operating the lithium/hydrogen galvanic cell in reverse) or sparged from the salt using DCl ($\text{DCl} + \text{LiT} \rightarrow \text{LiCl} + \text{DT}$). Procedures for collection and further processing of the evolved tritium have not been fully worked out, but on the surface, they appear to be relatively straightforward. A thorough analysis of this scheme in terms of materials problems, mutual solubilities, consequences to the overall neutronics of the blanket, the actual distribution coefficients, and selection of the optimum salt (constituents and composition) remains to be performed.

2. Studies of Tritium Distribution and Migration in Fusion Reactors (V. A. Maroni, E. Veleckis)

In the work conducted under this task, an attempt was made to evaluate the distribution and leakage profiles for tritium in two reference fusion reactor models--the PPL Tokamak Design,³⁰ and the LASL- θ -Pinch Design.³¹ The results of this study are expected to make a substantial contribution to the evaluation of important system features of these designs, such as hazards analysis, environmental impact, operational procedures, maintenance, and cost analysis.

Fig. 8. Solubility of Lithium Hydride in Lithium and in Lithium Chloride vs. Partial Pressure at 597°C

Fig. 9. Blanket Processing Loop for a Lithium-Cooled D-T Fusion Reactor

The motivation for investigating the location and quantities of tritium in currently conceived D-T-fueled fusion reactors can be simply stated as follows: Prototypical fusion power plants will require tritium inventories in excess of 10^7 Ci and it is likely that the permissible level for tritium release to the environment from such plants will be limited to about 1000 Ci/yr.²¹ This corresponds to a daily loss rate of 1 ppm or less of the total inventory. Based on anticipated standards, tritium releases in excess of the above figure could begin to constitute an objectionable radiologic hazard to the environment.

The important properties of the hydrogen isotopes that will determine their distribution and leakage characteristics in currently conceived fusion reactors are their solubilities in the materials with which they come in contact, their diffusion rates through the working fluids and structural components, and the stable chemical forms in which they exist. The formalisms which permit us to express these properties in terms of parameters that we expect to control are briefly outlined below.

To make a reasonable estimate of the tritium held up (dissolved) in the structure and fluids, we must have expressions for the solubility of tritium in the materials of construction. For the case of dilute solutions of gaseous hydrogen (H_2, D_2, T_2) in metals, the relationship between solubility and pressure is given by Sieverts' law

$$C = K_s \cdot \sqrt{P} \quad (17)$$

where C is the concentration, P is the H_2 partial pressure, and K_s is the Sieverts' constant. It can be further shown that K_s is exponentially dependent on temperature, hence the general expression relating concentration to H_2 pressure and temperature is given by

$$C = K_s^0 \cdot \sqrt{P} \cdot \exp (Q_s / kT) \quad (18)$$

in which K_s^0 is a constant, Q_s is the enthalpy of solution of hydrogen in the metal, k is the Boltzmann factor and T is the absolute temperature.

The solubilities of the important tritium-bearing species in a molten-salt blanket fluid (HT, T_2, TF , etc.) are directly related to their partial pressure in accord with Henry's law and can be expressed as follows:

$$C = K_H \cdot P \quad (19)$$

where C and P are the concentration and pressure of a given species in the blanket, and K_H is the Henry's law constant for that species. Since K_H is an exponential function of temperature, the general expression which relates concentration to temperature and pressure is given by Eq. 20

$$C = K_H^0 \cdot P \cdot \exp (Q_H / kT) \quad (20)$$

The rates of migration of H, D , and T through structural interfaces are determined from available permeation data for the materials

of construction. The expression which relates permeation to the operating parameters is given by Eq. 21

$$\Phi = \left(\frac{A}{X}\right) \cdot (\sqrt{P_H} - \sqrt{P_L}) \cdot B \cdot \exp(-Q_p/kT) \quad (21)$$

where Φ is the flux of hydrogen through the interface, A and X are the area and thickness of the interface, P_H and P_L are the hydrogen pressures on each side of the interface, ($P_H > P_L$), B and Q_p are parameters related to the material under consideration, and k and T are the Boltzmann factor and absolute temperature. In most cases, only limited data are available for deuterium and tritium permeation through the materials of interest; hence we have (of necessity) estimated the deuterium and tritium permeation rates by using the values of B and Q_p for protium and dividing the result obtained via Eq. 21 by the square root of the mass of the hydrogen isotope of interest.

The properties above, particularly the permeation rates for the hydrogen isotopes, are strongly affected²³ by the nature of the hydrogen-bearing species at various interfaces. Several species, notably H_2 , D_2 , and T_2 , have already been identified²⁵ as being important in any blanket system. The extent to which other species such as HD , HT and DT are formed is, of course, fixed by the concentrations of H_2 , D_2 , and T_2 .

In our study of the hydrogen-isotope distribution and migration characteristics of the two reference design models, we treat those primary reactor systems which come in contact with the most significant quantities of tritium, *i.e.*, the primary fuel loop, the blanket, and the heat-transfer and energy-conversion circuits. The important subsystems of each of these main systems are listed in Table 3. The hydrogen-isotope inventories and migration rates for these subsystems can be divided into N isothermal zones in such a way that the temperature drop, ΔT , across each zone is relatively small. (A ΔT of about $40^\circ C$ is used in most calculations.) The fractional area of a particular subsystem in each temperature zone is established by the temperature profile over the entire subsystem. In the calculational model, the subsystems are considered to fall into one of two categories--isobaric or interfacial. The isobaric systems are those throughout which the chemical activities, and hence the partial pressures of the hydrogen-bearing species, are assumed to be constant (*e.g.*, the blanket fluid). The interfacial subsystems are those through which there is a hydrogen concentration gradient (*e.g.*, heat-exchanger walls) and consequently a net flow of hydrogen through the interface. In most cases, we assume that the partial-pressure drop across the interface is greater than tenfold (*i.e.*, $P_H/P_L > 10$). As a result of this assumption, the concentration of each hydrogen isotope in the structural material of an interfacial subsystem is roughly one-half* that calculated by Eq. 17.

To calculate the amount of dissolved hydrogen, $S(I)$, in the I^{th} temperature zone, we use Eq. 22

$$S(I) = F(I) \cdot A \cdot X(I) \cdot d \cdot 0.5 \cdot (\sqrt{P_H} + \sqrt{P_L}) \cdot K_s^\circ \cdot \exp[Q_s/kT(I)] \quad (22)$$

* The average concentration in the interfacial material, C_{AVG} , is approximately given by

$$C_{AVG} \approx 0.5(\sqrt{P_H} + \sqrt{P_L}) \cdot K_s$$

TABLE 3. Important Reactor Systems and Subsystems
To Be Mapped for Hydrogen Isotopes

I. Primary Loop Processing System

Subsystems	Fuel Make-Up Equipment
	Injector
	Divertor
	Ducting to Vacuum Pumps
	Vacuum Pumps
	Compressor
	Isotope Separator
	Fuel Storage Container

II. Blanket System

Subsystems	Blanket Fluid
	Vacuum Wall (First Wall)
	Blanket Outer Wall
	Structural Material in the Blanket
	Coolant Ducts in the Blanket

III. Heat-Transfer and Energy-Conversion System

Subsystems	Outlet Ducting from Blanket to Heat Exchanger
	Inlet Ducting from Heat Exchanger to Blanket
	All Heat-Exchanger Walls
	All Ducting in the Heat-Transfer Equipment

where $F(I)$ = the fraction of the total interface area in the I^{th} zone,
 A = the total interface area,
 $X(I)$ = the thickness of the interface in the I^{th} zone,
 d = density of the interface material,
 $T(I)$ = the absolute temperature of the I^{th} zone,
and K_s° and Q_s are as given for Eq. 18.

The rate of hydrogen permeation, $\text{PERM}(I)$, through the interface in the I^{th} temperature zone is determined using Eq. 23

$$\text{PERM}(I) = \frac{A \cdot F(I)}{X(I)} (\sqrt{P_H} - \sqrt{P_L}) \cdot B \cdot \exp [-Q_p / kT(I)] \quad (23)$$

where the parameters on the right-hand side are the same as those defined for Eqs. 21 and 22.

The $S(I)$'s and $\text{PERM}(I)$'s are then summed over the N temperature zones to give the total concentration, C , and permeation rate, Φ , for the subsystem being investigated,

$$C = \sum_{I=1}^N S(I) \quad (24)$$

and

$$\Phi = \sum_{I=1}^N \text{PERM}(I) \quad (25)$$

Equations 22 through 25 were programmed into a computer code so that the large number of tedious calculations which needed to be made for the subsystems listed in Table 3 could be carried out rapidly. Another advantage of programming the calculations in this way is that it has been possible to test a large number of variations of dimensional and operational parameters for the reference models.

A sample computer output for the type of calculation being conducted under this task is shown in Table 4. This particular study was carried out for the heat-exchanger wall between the lithium circuit and the sodium circuit of the LASL- θ -Pinch Design as shown in Fig. 9. (The importance of understanding the solution and permeation characteristics of the hydrogen isotopes--particularly tritium--at these interfaces has been stressed above.) Those input data which determine the temperature profile, solubility, and permeability are listed under the caption in Table 4. Item 1 (in Table 4) gives the calculated temperature profile for the case selected in terms of the fractional area in each temperature zone. Item 2 contains a tabulation of the amount of tritium dissolved in each temperature zone (column 5) and a running summation of the cumulative tritium dissolved in the wall (column 6). Item 3 contains a tabulation of the tritium permeation rate in each temperature zone (column 4) and a running summation of the cumulative permeation rate through the wall (column 5).

TABLE 4. Sample of Typical Computer Output

TRITIUM MAPPING STUDY OF THE LITHIUM/SODIUM HEAT EXCHANGER
FOR THE LASL THETA PINCH DESIGN: MATERIAL=NIObIUM

NUMBER OF TEMPERATURE ZONES 8
 LOWEST TEMPERATURE 410.0 DEG C
 HIGHEST TEMPERATURE 541.0 DEG C
 SOLUBILITY CONSTANTS: KS = 6.000E-01 WPPM H/SQRT(TORR)
 QS = 8430. CAL/MOLE
 PERMEABILITY CONSTANTS: B = 2.700E-02 G-CM/SQ CM-DAY-SQRT(TORR)
 QP = 5200. CAL/MOLE
 UPSTREAM HYDROGEN PARTIAL PRESSURE 1.0E-11 TORR
 DOWNSTREAM HYDROGEN PARTIAL PRESSURE 0.0 TORR
 SURFACE AREA OF THE INTERFACE 3.7E 08 SQ CM
 THICKNESS OF THE INTERFACE 0.090 CM
 VOLUME OF THE INTERFACE STRUCTURE 3.34E 07 CU CM
 DENSITY OF THE INTERFACE MATERIAL 8.40 G/CU CM
 WEIGHT OF THE INTERFACE STRUCTURE 2.81E 08 G

ITEM 1. TEMPERATURE ZONING OF THE INTERFACE

ZONE	AREA FRACTION IN EACH ZONE	CUMULATIVE AREA FRACTION	AREA OF EACH ZONE (SQ CM)	AVERAGE TEMPERATURE (DEG C)
1	0.05	0.05	1.86E 07	413.275
2	0.10	0.15	3.72E 07	423.100
3	0.15	0.30	5.57E 07	439.475
4	0.20	0.50	7.43E 07	462.400
5	0.20	0.70	7.43E 07	488.600
6	0.15	0.85	5.57E 07	511.525
7	0.10	0.95	3.72E 07	527.900
8	0.05	1.00	1.86E 07	537.725

ITEM 2. HYDROGEN CONTENT OF THE INTERFACE STRUCTURE AT 1.0E-11 TORR

ZONE	AVERAGE TEMPERATURE (DEG C)	WEIGHT OF EACH ZONE (G)	HYDROGEN SOLUBILITY (WPPM H)	HYDROGEN IN EACH ZONE (MICROGRAMS)	CUMULATIVE AMOUNT OF H (MICROGRAMS)
1	413.3	1.40E 07	4.59E-04	6.44E 03	6.44E 03
2	423.1	2.81E 07	4.20E-04	1.18E 04	1.82E 04
3	439.5	4.21E 07	3.65E-04	1.54E 04	3.36E 04
4	462.4	5.62E 07	3.03E-04	1.70E 04	5.07E 04
5	488.6	5.62E 07	2.49E-04	1.40E 04	6.47E 04
6	511.5	4.21E 07	2.11E-04	8.91E 03	7.36E 04
7	527.9	2.81E 07	1.89E-04	5.32E 03	7.89E 04
8	537.7	1.40E 07	1.78E-04	2.49E 03	8.14E 04

ITEM 3. HYDROGEN PERMEATION THROUGH THE INTERFACE

ZONE	AVERAGE TEMPERATURE	AREA OF EACH ZONE (SQ CM)	PERMEATION RATE IN EACH ZONE (G/DAY)	CUMULATIVE PERM. RATE (G/DAY)
1	413.3	1.86E 07	3.89E-01	3.89E-01
2	423.1	3.72E 07	8.22E-01	1.21E 00
3	439.5	5.57E 07	1.34E 00	2.56E 00
4	462.4	7.43E 07	2.01E 00	4.56E 00
5	488.6	7.43E 07	2.27E 00	6.84E 00
6	511.5	5.57E 07	1.88E 00	8.72E 00
7	527.9	3.72E 07	1.34E 00	1.01E 01
8	537.7	1.86E 07	6.99E-01	1.08E 01

The set of data displayed in Table 4 allows examination of a number of consequences of the system design. The last number in column 6 of Item 2 and the last number in column 5 of Item 3 give the total dissolved tritium and total tritium permeation, respectively, for the wall. Inspection of column 5 under Item 2 permits one to examine the effect of temperature on total dissolved tritium in a given isothermal zone after the area fractions of the various zones have been properly taken into account. For example, in the case considered in Table 4, Zones 1 and 8 are equal in area; hence, one can see by direct comparison that the amount of tritium per unit area in the coldest zone is roughly three times the amount per unit area in the hottest zone. Similar comparisons relating to the tritium permeation rate can be made from inspection of column 4 under Item 3.

After a series of calculations (like the one in Table 4) for all the important subsystems listed in Table 3, it is possible to develop a model for the behavior of hydrogen isotopes in the particular fusion-reactor design under study. This model in turn reflects other criteria that must be applied in evaluating fuel-recovery schemes and tritium-containment systems. Typically, the hydrogen-isotope partial pressures at each important interface are varied in a manner which permits us to make iterations between specific fuel-processing methods and the degree of containment needed to limit tritium losses.

The overall implications of the results in Table 4 can be analyzed as follows: At a tritium partial pressure in the lithium of 10^{-11} Torr, which corresponds to a tritium concentration of ~ 100 ppb,^{2,32} a niobium heat exchanger operating with the temperature profile given under Item 1 will contain about 800 Ci* of dissolved tritium, but will pass upwards of 10^5 Ci* per day of tritium to the sodium circuit. If the sodium circuit interfaces with a steam system (as is the case for the LASL-0-Pinch Design) and if the amount of tritium permeating into the steam is restricted to ≤ 3 Ci per day ($\leq 0.003\%$ of the amount entering the sodium), serious consideration must be given to processes for recovery of tritium from sodium with high efficiency or (preferably) to methods of reducing the flux of tritium into the sodium.

The text of the computer code used in this study, additional details concerning the philosophy of the calculational model, restrictive assumptions pertinent to each of the reference designs, and the overall results of these analyses will appear in future publications^{30,31} resulting from the two cooperative conceptual design efforts.

* One gram of tritium $\approx 10^4$ Curies.

II. NUCLEATION STUDIES

Our experimental and theoretical studies of bubble nucleation have continued. Bubble nucleation and explosive boiling appear to be significant in safety problems of nuclear reactors, as well as in the transport of liquefied natural gas (LNG) and in the papermaking, steel, and other metallurgical industries. The detailed mechanisms for these dangerous explosions are not yet fully understood.

A. Measurement of the Limit of Superheat of Liquids (G. H. Kucera, T. A. Renner)

The experimental study of the homogeneous nucleation of vapor bubbles has continued with the determination of the limit of superheat of propane in an ethylene glycol-water medium (64:36 vol %). Since these measurements required the handling of liquefied propane, several test runs were undertaken with n-butane to familiarize ourselves with the use of the apparatus at temperatures below 0°C. The vaporization temperature, T_g , of n-butane was found to be $378.3 \pm 0.4^\circ\text{K}$, which agrees favorably with the value ($T_g = 378.2 \pm 0.5^\circ\text{K}$) obtained by Eberhart *et al.* (ANL-7878, p. 9).

Three separate experiments were carried out with propane and the limit of superheat was determined for each run.

<u>Propane T_g ($^\circ\text{K}$)</u>	<u>Number of Measurements</u>
1. 326.2 ± 0.5	98
2. 326.1 ± 0.3	155
3. 326.0 ± 0.3	189

The reduced limit of superheat, T_g/T_c , where T_c is the critical temperature, is 0.882 for propane and is consistent with values of T_g/T_c observed by Eberhart *et al.* (ANL-7923, p. 15) for other normal hydrocarbons.

Chromatographic analyses of the two tanks of propane used in these experiments indicated that the gas samples used in Runs 1 and 2 had parts-per-million quantities of both ethane and an unidentified constituent, whereas the gas samples used in Run 3 had parts-per-million quantities of ethane only. The values of T_g of all three runs are identical within experimental error, which suggests that the unknown component in the first two runs had no observable effect on the measured nucleation temperature.

Our value for the limit of superheat of propane, $326.1 \pm 0.4^\circ\text{K}$, agrees favorably with calculated values. The limit of superheat evaluated from homogeneous nucleation theory³³ is 328.5°K , and a similar value of 329.8°K is obtained from the mechanical stability condition and the equation of state.³⁴

B. Theoretical Calculation of Stability Limits (H. C. Schnyders)

During the course of our (J. G. Eberhart and H. C. Schnyders) previous work^{34,35} on the application of the mechanical stability

condition of thermodynamics [*i.e.*, $(\partial P/\partial V)_T > 0$ for mechanically unstable phases where P , V , and T are the pressure, volume, and temperature of the phase] to a number of equations of state to predict limits of superheat or tensile strength of metastable liquid phases, we discovered that all the empirical and model equations of state we examined³⁵ gave unreasonable predictions of the upper bound to the supersaturation ratio, S_* at temperatures for which experimental data are available. On the other hand, the same equations of state gave fair-to-excellent predictions for the liquid-phase spinodal [the curvilinear path in PVT space along which $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T > 0$], which describes the limit of metastability for the liquid phase beyond which it must transform to the stable vapor phase. This latter success is understandable since all of these equations of state were based, more or less, on the van der Waals uniform average potential concept, which assumes that the molecules experience a constant attractive potential which is proportional to the density. This assumption is good at the high densities found along the liquid-phase spinodal³⁵ which describes an upper bound to the limit of superheat or tensile strength of the liquid phase. However, the vapor-phase spinodal traces a path through the low-density regions of PVT space along which $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T > 0$. At these densities the uniform average potential concept is unrealistic, but the assumption of pairwise additivity of forces is excellent. All one needs to generate reasonable PVT properties in the neighborhood of this spinodal is a physically realistic pairwise interaction potential. We have chosen the Lennard-Jones potential because the PVT properties of this fluid have been calculated "exactly" (with the assumption of pairwise additivity of forces) over a wide range of densities and temperatures in the liquid and dense gas regions of PVT space using Monte Carlo calculational techniques.³⁶ In addition, perturbation theories³⁷ provide an equation of state for this model fluid which is in very good agreement with the Monte Carlo calculations and permit the easy evaluation of the pressure of the fluid at almost any desired density in the fluid phase.

Significantly, the Monte Carlo calculations³⁶ have also been carried out in metastable regions of the Lennard-Jones fluid (see Fig. 2 of Ref. 35) by the imposition of a constraint which suppresses large fluctuations in density. This constraint is essential, since, if it were not imposed, states representing the equilibrium two-phase system would be included in the ensemble over which the statistical averages of the properties of the system are taken. The local maximum, P_{CS} , in the pressure along the van der Waals loop (see Fig. 10) of the Lennard-Jones isotherm represents an upper bound to supersaturation (with the possible exception of transient supersaturations achieved in supersonic nozzle experiments) at a given temperature. For this model the ratio of P_{CS} to the equilibrium vapor pressure, P_e , is the critical supersaturation ratio, S_m . The quantities P_{CS} and P_e were both determined from the calculated properties of the Lennard-Jones fluid and were reduced by the known critical pressure for the Lennard-Jones fluid. The calculated critical properties of the Lennard-Jones fluid are $P_c = 0.148 \epsilon/\sigma^3$, $kT_c = 1.36\epsilon$, and $\rho_c = 0.36/\sigma^3$, where ϵ and σ are the energy and length parameters characterizing the familiar Lennard-Jones pair potential

* The supersaturation ratio is defined to be the ratio of the pressure of the supersaturated (metastable) vapor, P_s , to the equilibrium vapor pressure, P_e , of the liquid.

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (26)$$

and r is the internuclear separation of a pair of molecules. All the PVT properties of the Lennard-Jones fluid have been reduced by the critical properties for this fluid, as given above. The critical supersaturation ratios, *i.e.*, S_m , for the Lennard-Jones, van der Waals,³⁸ and Berthelot³⁸ equations of state are given, respectively, in the third, fourth, and fifth columns of Table 5 as a function of the reduced temperature, $\theta = T/T_c$, where T_c is the critical temperature of the fluid. The second column of the table gives our calculated results for the reduced vapor pressures $\Pi_v = P/P_c$, of the Lennard-Jones fluid. The critical values of S at which the liquid phase appears in supersaturated vapors³⁹ of *n*-hexane and *n*-octane are presented in columns six and seven of Table 5. The values of S_m^{LJ} for the Lennard-Jones fluid are about a factor of 2 or 3 larger than the experimental measurements of the critical supersaturation ratio in *n*-hexane and *n*-octane. This correspondence is approximately what is expected when one considers the work of Strickfaden and de Sobrino.⁴⁰ These authors studied the growth of liquid droplets in the metastable vapor phase of the van der Waals fluid by the solution of a Boltzmann-type transport equation. They found that the homogeneous nucleation of the liquid phase occurs at an appreciable rate at super-

Fig. 10. Schematic Diagram of a Model Isotherm Showing the Equilibrium Vapor Pressure, P_e , and the Critical Supersaturation Pressure, P_{cs} . (The critical supersaturation ratio is defined as $S_m = P_{cs}/P_e$.)

TABLE 5. The Reduced Temperature Dependence of Critical Supersaturation Ratios for Model Fluids,^a n-Hexane, and n-Octane

Reduced Temperature, θ	Reduced Pressure, π_v	S_m^{LJ}	S_m^v	S_m^B	S (n-Hexane)	S (n-Octane)
0.404	8.642×10^{-4}	92.60				
0.42						25
0.441	2.385×10^{-3}	41.9				
0.45			11		8	14.7
0.478	5.581×10^{-3}	21.94				
0.50			6.4	900	4.8	7
0.515	1.144×10^{-2}	12.95				
0.55		8.34	4.4	170	3.2	
0.588	3.63×10^{-2}	5.769				
0.60			3.2	40		
0.625	5.808×10^{-2}	4.22				
0.65			2.7	15		

^a LJ = Lennard-Jones model fluid
v = van der Waals equation of state
B = Berthelot equation of state

saturation pressures which are factors of two to three less than the upper bound values we derive from the equation of state. This correspondence adequately demonstrates that the mechanical stability condition may be applied to equations of state which are accurate in the metastable vapor-phase regions to provide reliable upper bounds to critical supersaturation pressure, and if accurate pair potentials were known for the substance in question, the kinetic equations could conceivably be solved numerically to give good estimates of critical supersaturations to be achieved in actual experiments.

Even though the supersaturation ratios correspond well with experimental results, the vapor pressures and critical supersaturation pressures for the Lennard-Jones fluid are much higher (factors of ten to one hundred) than the experimental ones at these low temperatures (near the triple point). Among other things, this indicates that the Lennard-Jones potential is not a good effective potential for the calculation of thermodynamic properties of normal hydrocarbons, whereas the supersaturation ratio, being a relative property, appears to mimic their behavior. However, a convincing demonstration can be given for the proposition that the mechanical stability condition of thermodynamics may be applied to accurate equations of state for the prediction of absolute upper bounds to the supersaturations that can be achieved in metastable vapors. The local maximum in the "van der Waals-type loop" at a subcritical isotherm is the point at which the fluid becomes mechanically unstable ($\partial P/\partial V > 0$) upon a further increase in pressure, and the stable liquid phase must form. This point on the isotherm is the maximum attainable supersaturation.

According to classical homogeneous nucleation theory,⁴¹ the homogeneous nucleation rate $J(P, T)$, defined to be the number of critical-sized liquid- (or solid-) phase nuclei formed per cubic centimeter per second, is proportional to the quantity $G^+(n^*, P, T) \exp[-G^+(n^*, P, T)/k_B T]$. $G^+(n, P, T)$ is the Gibbs free energy of formation for a liquid- or solid-phase cluster of n molecules from n monomers in the vapor at the same temperature T and pressure P . The number of molecules in the critical-sized cluster is n^* , and $G^+(n^*, P, T)$ has its maximum value for this cluster. McGinty⁴² has evaluated G^+ for microcrystals of molecules interacting via pairwise Lennard-Jones forces (Eq. 26) for sizes of $n = 2$ to 100, using molecular dynamics techniques. The total partition function for the cluster is assumed to be separable into translational (center of mass), rotational, and vibrational (harmonic approximation) partition functions. (The interested reader is referred to the original paper⁴² for further details). From our point of view, the significance of this work is that a kinetic theory of homogeneous nucleation is used to predict critical supersaturation pressures for a model fluid (Lennard-Jones) for which an accurate description of metastable thermodynamic states in the vapor is known from Monte Carlo calculations,⁴³ and is accurately and straightforwardly described by Barker-Henderson perturbation theory in the Percus-Yevick approximation.⁴⁴ As expected, McGinty⁴² found a rapid increase in J from 1 to 100 with an increase of pressure of 10%. Consequently, the estimated critical supersaturation pressure is relatively insensitive to the arbitrary choice of that nucleation rate which corresponds to critical supersaturation. It is conventional to choose that pressure of the vapor at which the rate of nucleation of critical-sized clusters of the stable dense phase, J , is equal to one to be the critical supersaturation pressure, P_s . Using this criterion,

McGinty found a critical supersaturation ratio (the ratio of P_s to P_e , the equilibrium vapor pressure of the condensed Lennard-Jones fluid) of 33 at a reduced temperature of $T^* = k_B T / \epsilon = 0.584$. Our application of the mechanical stability condition to this isotherm for the Lennard-Jones fluid yields an upper bound to critical supersaturation of 52. This result supports the claim that, given an accurate equation of state for the metastable vapor, an accurate upper bound may be calculated for the maximum supersaturation which can be sustained by a metastable vapor before it spontaneously transforms to the stable condensed phase, and that a good estimate of the observed critical supersaturation ratio can be made.

Finally, the reduced superheating (liquid-phase) spinodal for the Lennard-Jones fluid has also been calculated; it is presented in Table 6 (column 3), along with the spinodal derived from the augmented van der Waals (Av) equation of state³⁴ for hard spheres (column 2). The correspondence to the augmented van der Waals equation of state (which is a good representation of reduced limit-of-superheat spinodals for n-hydrocarbons³⁴) is good.

TABLE 6. Reduced Superheating Spinodals for the Augmented van der Waals and Lennard-Jones Fluids

Reduced Temp., Θ	π_{ℓ}^{Av}	π_{ℓ}^{LJ}
1.000	1.000	1.000
0.985		0.887
0.971	0.819	0.786
0.941	0.580	0.560
0.926	0.451	0.436
0.912	0.311	0.306
0.897	0.161	0.169
0.882	0.001	0.025
0.868		-0.126
0.838		-0.447
0.809		-0.793
0.794		-0.976

C. The Role of Bubble Nucleation in Explosive Boiling (M. Blander)

One mechanism for direct contact vapor explosions, which pose a safety problem in nuclear reactors as well as in industry, involves bubble nucleation in superheated fluids. Nucleation theory leads to the prediction that many liquids may be heated to a temperature, T_{ℓ} , which is about 90% of their critical temperature, before bubbles nucleate homogeneously and grow explosively. Such high limits of superheat may be attained if a volatile fluid wets a hot substrate which it contacts accidentally. This leads to the most violent explosion possible by this mechanism. If the hot substrate is wet poorly, then boiling will occur well below the limit of superheat and will be less violent than when wetting occurs. The wetting characteristics are

crucial in determining the relative violence of direct-contact vapor explosions.

When the hot substrate is wet by the volatile fluid such that the wetting angle, θ , is zero, then the fluid will reach the homogeneous limit of superheat. For solid surfaces with cracks and crevices, one is unlikely to achieve the limit of superheat. Consequently, one expects a higher probability for superheat explosions for liquid-liquid, liquid-glass, and liquid-polymer contacts. With these concepts in mind we can examine some examples. If there is no boiling, the temperature, T_i , at an interface between a hot substrate and a fluid is given by

$$T_i = \frac{T_v d_v + T_s d_s}{d_v + d_s} \quad (27)$$

where $d = \sqrt{\kappa \rho C}$, κ is the thermal conductivity, ρ the density (g/cm^3), C the specific heat, v designates the volatile fluid and s the hot substrate. If the volatile fluid wets the hot substrate, film boiling will occur if T_i exceeds the limit of superheat, T_ℓ . The boiling will cool the interface and if T_i then goes below T_ℓ , the volatile liquid may settle down and wet the substrate. This situation may also occur if the initial value of T_i is less than T_ℓ but T_s is greater than T_ℓ . If the volatile fluid layer is not too thick (*i.e.*, not effectively infinitely thick on the time scale of the observations), then T_i will ultimately rise until T_ℓ is reached, at which time the fluid will nucleate homogeneously and boil explosively. The conditions under which this may occur for a mutually immiscible pair are as follows: (a) $T_\ell > T_i \geq$ the temperature at which the substrate freezes. If the substrate freezes, it is likely to contain cracks and crevices and not be completely wetted. Thus T_ℓ should generally be greater than the freezing point (perhaps even the metastable freezing point) of the substrate. (b) θ must be small enough for the probability of homogeneous nucleation to be greater than that for heterogeneous nucleation.

We may apply this to understanding boiling at a hydrocarbon-water interface. The measured value of T_ℓ for propane, for example, is 53°C . Light hydrocarbons which have been measured (below C_9H_{20}) wet liquid water. Consequently, since d for water is larger than for hydrocarbons, one might expect propane to boil explosively when poured on hot water. The explosive boiling of propane on water at temperatures between 53 and 70°C (but not at lower temperatures) has been observed by Enger and Hartman.⁴⁵ The lower limit of 53° is equal to T_ℓ . Analogous observations were made for isobutane. Thus, although the limit of superheat was not reached at the interface in the entire range of temperatures, it was approached in these cases, indicating small wetting angles. For Freon 22 and propylene, the lower temperature of the range for explosions was about 10 - 15° below T_ℓ , indicating a fairly small non-zero wetting angle. On the other hand, methane and ethane did not explode upon contact with water.⁴⁵ For both methane and ethane, the temperatures T_ℓ are low enough for ice to form at the interface. This non-explosive behavior can be understood if the ice is not wet or contains crevices which are not completely wet, as is discussed above.

When liquid methane or ethane was poured onto a higher hydrocarbon (butane, pentane or hexane), explosions always occurred.⁴⁶ These hydrocarbons have a mutual solubility with methane and ethane, so that there

is a continuous range of liquid compositions with each successive layer wetting the layer below it, thereby leading to conditions appropriate for homogeneous nucleation. Explosions may also occur when impure methane or ethane containing propane or butane impurities is poured on water. In some ranges of composition and water temperatures, the initial boiling at the interface will increase the concentration of the higher boiling constituent so that the value of T_ℓ of the composition near the interface is above 0°C . Under these conditions a vapor explosion may occur. To understand this type of explosive behavior, one requires an understanding of the nucleation properties of mixtures.

Eberhart, Kremsner, and Blander⁴⁷ have studied nucleation in hydrocarbon mixtures. The limits of superheat at intermediate compositions are intermediate between the limits of superheat of the end members, and do not deviate greatly from being linear in mole fraction. Thus, if one has a pentane layer wetting a substrate such as water at 25°C and pours liquid methane onto it, the two hydrocarbons will form a solution at the interface and T_ℓ will vary from about 147°C at the water-pentane interface to about -100°C in the pure methane. The initial temperature at the water-pentane interface is, ideally, 25°C and in the methane, about -164°C . Schematic profiles of T_ℓ and T are shown as a solid line in Fig. 11 for an idealized initial state soon after pouring the methane and as dashed lines for a later time. Since T_ℓ is fixed by the composition of the hydrocarbon mixture, the flattening of the profile of T_ℓ will be a function of the magnitude of the interdiffusion coefficients, D , of methane in pentane. The actual temperature, T , will be governed by the magnitude of $\kappa/\rho C$ which is generally much larger than D . Consequently, T will rise and the profile will straighten more rapidly than the profile of T_ℓ and ultimately, at some depth, will become tangent to T_ℓ . The mixture will nucleate at this depth and initiate the vaporization of that liquid which is metastable. The energy released in this initiating explosion will be a function of the total excess energy stored in the metastable hydrocarbon. This is a function of the thermal histories, properties, and compositions of the fluids.

It is possible that the mechanism for the destructive water-smelt explosions caused by leakage of water into a papermaking smelt may be analogous to the mechanism for methane poured on pentane. Smelts are alkali carbonates containing some sulfides. If water in a smelt can form a continuum of liquid solutions ranging from the very hot smelt containing no water to much cooler water containing no smelt (or if there is a compositional gap and the water-rich composition wets the smelt-rich composition), then upon leakage of water into a smelt each successive layer between the two phases wets the one below. If in the state reached (perhaps after some film boiling of the water), the temperature, T , does not exceed T_ℓ anywhere ($300\text{--}310^\circ\text{C}$ for pure water and increasing with the concentration of salt), then the water will not explode. As heat is conducted toward the water, the temperature will rise until, at some intermediate composition, T_ℓ is exceeded. The liquid will nucleate at this point. Sufficient data are not available to check this hypothesis.

Since T_ℓ for sodium in the system sodium-molten UO_2 is below the melting point of UO_2 , the limit of superheat for sodium is probably not reached unless these two materials are mutually soluble or form compounds that form a continuum of liquids between the two phases. No evidence for this exists at present.

Fig. 11. Schematic Idealized Profiles of the Limit of Superheat, T_l , and the Temperature, T , at a Methane-Pentane-Water Interface. (Solid lines represent profiles at an initial time t^0 and dashed lines represent profiles at a later time t' when $T' = T'_l$ at one height above the water interface.)

Even when the limit of superheat is not attained, the explosion can be violent. The violence of the explosion for a given substance is a function of the total enthalpy involved in superheating the liquid before the metastable liquid is nucleated. The closeness of the approach to the limit of superheat will be one factor governing the energy in the initiating explosion. A characteristic of these superheating explosions is the time lag until some portion of the volatile fluid is sufficiently superheated. This time lag permits a large amount of heat to be transferred to the fluid before boiling is initiated and obviates the need for unusual rates of heat transfer. The greater the time lag the closer to the limit of superheat one gets in a given situation and the greater the total energy of the initial explosion. Fragmentation after

the initial explosive boiling will increase surface areas of the volatile fluid, enhancing the total heat transferred to the vaporizing fluid. Thus, nucleation theory permits one to examine a possible mechanism for contact vapor explosions based on approaching the limit of superheat before boiling is initiated. For some hydrocarbons on water or on other hydrocarbons, this initiating mechanism appears likely. For water-smelt explosions, this mechanism is possible, but adequate data are not available for testing this speculation. For the sodium-molten UO_2 system, it appears unlikely that one may achieve the limit of superheat, but data to support this are not available.

If the limit of superheat is reached, then a large fraction of the maximum energy available for an explosion is contained in the metastable fluid before initiation. More energy can be picked up if the initial explosion fragments the fluid, and for any given situation, fragmentation and the enthalpy input are likely to be greater the closer one approaches the limit of superheat. Further detailed studies are required to investigate these hypotheses.

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III. LASER-RAMAN SPECTROSCOPY OF MOLTEN SALTS

(E. J. Hathaway, G. N. Papatheodorou,* V. A. Maroni)

In the past our structure studies of molten salts have been confined to binary systems containing a divalent metal cation, an alkali-metal cation, and a single halide anion.⁴⁸⁻⁵¹ Recent interest⁵² in other charge unsymmetrical systems involving trivalent metal cations has prompted us to carry out a Raman study of a series of molten LaCl_3 -KCl mixtures.

Laser-Raman spectra of seven compositions in the LaCl_3 -KCl system obtained in our laboratory are shown in Fig. 12. The curves for samples

Fig. 12. Laser-Raman Spectra of Molten LaCl_3 -KCl Mixtures. [Curves for $M = 10$ through 53.3 were recorded at 700°C . The curve for $M = 65$ was recorded at its melting point ($\sim 730^\circ\text{C}$). The laser line ($4880 \text{ \AA}$) was polarized perpendicular to the direction of observation.]

containing from 10 to 53.3 mol % LaCl_3 were recorded at 700°C ; the curve for 65 mol % LaCl_3 was recorded near its melting point ($\sim 730^\circ\text{C}$). The $4880 \text{ \AA}$ line of an argon-krypton ion laser was used for excitation, and the spectra were scanned on the anti-Stokes side where the fluorescence background (presumably due to a rare earth element impurity) was less

* Postdoctoral fellow, University of Chicago. The work reported under this task was suggested by Papatheodorou and was performed in conjunction with him.

severe. Other details of the experimental procedure and the instrumentation were the same as reported elsewhere.^{48,49,53}

The spectral changes that take place over the composition range investigated indicate the presence of a complex equilibrium, but the number of species involved can not be determined reliably from a simple inspection of the data in Fig. 12. Studies of the depolarization characteristics of the spectra in Fig. 12 show that the band which peaks near 250 cm^{-1} for the mixtures containing from 10 to 33.7 mol % LaCl_3 is strongly polarized; hence we assume that the complex from which it originates is highly symmetric. Furthermore, this band appears to reach maximum intensity around 25 mol % LaCl_3 in consonance with the contention of other investigators⁵² (based on emf and calorimetric data) that LaCl_6^{3-} is a stable species in $\text{LaCl}_3\text{-KCl}$ melts.

Curve resolution analyses of Raman data collected using both perpendicular and parallel polarized exciting radiation are in progress. The procedures we are using are similar to those used in our previous study of $\text{SnCl}_2\text{-KCl}$ melts.⁴⁹ Results of these analyses will be presented in a subsequent progress report.

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IV. PHASE EQUILIBRIA

The fundamental study of phase equilibria of reciprocal systems has continued in order to derive a deeper understanding of their properties. Such systems are of a general type which are significant in a variety of technologies.

A. Liquidus Temperatures of Reciprocal Systems (M. Blander, M. L. Saboungi)

The conformational ionic solution (CIS) theory⁵⁴ was utilized to calculate liquidus temperatures in the Na, Tl || NO₃, Cl and Li, K || NO₃, Cl systems. The method of calculation has been described,^{54,55} and requires a knowledge of ΔG° , the free energy of the metathetical exchange reaction of the constituent salts; λ_i , the interaction parameters in binary molten salt systems with a common ion *i*; *L*, the heat of fusion; and *T*₀, the melting temperature of constituents. These parameters are available or have been calculated for the systems considered.

The phase diagram for the system Na, Tl || NO₃, Cl has been measured by Luzhnaya.^{56,57} Calculated values of λ_i and of the eutectic compositions of the four binaries are reasonably consistent with other data. The differences in λ_i for the TlCl-NaCl system may reflect some solid solution. From tabulated values of free energies of formation,^{58,59} a value of 5000 cal/mol⁻¹ was calculated for ΔG° (for the reaction TlCl + NaNO₃ $\rightleftharpoons$ TlNO₃ + NaCl), and using this value of ΔG° and the calculated values of λ_i , the phase diagram in Fig. 13 was calculated for comparison with the measured phase diagram in Fig. 14.

The liquidus contours of Fig. 14 for the Na, Tl || NO₃, Cl system are in excellent agreement with the calculated contours of Fig. 13. This system is an intermediate type between those having two ternary eutectics (E-E) discussed previously⁵⁵ and those rare types having one peritectic and one ternary eutectic (P-E). Within the uncertainties in the measurements and the calculations for this system, these can not be distinguished.

The phase diagram for the system Li, K || NO₃, Cl has been measured by Il'yasov and Litvinov.⁶⁰ Calculated values of λ_i and the eutectic compositions are reasonably consistent with other data. For this system $\Delta G^\circ = \sim 0$ and calculations for small values (near zero) for ΔG° exhibited negligible differences in liquidus contours. The calculated liquidus temperatures for $\Delta G^\circ = 100$ cal/mol⁻¹ (for the reaction LiCl + KNO₃ $\rightleftharpoons$ LiNO₃ + KCl) are given in Fig. 15 for comparison with the measurements in Fig. 16. This system is a rare P-E type discussed by Ricci.⁵⁸ As can be seen, this phase diagram is characterized by a ternary peritectic P and a ternary eutectic E. ΔG° is so small that, within the error in its value, one can not be certain whether LiCl + KNO₃ or LiNO₃ + KCl is the stable pair. If LiCl + KNO₃ is the stable pair, the peritectic reaction at P is

and if LiNO₃ + KCl is the stable pair, the peritectic reaction is

The measured phase diagram in Fig. 16 is more complex than the

Fig. 13. Calculated Liquidus Phase Diagram of the Na, Tl || NO₃, Cl System.
ANL Neg. No. 308-3279.

Fig. 14. Measured Liquidus Phase Diagram of the Na, Tl || NO₃, Cl System.
ANL Neg. No. 308-3281.

Fig. 15. Calculated Liquidus Phase Diagram of the Li, K || NO₃, Cl System.
ANL Neg. No. 308-3278.

Fig. 16. Measured Liquidus Phase Diagram of the Li, K || NO₃, Cl System.
ANL Neg. No. 308-3280.

calculated diagram in Fig. 15 because of the reported binary compounds $4\text{LiNO}_3 \cdot \text{LiCl}$, $\text{LiNO}_3 \cdot \text{KNO}_3$ and $4\text{KNO}_3 \cdot \text{KCl}$. The phase fields for these compounds subtend only a small area in the phase diagram, and liquidus temperatures calculated taking these compounds into account would differ little from the calculated diagram in Fig. 15. Except for these small differences, the agreement between the calculated and measured phase diagrams in Figs. 15 and 16 is excellent. Similar calculations for values of ΔG° of 0 and $-100 \text{ cal mol}^{-1}$ ($\text{LiNO}_3 + \text{KCl}$ is the stable pair) differed little from those shown in Fig. 15, indicating that the phase diagram is relatively insensitive to small changes in ΔG° .

The CIS theory leads to excellent predictions of the liquidus temperatures in a broad variety of simple reciprocal molten-salt systems without miscibility gaps. The theory utilizes data for pure salts and for binary systems to calculate *a priori* thermodynamic properties of multicomponent systems. The theory provides insights into the relationship between these thermodynamic parameters for lower order systems and particular topological features in phase diagrams and should be an aid in predictions and interpretations of phase diagrams of reciprocal systems.

B. Miscibility Gaps (M. Blander, M. L. Saboungi, H. C. Schnyders)

We have previously discussed miscibility gaps⁵⁵ and, for some values of the thermodynamic parameters ΔG° and λ , we had encountered problems in computer calculations from the CIS. To gain insight into the source of these problems, we will consider in detail the stable diagonal for a mixture of salts AC-BD for the case in which all the binary interaction parameters (λ) are zero. The shape of the miscibility gaps will be shown to be dependent on the parameter Z, the coordination number, which governs the relative values of the theoretical terms. These considerations provide an insight into the limitations of the theory and its ability to describe real systems, and should be an aid in extending the theory to systems in which deviations from ideality are large enough to exhibit liquid-liquid miscibility gaps.

If AC is component 1 and BD component 2, then the molar free energy of mixing of a mixture of AC and BD is

$$\begin{aligned} \Delta G_m = & X_1 X_2 \Delta G^\circ + X_2^2 X_1 (\lambda_D + \lambda_B) + X_1^2 X_2 (\lambda_C + \lambda_A) + X_1^2 X_2^2 \Lambda \\ & + 2X_1 RT \ln X_1 + 2X_2 RT \ln X_2 \end{aligned} \quad (28)$$

where $\Lambda = -(\Delta G^\circ)^2 / 2ZRT$. The condition for immiscibility on the AC-BD diagonal is that a single plane be tangent at two points on the diagonal to an isothermal plot of ΔG_m versus composition. The compositions at the two tangent points define the miscibility gap at the temperature of ΔG_m . For the case in which all λ 's are zero, because of symmetry, the line is horizontal and the condition reduces to $(d\Delta G_m/dX_2) = 0$. If we define $(\Delta G^\circ/RT) \equiv 1/\tau$, where τ is a reduced temperature and $y \equiv (X_1 - 1/2)$, then we obtain an equation

$$\frac{2y}{\tau} + \frac{y(4y^2 - 1)}{2Z\tau^2} - 2 \ln \left(\frac{y + 1/2}{1/2 - y} \right) = 0 \quad (29)$$

which defines the miscibility gap. Values of the reduced temperature τ , calculated at various compositions for values of $Z = 5.0, 5.5$ and 6.0 , are plotted in Fig. 17. As Z decreases, the top of the curve flattens and for $Z < 5.3$, there is a dip (which can be seen on the curve for $Z = 5.0$). This dip is an artifact of the theory, which has been derived only to second order. As has been discussed,⁵⁴ the higher order terms partly cancel the term in $(\Delta G^\circ)^2$. This can be partly compensated for by using values of Z somewhat larger than structural considerations would suggest. Thus, $Z \geq 5.3$ must be used to obtain thermodynamically consistent results.

The influence of a decrease of Z is to increase the magnitude of the term in Λ relative to the term in ΔG° in Eq. 1 [note that Λ is proportional to $(\Delta G^\circ)^2/Z$]. Similar changes in relative magnitude of the different terms can be effected by changes in the λ terms. For example, for the symmetric case in which

$$\lambda = \lambda_A = \lambda_B = \lambda_C = \lambda_D$$

then

$$\Delta G_m = X_1 X_2 (\Delta G^\circ + 2\lambda) + X_1^2 X_2^2 \Lambda + 2X_1 RT \ln X_1 + 2X_2 RT \ln X_2 \quad (30)$$

When the λ 's are positive, the first term becomes larger relative to the second term on the right-hand side of the equation. This is analogous to an increase of both Z and ΔG° in Eq. 1 such that $(\Delta G^\circ)^2/Z$ is constant. The influence of negative λ 's is equivalent to a decrease of ΔG° and Z [such that $(\Delta G^\circ)^2/Z$ is constant]. We have found in computer calculations that if the λ 's are negative enough, artifacts with $Z = 6$ similar to the plot for $Z = 5$ occur. These artifacts do not occur for cases where λ is positive. Undoubtedly, the inclusion of higher order terms will suppress this artifact. Consequently, without higher order terms, the theory should prove useful for cases where the λ 's are positive or are small relative to ΔG° .

The shapes of the curves in Fig. 17 may be compared with measurements, where available. One of the most carefully measured systems is the Na, Tl || Br, NO₃ system.⁶² The miscibility dome is quite flat and closer in shape to the curve for $Z = 5.5$ than to the curve for $Z = 6$. Since the λ terms for this system are positive, this means that the value of Z which will lead to a miscibility dome of this shape will be less than 5.5. We have found⁵⁵ that calculations for this system correspond well with measurements when $Z = 5$.

Fig. 17. Calculated Miscibility Gap at Reduced Temperatures $\tau = (RT/\Delta G^\circ)$. ANL Neg. No. 308-3282.

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

In a previous report⁶³ we stated that our proposed method of constructing nonempirical pair potentials was apparently accurate for argon and for the hydrogen molecule in its triplet state. An even more demanding test of accuracy is provided by the helium pair potential because all the quantities needed to specify the potential are more accurately known (from experiment or calculation) and because the large quantum effects associated with light atoms at low temperatures provide great sensitivity. (The latter is so because the quantum effects depend not only on the potential but also on its derivatives.)

The present calculations for helium employ a potential slightly different from that displayed in Fig. 18 of Ref. 63. The principal change is that Gilbert and Wahl's⁶⁴ calculation of the Hartree-Fock energy of (He)₂ has been replaced by the more recent calculations of McLaughlin and Schaeffer,⁶⁵ which were done with a larger basis set of functions. The necessity of accounting for large quantum effects in the calculation of the transport properties (viscosity, thermal diffusion ratio, self-diffusion, spin-diffusion, thermal conductivity, total and differential elastic scattering cross sections) and thermodynamic (e.g., second virial coefficients) properties of helium requires that the calculations be done in a framework quite different from that used in the near-classical regime.⁶⁶ The quantal calculations⁶⁷ are most conveniently done by an analysis of the molecular collision process in terms of a set of phase shifts, $\eta_\ell(E)$. These phase shifts depend on the molecular angular momentum quantum number, ℓ , the relative kinetic energy, E , of the colliding pair, and their mutual potential energy, $U(r)$, at a distance, r ; they correspond in a general way with classical deflection angles, and are determined by a comparison of the asymptotic ($r \rightarrow \infty$) solutions of the radial Schrödinger equation

$$\frac{d^2 G_\ell(x)}{dx^2} + \left\{ [2\pi/\Lambda^*]^2 [E - U(x)]/\epsilon - \frac{\ell[\ell+1]}{x^2} \right\} G_\ell(x) = 0 \quad (31)$$

for $U(x)$ as written, and for $U(x) = 0$. In Eq. 31, x is equal to r/σ , the reduced interatomic distance. The reducing parameters σ and ϵ are defined by the relations, $U(\sigma) = 0$, and minimum $[U(r)] = -\epsilon$. Λ^* is the deBoer quantum parameter⁶⁷ given by $h/\sigma(2\mu\epsilon)^{1/2}$, where μ is the reduced mass of the colliding pair. The transport cross sections^{68,69} are calculable in terms of the phase shifts

$$S^{(0)}(E) = \frac{h^2}{2\mu\pi E} \sum_\ell \sin^2[\eta_\ell(E)] \quad (32a)$$

$$S^{(1)}(E) = \frac{h^2}{2\mu\pi E} \sum_\ell \sin^2[\eta_{\ell+1}(E) - \eta_\ell(E)] \quad (32b)$$

$$S^{(2)}(E) = \frac{h^2}{2\mu\pi E} \sum_\ell \sin^2[\eta_{\ell+2}(E) - \eta_\ell(E)] \quad (32c)$$

The total elastic scattering cross section is given by $S^{(0)}(E)$, while $S^{(1)}(E)$ and $S^{(2)}(E)$ determine diffusional transport, and viscosity or thermal conductivity, respectively. Calculation of these quantities is conveniently done via the intermediate quantities, the reduced collision integrals,^{6,9} defined by the relations

$$\Omega^{*(i,j)}(T^*) = \frac{1}{(j+1)!} \int_0^\infty \exp(-y) y^{j+1} S^{(i)}(T^* y) dy \quad (33)$$

where $y = E^*/T^*$, and E^* and T^* are the reduced relative kinetic energy (E/ϵ) and temperature (kT/ϵ), respectively.

The complexity of the calculations may be readily appreciated.

(a) The numerical evaluation of the collision integrals needed ($i = 1, 2, 3, 4$; $j = 1, 2, 3, 4, 5$) requires the evaluation of $S^{(i)}(E)$ at approximately one hundred values of E^* at each temperature. (b) For each of these values of E^* the differential equation (Eq. 31) must be solved numerically (at 400 to 2000 values of x) to obtain the asymptotic solution, and thus $\eta_\ell(E^*)$ for each integer value ℓ , starting with $\ell = 0$. This procedure is followed until $\eta_\ell(E)$ is less than 0.05 radian. (For smaller phase shifts the well-known Born approximation⁷⁰ may be used with an accuracy of better than a few percent, and greater speed of computation, to generate additional phase shifts until for four successive values of ℓ the phase shifts are less than 0.001 radian.) For the larger values of E^* one may have to calculate as many as 80 phase shifts. (c) These phase shifts are then appropriately summed via Eqs. 32a, 32b, and 32c to give the transport cross sections at one of the energies needed for the numerical integrations of Eq. 33.

Clearly, efficiency in calculation without sacrifice of accuracy is essential. We have adopted some of the computational techniques of authors who have done similar calculations, and combined them with our own modifications into a useful computational scheme. We solve Eq. 31 numerically by Numerov integration at an interval of integration, Δx , which is decreased with increasing E^* according to the scheme suggested by Keller and Taylor⁷¹

$$\Delta x = \frac{0.025 \Lambda^*}{(E^* + 1)^{1/2}} \quad (34)$$

Accurate calculations at high values of T^* require the integration in Eq. 33 to be carried out to E^* values of greater than 1000. At large values of E^* the classical calculation of transport cross sections is sufficiently accurate and can be done with great speed. In fact, the classical calculation of transport cross sections agrees with the quantal calculation at $E^* = 102.35$ to better than 2 parts per 1000. Hence, classical calculations of $S^{(\ell)}(E^*)$ were performed to complete the integration in Eq. 33 for values of E^* between 102.35 and 1638.35.

Another complicating feature of these calculations is the occurrence of large differences in the reduced masses (and Λ^*) for the three isotopic pairs $^3\text{He}-^3\text{He}$, $^4\text{He}-^4\text{He}$, and $^3\text{He}-^4\text{He}$. This fact necessitates the complete evaluation of Eqs. 31-33 for each pair. These differences are accentuated at low temperatures where there are large differences in the viscosities and second virial coefficients of ^3He and ^4He .

Our results for the low-temperature second virial coefficients of ^3He and ^4He (in cm^3/mol) over the range 1.6–10°K are plotted (solid lines) versus $1/T$ in Fig. 18. The data are those of Keesom and Walstra^{72,73} and of W. E. Keller⁷⁴⁻⁷⁶ as corrected by T. R. Roberts *et al.*⁷⁷ Smoothed values given by Dymond and Smith⁷⁸ are also included. The agreement is excellent, in fact, as good as previous calculations using empirical potentials^{79,80} fitted to the data.

Fig. 18. Second Virial Coefficients of ^3He and ^4He

In Fig. 19 we compare the experimental data of Bendt⁸¹ and DuBro and Weissman⁸² for the ^3He - ^4He gas-diffusion coefficients from 1.7 to 900°K with our calculated curve (solid line). The plot shows the quantity $\rho\mu_{34}D_{34}/T^{1/2}$ versus the temperature T , where ρ is the number density of the gas, μ_{34} is the reduced mass of the ^3He - ^4He pair, and D_{34} is the diffusion coefficient in units of $10^{-6} \text{ cm}^2/\text{sec}$. The agreement is as good as the results for various semiempirical potentials

Fig. 19. Isotopic Diffusion of ^3He in ^4He in the Gas Phase

tested to date.^{79,80,83} In Fig. 20, we present our calculated curve for the viscosity of helium gas from 100–2000°K. The agreement with the data of Clarke and Smith,⁸⁴ Dawe and Smith,⁸⁵ Kalelkar and Kestin,⁸⁶ Kestin and Whitelaw,⁸⁷ and Guevera *et al.*⁸⁸ up to 1800°K is excellent. The Guevera⁸⁸ results above 1800°K show a nearly constant reduced viscosity which is not predicted by our model potential or any other; they should be looked at with suspicion as a possible experimental artifact.

Fig. 20. Viscosity of ^4He Gas

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VI. METEORITIC STUDIES
(L. Fuchs*, M. Blander)

Calcium-Aluminum-Rich Inclusions in the Allende Meteorite: Textural and Mineralogical Evidence for a Liquid Origin. Calcium-aluminum-rich inclusions in the Allende meteorite are thought to be high-temperature condensates from the solar nebula. They took on added importance when it was realized that lunar return samples are or were derived from similar materials. Thus, these Allende inclusions are considered to be an important analogue of the nonvolatile materials which may have formed the lunar surface layers or perhaps even the entire moon.

We have made a detailed study of the mineralogy, textures, and assemblages of twenty such inclusions and observed many which appear to have crystallized from a liquid and which could not be an agglomeration of solid nebular condensates. The evidence for this is the presence of (a) spherical and ovoid shapes; (b) rims containing minerals (*e.g.*, hibonite or perovskite) which one calculates should condense at higher temperatures than the minerals inside the inclusion; (c) eutectic intergrowths (*e.g.*, diopside + anorthite and anorthite + gehlenite in the same inclusion); (d) fine-grained grossular stringers within a crystal and filling interstices between crystals; (e) minerals which one calculates should condense at lower temperatures than the mineral enclosing it (*e.g.*, rounded euhedral spinel crystals in gehlenite, euhedral olivine in diopside). These observations as well as the textures and the departures from equilibrium often support the conclusion that these inclusions crystallized (probably rapidly) from liquid drops.

Possible mechanisms for the formation of liquids of these compositions are

1. Direct condensation from the solar nebula at high hydrogen pressures (>1 atm).
2. Direct condensation from the nebula of metastable subcooled liquids.⁸⁹
3. Melting of solids on a planetary body by the impact of bolides ("meteorites").

We favor the second mechanism which is consistent with the broadest range of observations.

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VII. CHEMISTRY OF AIRBORNE PARTICULATES

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A detailed understanding of the chemistry of airborne particulate (aerosol) pollutants is essential to the establishment of ambient air quality and control standards appropriate for these substances. At present, most of the available data are based on samples collected using high-volume sampling techniques by which particulate material of all sizes is collected on a glass-fiber filter for an extended period of time (usually 24 hr). Typically, sufficient material is collected so that standard wet-chemical methods of analysis can be used. A well-recognized shortcoming in this method is that it does not permit chemical analysis of particulates as a function of particle size and time, but only gives values averaged over particles of all sizes and over the entire collection period. Data of this kind are useful for establishing long-term trends but seem to be inadequate for setting standards because the extent of the potential health hazard is a strong function of particle size and possible short-term high-level concentration of pollutants.

The desirability of detailed data on the chemistry of airborne particulates as a function of particle size and time has been enhanced by the recent findings of Whitby *et al.*⁹⁰ Based on careful measurement of particle-size distribution and variations in the distribution with time, they have concluded that the mechanism producing airborne particles of less than about one micron in diameter is quite different from that producing particles of larger size. The smaller particles are presumably formed by a condensation and coagulation mechanism whereas the larger particles are produced by mechanical injection into the atmosphere. If these mechanisms are correct, then one would expect the chemistry of small particles (*i.e.*, less than about one micron) to be quite uniform and to show some diurnal variation. Larger particles would have a widely differing chemistry, reflecting the diversity of their sources.

To provide data on the chemistry of particles as a function of both size and time, we have initiated a program to develop the necessary sampling, sample handling, and analytical techniques. Preliminary results show that there are indeed some very significant differences in the chemistry of particles as a function of size and time, which should be considered in formulating theories on particle formation and in assessing the potential health hazard of airborne particulates.

A. Impactor Collection of Airborne Particulate Material (P. T. Cunningham, S. A. Johnson)

A Lundgren-type inertial impactor⁹¹ was selected to collect samples of airborne particulates for this study. A schematic drawing of the impactor is shown in Fig. 21. The basic principles underlying the operation of inertial impactors have been discussed in detail in the literature.⁹² Simply stated, air is drawn through a series of nozzles or jets (stages) which have successively smaller cross sections. An impaction surface after each jet causes the air flow to change direction and those particles with an inertia too great to follow the lines of flow strike the impaction surface and are collected. Consequently, smaller particles are collected on successive stages. The details of the size distribution of particles collected on each stage can be very complicated due to nonuniform particle density and shape, particle-bounce

characteristics, nonuniform flow, and a host of other variables, but in general, each stage can be characterized by an effective cutoff diameter (ECD), which is that mean aerodynamic particle diameter for which one half of the particles are impacted. For the Lundgren impactor used in this work, the ECD is 12, 3, 1.2 and 0.3 μm for stages I through IV, respectively, at a nominal flow rate of 4 cfm. Particles of less than 0.3 μm dia are collected on the backup filter (see Fig. 21). The

Fig. 21. Schematic Diagram of Lundgren Impactor.
(Air flow is from left to right.)

basic reason for selecting the Lundgren impactor for these studies is its feature of having rotating drums as impaction surfaces. Because of this, the instrument provides for both size and time classification of the collected particles.

Samples were collected on Mylar or aluminized Mylar films that were stretched over the surface of the impactor drums. Some interesting data relating to the change in particle concentration with time can be obtained by examination of the samples thus obtained. Figure 22 shows the variation with time of the particle density on the surface of the Mylar films taken from stages II, III, and IV, as determined with an optical densitometer. From microscopic examination of the samples, the optical density appears to be a reasonably good indication of particle density on the surface of the Mylar film for a particular impactor stage. Comparison between different stages is not so reliable. It is clear from Fig. 22 that the variation in the concentration of submicron (stage IV) particles with time is considerably greater than that for the larger particles. This is in agreement with results observed by Whitby *et al.*^{90,93}

In collecting samples for infrared spectrophotometric analysis, it was found desirable to operate the impactor so that the impaction drums rotated in a stepwise fashion rather than continuously. A sample was

Fig. 22. Variation of Concentration of Impactor-Collected Airborne Particulate Material as a Function of Particle Size and Time as Measured by Optical Density Technique

collected for periods of from one to three hours with the drums stationary, thereby collecting a heavy band of material. The drums were then rotated quickly about 15 degrees and another band collected. In this mode of operation, more than 20 bands could be collected, permitting continuous sampling for nearly three days and still providing three-hour time resolution.

An indication of the distribution of the mass of the airborne particulate can be obtained by weighing the material collected on each stage and on the after-filter. A comparison of selected results from this

work and some data found in the literature⁹⁴ is presented in Table 7. There is some question concerning the absolute accuracy of these data because the problem of particle bounce in the impactor and particle-density and shape effect can not be accurately assessed. Nevertheless, the trends observed seem to be real and may be of considerable importance in evaluating health effects.

B. Elemental and Chemical Analysis of Airborne Particulate Material
(P. T. Cunningham, S. A. Johnson, R. Yang)

Particulate samples collected using the techniques described above in Section VII.A have been analyzed for their elemental and chemical composition using a number of techniques. Most of the techniques are not new, that is, they have previously been used in the analysis of particulate pollution samples. However, the main purpose of this program is to provide for the analysis of size- and time-classified material, which means that the available samples are typically much smaller than those used in other studies. Another consequence of classifying the samples with respect to size and time is the great increase in the number of samples that must be analyzed. The consequent necessity of handling a large number of samples, each containing only a small amount of material, has been constantly considered in developing the analytical procedures described here.

Elemental analysis has been performed using X-ray fluorescence and the ion microprobe mass analyzer (IMMA).⁹⁵ The data obtained from IMMA consists of a mass spectrum that is characteristic of the sample and covers the range from 1 to 300 atomic mass units for either positively or negatively charged masses. Analysis using IMMA has a great advantage over other methods of elemental analysis that might be used, in that IMMA analysis has very high sensitivity and is a rapid technique. A summary of some qualitative data obtained using IMMA is presented in Table 8. The samples used were obtained at ANL using a Lundgren impactor with the drum surface covered with aluminized Mylar. Small pieces, about 2 mm square, were cut from the Mylar films recovered from stages III and IV at positions corresponding to the times shown in Table 8 and mounted for IMMA analysis. The great sensitivity of the IMMA machine is demonstrated by the fact that the average weight of sample on the Mylar film within the area scanned by IMMA is about 5 ng. Trace elements present in the ppm level in this sample can be detected.

The detailed effects of a number of IMMA operating variables on the absolute sensitivity of the machine with respect to various elements are still not well understood. To overcome this problem, it is common to use internal standards or to obtain a quantitative analysis of one or more elements in the sample by an independent method and then use these known elements as internal standards for the IMMA data. In an effort to evaluate this latter procedure for particulate material, nondispersive X-ray fluorescence⁹⁶ has been used to examine a limited number of samples. Results are tabulated in Table 9. Since the sensitivity of this technique is much less than that for IMMA, the samples were obtained using the Lundgren impactor in the stepwise mode of operation with a three-hour sampling time. A portion of the samples collected on stages II, III and IV was used for the analysis. This experiment demonstrated that X-ray fluorescence could be used to establish iron, zinc, lead, and bromine (and probably other elements) as internal standards in the particulate samples.

TABLE 7. Size Distribution of Particulate Mass

Impactor Stage	This Work (based on 3-day sample)			National Air Surveillance Cascade Impactor Network Data for 1970 Calculated from Data Presented in Ref. 89, % of Total Weight in Size Range					
	Nominal ECD, μm	Weight Collected on Stage, mg	% of Total Weight on Stage	Chicago	Cincinnati	Philadelphia	Denver	Wash. D.C.	St. Louis
I	12.0	0.46	1.7	10	5	4	7	3	8
II	3.0	1.63	6.1	18	15	11	13	12	18
III	1.2	3.10	11.5	14	17	15	12	13	16
IV	0.3	9.86	36.6	26	32	30	22	32	28
After-Filter		11.87	44.1	32	31	40	46	40	30
Percent of particle mass $\leq 1 \mu\text{m}$		76		55	59	67	65	68	54
Percent of particle mass $\leq 2 \mu\text{m}$		87		68	74	80	75	81	68
Average Particulate Concentration, $\mu\text{g}/\text{m}^3$		64.5		86.5	74.3	58.5	59.7	56.3	73.1

TABLE 8. Variation in the Elemental Composition of Airborne Particulate as Measured by IMMA^a

Element ^b	5:00 PM	7:00 PM	8:50 PM	11:45 PM	1:45 AM	4:00 AM	6:45 AM	8:20 AM	9:30 AM	12:00 noon
Li	W W	M M	M W	M M	M M	M W	W VW	M M	VW M	M VW
Be	VW VW	VW N	N N	VW N	VW N	VW N	VW N	VW VW	N VW	VW VW
B	W W	W W	M VW	M W	M W	M VW	W VW	M W	N W	M W
C	M M	M S	S S	S S	S M	S M	M M	S S	M M	S M
Na	S VS	VS VS	VS VS	VS VS	VS VS	VS VS	VS M	VS VS	VS VS	VS VS
Mg	S S	VS VS	VS S	VS VS	VS S	VS M	S N	VS VS	S VS	VS M
Si	VS VS	VS VS	VS VS	VS VS	VS VS	VS S	VS VW	VS VS	M VS	VS VS
S	W W	W M	W W	S M	M M	W W	W VW	M M	VW S	W W
K	VS VS	VS VS	VS VS	VS VS	VS VS	VS VS	VS W	VS VS	M VS	VS VS
Ca	VS VS	VS VS	VS VS	VS VS	VS VS	VS VS	VS W	VS VS	VS VS	VS S
Sc	W W	VW M	W W	W W	W W	W VW	M N	M M	N S	W VW
Ti	M W	M W	M W	M M	M M	M W	S VW	VS VS	VW VS	M W
V	W W	W W	M W	S M	M M	M W	M N	M M	VW M	W VW
Cr	W W	W W	W W	W M	M M	M W	M N	M S	VW M	W VW
Mn	W M	M M	S M	S VS	S S	S W	M VW	M S	VW S	M W
Fe	S S	S S	VS S	VS VS	VS VS	VS S	VS VW	VS VS	M VS	VS M
Co	W VW	W W	M VW	M VW	S VW	M N	VW VW	S W	N M	W VW
Ni	VW W	W W	W W	W W	W W	W VW	W VW	M W	VW M	W VW
Cu	W W	VW W	W W	M M	M M	W VW	W N	M M	VW S	W W
Zn	W W	W M	W M	S S	S W	S VW	M N	M M	VW M	W W
Ga	W VW	VW W	W VW	W W	W W	W VW	W N	W W	N M	W VW
Ge	W VW	N VW	N N	N VW	VW VW	VW N	VW N	VW VW	N VW	VW VW
As	W VW	W VW	W VW	W VW	M VW	W VW	VW VW	W W	N W	W VW
Se	VW VW	VW VW	W VW	W W	W VW	W VW	VW N	W W	N W	VW N
Rb	VW W	VW W	W W	W M	W M	W W	W N	W M	VW M	W VW
Sr	W VW	VW VW	M M	M M	W W	M VW	M N	VS VS	W VS	M VW
Y	VW VW	VW VW	VW N	W W	VW VW	VW VW	VW N	W W	VW W	VW VW
Ba	W W	W W	M W	S S	M W	M W	S M	VS VS	W VS	M W
Pb	-- --	-- --	-- --	-- --	M VS	S M	M N	M VS	N VS	M N

^aData are only relative. Notation refers to the intensity of the peaks observed: N - not observed, VW - very weak, W - weak, M - moderate, S - strong, VS - very strong.

^bThe upper entry for each element refers to sample collected on stage III (ECD = 1.2 μ m), the lower entry refers to sample collected on stage IV (ECD = 0.3 μ m).

TABLE 9. Results of X-Ray Analysis

Sample Data			X-Ray Data ^a Total number of counts observed ^b			
Stage Number	ECD, μm	Sample Weight, μg	FeK_{α}	ZnK_{α}	PbL_{α}	BrK_{α}
II	3.0	8.8	330 (37.5)	380 (43.2)	182 (20.7)	84 (9.6)
III	1.2	19.2	603 (31.4)	623 (32.4)	845 (44.0)	554 (28.8)
IV	0.3	42.6	368 (8.7)	1283 (30.0)	2945 (69.2)	1941 (45.6)

^a NbK_{α} excitation, 60-min counting time.

^b Numbers in parentheses represent counts per microgram of sample.

It can also be noted from the parenthetical values in Table 9 that the concentration of lead and bromine in the sample decreases with increasing particle size and that the reverse is true for iron and, to a lesser extent, for zinc. This observation is in general agreement with other results.⁹⁷

The analytical methods described above provide a very powerful technique for the rapid elemental analysis of large numbers of samples. They do not, however, provide chemical analysis, that is, the nature of the chemical compounds present in the sample is not identified. Some work which provides chemical data on particulate material as a function of particle size and time has been reported, most notably that of Novakov *et al.*⁹⁸ They used photoelectron spectroscopy to identify the chemical states of nitrogen and sulfur in particulates present in photochemical smog. The photoelectron spectroscopic technique, however, requires considerable time for each sample.

Consideration of the sensitivity usually associated with infrared spectroscopy and the amount of sample typically collected using the Lundgren impactor indicated that compounds present in the particulate sample at concentrations as low as one percent should be detectable. Efforts to obtain spectra from material impacted on the surface of Mylar film were, however, not successful. A partial solution to the problem came with the realization that the size of the particles of interest is on the order of the wavelength of infrared light and therefore would scatter much of the infrared light in air, owing to the large difference in index of refraction between the particles and air. The situation would be ameliorated if the difference in index of refraction could be reduced by embedding the particles in a suitable matrix. A potassium bromide pellet was prepared in which the impacted material on a disk of Mylar was impressed into the surface of the pellet and the Mylar was then peeled away, leaving the particles embedded in potassium bromide. By using this procedure, spectra were obtained. Subsequently, the Lundgren impactor was operated in the stepwise mode and the band of particulate material collected was carefully scraped from the Mylar and mixed with potassium bromide, and the mixture pressed into a pellet using conventional techniques. Selected spectra obtained in this way are shown in Fig. 23, together with the assignments that were made.

It is clear from Fig. 23 and from examination of other spectra that significant differences do exist in the chemistry of particles of different size classifications and that the chemistry of the particles varies as a function of time. In addition, a greater variety of compounds is detected in the particles having diameters greater than one micron than in smaller particles, as one might expect from Whitby's observations.⁸⁵ Sufficient data are not yet available to make any firm statements regarding the mechanism of particulate formation or the effects of meteorological variables on particulate composition, but some possible correlations have been noted. Figure 24 shows data obtained over a 27-hr period with 3-hr time resolution. What is first noted is the considerable increase in the total weight collected on stage IV (ECD = 0.3 μm) during the nighttime hours, which is at variance with data obtained in areas (unlike the area where these samples were obtained) where photochemical smog is believed to be a major source of particulates. Also of interest is the increase in ammonium-ion absorbance relative to that of sulfate ion collected

	NH_4^+
a ₁	3140 ν_3
a ₂	3020 $\nu_2 + \nu_4$
a ₃	2800 $2\nu_4$
a ₄	1720 $\nu_4 + \nu_6$
a ₅	1400 ν_4

	$\text{SO}_4^{=}$
d ₁	1110 ν_3
d ₂	980 ν_1
d ₃	620 ν_4

	NO_3^- (ADSORBED)
g	1384 ν_3

	NO_2^{+*}
h	2428 ν_3
* UNCERTAIN	

	$\text{CO}_3^{=}$ (CALCITE)
b ₁	1435 ν_3
b ₂	880 ν_2
b ₃	728 ν_4

	C-H
e ₁	2920 ν_3
e ₂	2860 ν_1

	NO_3^{+*}
j ₁	1768 $2\nu_2$
j ₂	1360 ν_3
j ₃	840 ν_2

	$\text{SiO}_2, \text{SiO}_4^{=}$
c ₁	1035 ν_3
c ₂	800 ν_1
c ₃	780 ν_1
c ₄	470 ν_4

	H_2O (ADSORBED)
f ₁	3420 ν_3
f ₂	1620 ν_2

	PO_3^{+*}
k ₁	1190 ν_3
k ₂	1140 ν_3
k ₃	1120 ν_3
k ₄	670 ν_2
k ₅	627 ν_2
k ₆	600 ν_2

Fig. 23. Selected Infrared Spectra of Airborne Particulate Material Showing Observed Bands and Assignments

Fig. 24. Variation of Selected Meteorological, Particulate, and Spectral Data with Time

during the night. The cross-hatched area of Fig. 24 shows the $\text{NH}_4^+/\text{SO}_4^{2-}$ absorbance ratio found for standard ammonium sulfate samples. The correlation of these effects with relative humidity is suggested by the data in Fig. 24.

The very sharp and strong peak at 1384 cm^{-1} shown in Fig. 23 is a prominent feature in the spectra of many samples obtained from stage II, but is rarely present in the spectra of samples obtained from stage IV. Boehm⁹⁹ observed a similar spectral feature and suggested that it might be due to nitrate ion formed on the hydroxylated surface of oxides (or other materials) from adsorbed nitrogen dioxide. Our observation of this feature in the spectrum of a mixture of sea sand, ammonium sulfate, and carbon black that had been briefly exposed to nitrogen dioxide suggests that it is indeed due to adsorbed nitrogen dioxide.

Work is continuing on the development of the techniques necessary to determine the chemistry of airborne particulates as a function of particle size and time. It is hoped that the methods now at hand will begin to provide some further insight into the mechanism of particle formation in the atmosphere and that this in time will provide guidance in determining potential health hazards and appropriate control measures.

REFERENCES

1. V. A. Maroni, E. J. Cairns, and F. A. Cafasso, A Review of the Chemical, Physical, and Thermal Properties of Lithium That Are Related to Its Use in Fusion Reactors, USAEC report ANL-8001 (1973).
2. Chemical Engineering Division Physical Inorganic Chemistry Semi-annual Report, July-December 1972, USAEC report ANL-7978 (1973).
3. See, *e.g.*, J. H. Hildebrand and R. L. Scott, The Solubility of Non-electrolytes, 3rd Ed., p. 34, Reinhold Publishing Co., New York (1950).
4. C. E. Messer, E. B. Damon, P. C. Maybury, J. Mellor, and R. A. Seales, *J. Phys. Chem.* 62, 220 (1958).
5. C. E. Messer, A Survey of Lithium Hydride, USAEC report NYO-9740 (1960).
6. F. K. Heumann and O. N. Salmon, The Lithium Hydride, Deuteride, and Tritide Systems, USAEC report KAPL-1667 (1956).
7. JANAF Thermochemical Tables, U.S. Department of Commerce (1967).
8. R. W. Webb, Permeation of Hydrogen Through Metals, USAEC report NAA-SR-10462 (July 1965).
9. A. Sieverts and E. Jurisch, *Ber. Deut. Chem. Ges.* 45, 221 (1912).
10. E. Veleckis and R. K. Edwards, *J. Phys. Chem.* 73, 683 (1969).
11. Ref. 1, pp. 25-37.
12. G. J. Moody and J. D. R. Thomas, *J. Chem. Ed.* 43, 205 (1966).
13. C. E. Sessions and J. H. DeVan, *Nucl. Appl.* 9, 250 (1970).
14. K. A. Bolshakov, P. I. Federov, and L. A. Stepina, *Izvest. Vyschikh. Ucheb. Zavedenii, Tsvetnaya Met.* 2(4), 52 (1959).
15. E. E. Hoffman, in Newer Metals, ASTM Spec. Tech. Publ. 272, pp. 195-206 (1960).
16. W. D. Weatherford, R. K. Johnston, M. L. Valtierra, and J. W. Rhoades, Contamination Effects in Liquid Rubidium and Liquid Lithium Systems, Report No. ASD-TDR-63-413 (May 1963).
17. R. Hultgren, R. L. Orr, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, January 1970 Supplement, Lawrence Radiation Laboratories, Berkeley, Calif.
18. C. C. Addison and B. M. Davies, *J. Chem. Soc.* 1969A, 1822.

19. M. D. Lyutaya and T. S. Bartnitskaya, Izv. Akad. Nauk SSSR Neorg. Mater. 6, 1763 (1970).
20. M. Fromont, Rev. Chim. Minerale 4, 447 (1967).
21. D. Steiner and A. P. Fraas, Nucl. Safety 13, 353 (1972).
22. E. F. Johnson, Fusion Reactor Fuel Processing, USAEC report MATT-901 (June 1972).
23. R. G. Hickman, Some Problems Associated with Tritium in Fusion Reactors, USAEC report UCRL-74057 Rev. 1 (September 1972).
24. J. S. Watson, A Summary of Tritium Handling Problems in Fusion Reactors, USAEC report ORNL-TM-4022 (November 1972).
25. V. A. Maroni, "Selected Problems of Tritium Management Related to CTR," presented at The Short Course in Fusion Power, Princeton University, Princeton, New Jersey, Oct. 30-Nov. 3, 1972.
26. R. Faroskhi and J. E. Rogers, Methods of Tritium Recovery from Molten Lithium, USAEC report ORNL-MIT-66 (December 1968).
27. G. J. Bernstein *et al.*, Development and Performance of a High-Speed Annular Centrifugal Contactor, USAEC report ANL-7969 (January 1973).
28. J. B. Knighton *et al.*, Development of a Mixer-Settler for Liquid Metal-Salt Systems, USAEC report ANL-7810 (June 1971).
29. E. J. Cairns *et al.*, Galvanic Cells with Fused-Salt Electrolytes, USAEC report ANL-7316 (November 1967).
30. R. G. Mills *et al.*, Reference Design Model of a Fusion Power Plant, Princeton Plasma Physics Laboratory (report in preparation-title is tentative).
31. F. Ribe *et al.*, Reference Theta Pinch Fusion Reactor Design Report, Los Alamos Scientific Laboratory and Argonne National Laboratory (report in preparation-title is tentative).
32. Ref. 1, p. 13.
33. J. L. Katz and M. Blander, J. Colloid Interfac. Sci. 42, 496 (1973).
34. J. G. Eberhart and H. C. Schnyders, J. Phys. Chem., in press.
35. J. G. Eberhart and H. C. Schnyders, in Chemical Engineering Division Physical Inorganic Chemistry Semiannual Report, January-June 1972, USAEC report ANL-7923, p. 16 (1972).
36. J. P. Hansen and L. Verlet, Phys. Rev. 184, 151 (1969).
37. G. H. Mansoori, J. A. Provine, and F. B. Canfield, J. Chem. Phys. 51, 5295 (1969).

38. S. W. Benson and E. Gerjuoy, J. Chem. Phys. 18, 215 (1950).
39. J. L. Katz, J. Chem. Phys. 52, 4733 (1970).
40. W. B. Strickfaden and Luis de Sobrino, Can. J. Phys. 48, 2507 (1970).
41. J. Lothe and G. M. Pound, Nucleation, p. 118, A. C. Zettlemeyer, ed., Bekker, New York (1969).
42. D. J. McGinty, J. Chem. Phys. 55, 580 (1971).
43. J. P. Hansen and L. Verlet, Phys. Rev. 184, 151 (1969).
44. G. A. Mansoori, J. A. Provine, and F. B. Canfield, J. Chem. Phys. 51, 5295 (1969).
45. T. Enger and D. E. Hartmann, Rapid Phase Transformation During LNG Spillage on Water, presented at the 3rd International Conference and Exhibition on LNG, Washington, D.C., Sept. 24-28, 1972.
46. E. Nakanishi and R. C. Reid, Chem. Eng. Prog. 67, 36-41 (1971).
47. J. G. Eberhart, W. Kremsner and M. Blander, "Homogeneous Bubble Nucleation in Superheated Hydrocarbons and Their Mixtures," International Workshop on Nucleation Theory, Clark College, Atlanta, Georgia (1972) pp. 45-55.
48. V. A. Maroni, E. J. Hathaway, and E. J. Cairns, J. Phys. Chem. 75, 155 (1971).
49. E. J. Hathaway and V. A. Maroni, J. Phys. Chem. 76, 2796 (1972).
50. V. A. Maroni, J. Chem. Phys. 54, 4126 (1971).
51. V. A. Maroni and E. J. Hathaway, Electrochim. Acta 15, 1837 (1970).
52. G. N. Papatheodorou and T. Ostvold, Thermodynamic Studies of Binary Charge Unsymmetrical Fused Salt Systems: Calorimetric and E.M.F. Measurements of Liquid Lanthanum (III) Chloride-Alkali Chloride Mixtures (paper being prepared for publication).
53. V. A. Maroni and P. T. Cunningham, "Laser-Raman Spectra of Gaseous BiBr₃ and PbCl₂" (submitted for publication in Applied Spectroscopy).
54. M. Blander and S. J. Yosim, J. Chem. Phys. 39, 2610 (1963); M. Blander and L. E. Topol, Inorg. Chem. 5, 1641 (1966).
55. M. Blander and M. L. Saboungi, Chemical Engineering Division Physical Inorganic Chemistry Semiannual Report, July-December 1972, USAEC report ANL-7978, p. 20 (Jan 1973).
56. Handbook of Solid-Liquid Equilibria in Systems of Anhydrous Inorganic Salts, Vols. I and II, N. K. Voskresenskaya, ed., Izdatel'stvo Akademii Nauk SSSR, Moskva-Leningrad (1961) [English Translation].

57. N. P. Luzhnaya, Trudy Instituta Prikl. Khim. 23, 34 (1935).
58. JANAF Thermochemical Tables (2nd Edition) N.B.S. 37 (1971)
Superintendent of Documents, U.S. Govt. Printing Office, Washington, D.C. 20402.
59. F. D. Rossini *et al.*, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, U.S. Govt. Printing Office, Washington, D.C. (1952).
60. I. Il'yasov and Yu. G. Litvinov, Russ. J. Inorg. Chem. (English Transl.) 17, 607 (1972).
61. J. E. Ricci, "Phase Diagrams of Fused Salts," in Molten Salt Chemistry, M. Blander, ed., Interscience Publishers, New York (1964).
62. C. Sinistri, P. Franzosini, and G. Flor, Gazz. Chim. (Rome) 97, 275 (1967).
63. Chemical Engineering Division Physical Inorganic Chemistry Semi-annual Report, July-December 1972, USAEC report ANL-7978, p. 28 (Jan 1973).
64. T. L. Gilbert and A. C. Wahl, J. Chem. Phys. 47, 3425 (1967).
65. D. R. McLaughlin and H. F. Schaeffer III, Chem. Phys. Letters 12, 244 (1971).
66. J. A. Barker, W. Fock, and F. Smith, Phys. Fluids 7, 897 (1964).
67. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, J. Wiley and Sons, New York (1954).
68. R. J. Munn, E. A. Mason, and Francis J. Smith, J. Chem. Phys. 41, 3978 (1964).
69. R. J. Munn, Francis J. Smith, and E. A. Mason, J. Chem. Phys. 42, 537 (1965).
70. B. H. Bransten, Atomic Collision Theory, p. 15, W. A. Benjamin, New York (1970).
71. J. M. Keller and W. L. Taylor, J. Chem. Phys. 51, 4829 (1969).
72. W. H. Keesom and W. K. Walstra, Physica 13, 225 (1947).
73. W. H. Keesom and W. K. Walstra, Physica 7, 985 (1940).
74. W. E. Keller, Phys. Rev. 97, 1 (1955).
75. W. E. Keller, Phys. Rev. 100, 1970 (1955).
76. W. E. Keller, Phys. Rev. 98, 1571 (1955).

77. T. R. Roberts, R. H. Serman, and S. G. Sydoriak, J. Res. Nat. Bur. Std. 68A, 567 (1964).
78. J. H. Dymond and E. B. Smith, The Virial Coefficients of Gases: A Critical Compilation, Clarendon Press, Oxford (1969).
79. J. M. Keller and W. L. Taylor, J. Chem. Phys. 51, 4829 (1969).
80. L. W. Bruch and I. J. McGee, J. Chem. Phys. 52, 5884 (1970).
81. P. J. Bendt, Phys. Rev. 110, 85 (1958).
82. G. A. DuBro and S. Weissman, Phys. Fluids 13, 2682 (1970).
83. W. L. Taylor and J. M. Keller, J. Chem. Phys. 54, 647 (1971).
84. A. G. Clarke and E. B. Smith, J. Chem. Phys. 51, 4156 (1969).
85. R. A. Dawe and E. B. Smith, J. Chem. Phys. 52, 693 (1970).
86. A. S. Kalelkar and J. Kestin, J. Chem. Phys. 52, 4248 (1970).
87. J. Kestin and J. H. Whitelaw, Physica 29, 335 (1963).
88. F. A. Guevera, B. B. McInteer, and W. E. Wageman, Phys. Fluids, 12, 2493 (1969).
89. M. Blander and J. L. Katz, Geochim. Cosmochim. Acta 31, 1025 (1967).
90. K. T. Whitby, R. B. Husar and B. Y. H. Liu, J. Colloid Interfac. Sci. 39, 177 (1972); R. B. Husar, K. T. Whitby and B. Y. H. Liu, J. Colloid Interfac. Sci. 39, 211 (1972).
91. D. A. Lundgren, J. Air Pollut. Contr. Assoc. 17, 225 (1967); D. A. Lundgren, Atmos. Environ. 5, 645 (1971).
92. W. E. Ranz and J. B. Wong, Ind. and Eng. Chem. 44, 1371 (1952); W. E. Ranz, Principles of Inertial Impaction, Engineering Research Bulletin No. 66, Pa. State Univ. (1956).
93. K. T. Whitby, University of Minnesota, private communication.
94. R. E. Lee, Jr. and S. Goranson, Environ. Sci. Tech. 6, 1019 (1972).
95. H. Liebl, J. Appl. Phys. 38, 5277 (1967).
96. J. A. Cooper, Nucl. Instr. and Meth. 106, 525 (1973).
97. R. E. Lee, Jr., S. S. Goranson, R. E. Enrione, and G. B. Morgan, Environ. Sci. Tech. 6, 1025 (1972).
98. T. Novakov, P. K. Mueller, A. E. Alcocer and J. W. Otvos, J. Colloid Interfac. Sci. 39, 225 (1972).
99. H. P. Boehm, Discuss. Faraday Soc. 52, 264 (1971).