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**Mound Facility Activities in Chemical
and Physical Research:
January-June 1978**

September 18, 1978

Monsanto

MOUND FACILITY

Miamisburg, Ohio

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

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Foreword

This report is issued semiannually by Mound Facility. Under the sponsorship of the DOE Division of Basic Energy Sciences, Mound Facility is responsible for producing materials for use in the physical sciences to further the progress of science and technology in the public interest. Additional research activities of related interest under the sponsorship of the Division of Military Application are also reported here.

This report is submitted by W. T. Cave, Director of Nuclear Operations, and R. E. Vallee, Manager of Technology Applications and Development, from contributions prepared by W. M. Rutherford, Science Fellow (Thermal Diffusion); W. L. Taylor, Science Fellow (Gas Dynamics and Cryogenics); G. L. Silver, Senior Research Specialist (Separation Chemistry); R. C. Bowman, Leader, Metal Hydride Research, and from members of the Isotope Separation Section: R. A. Schwind, Isotope Separation Manager; E. D. Michaels, Leader, Isotope Separations Development; W. J. Roos, Leader, Stable Isotopes Production; B. E. Jepson, Leader, Metal Isotope Separation; R. M. Watrous, Leader, Radioisotopes Separation; and V. L. Avona, Leader, Stable Isotope Sales.

These reports are not intended to constitute publication in any sense of the word. Final results will either be submitted for publication in regular professional journals or be published in the form of MLM topical reports.

Previous reports in this series are:

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Process automation has continued in HH Building; recently completed projects include: the addition of a microcomputer development facility and the implementation of a small BASIC interpreter for high-level programming on these systems; the installation of completely redesigned electronics for the CEC cycloidal mass spectrometer, including the incorporation of a microcomputer for local control functions; and the installation of an analyzer, used for detecting ppm levels of helium-3 in helium-4 gas, on the helium separation system.

II. Isotope separation

ARGON.	10
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Production of 7% argon-38 and 99.5% argon-36 continued during this period.

CARBON	10
------------------	----

During this period 128 g of 90+% carbon-13 as elemental carbon and 445 g of 90+% carbon-13 as methane were produced by conversion from carbon monoxide and carbon dioxide. Approximately 125 g of 99+% carbon-13 was produced by thermal diffusion of methane. A total of 102 g of elemental carbon at 99+% carbon-13 enrichment was produced by conversion from carbon dioxide.

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Approximately 3350 STP liters of 99.9% helium-3 and 100 STP liters of 99.9995% helium-3 were produced.

KRYPTON.	10
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Production of 99% krypton-86 and 70% krypton-82 has continued during this period.

NEON	10
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Approximately 100 liters of neon-22 has been upgraded to product specifications.

XENON.	11
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Approximately 0.4 STP liter of 40% xenon-124, 0.3 STP liter of 5% xenon-124, 0.2 STP liter of 20% xenon-124, and 8.5 STP liters of 80% xenon-136 were produced during this period.

III. Low temperature research

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We have proposed a new intermolecular potential function for helium which relies upon theoretical parameters for the short-range exponential and long-range dispersion regions. One disposable parameter describes the region of electronic overlap. This Hartree Fock Dispersion form produces a superior description of second virial and transport data over the temperature range from 1.5 to 1200 kelvins.

IV. Separation chemistry

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A total of 23 grams of chlorine-37 enriched to 90+% has been produced in the experimental chlorobenzene liquid thermal diffusion cascade. Changes on the cascade are being made to increase the production rate at a higher enrichment of 95+% chlorine-37.

THORIUM-229.	23
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A total of 20.9 mg of thorium-229 has been separated from aged UF_4 in FY-1978. Of this total, 8.3 mg was shipped to Isotope Sales at ORNL, and 12.6 mg has been prepared for shipment and awaits analysis by mass spectrometer.

PROTACTINIUM-231 AND THORIUM-230	23
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A shipment of 35,974 mg of thorium was made to Isotope Sales at ORNL in partial fulfillment of the FY-1978 quota. An additional 11,385 mg is on hand. Approximately 150 mg of partially purified protactinium-231 is being processed.

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The initial separation, by oxalate precipitation, of an estimated 4.2 g of uranium-234 from 72.4 g of aged plutonium-238 was completed. Dissolution was completed for another 19.9 g of plutonium-238 containing an estimated 1.5 g of uranium-234.

V. Separation research

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Isotopic separation experiments performed with two types of modified thermal diffusion columns, one type having a narrow coolant annulus, the other having the coolant annulus packed with spherical particles, gave very high separation factors at total reflux. The initial transport coefficient was

much larger for columns with narrow coolant annuli. Calculations relating to the separation of isotopes as solutes dissolved in a solvent proved that a counterflow of solvent could be used to eliminate the solute-solvent concentration gradient in a thermal diffusion column.

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The new, cooled, target gas cell was installed and its associated feed/flow system calibrated for the various gases to be used in upcoming total cross section experiments. The velocity selector system was assembled for high-speed testing and velocity distribution measurements with its own effusive beam production system.

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The mutual diffusion coefficients of krypton-noble gas mixtures have been measured as a function of temperature from approximately 300 to 1200 K. A dual chamber apparatus with no moving parts is used with an experimental procedure which is independent of the initial conditions. The results extend the temperature range of any previously reported values using a similar method by approximately 400 K. Transport collision integrals have been computed for several intermolecular potential functions and used to calculate theoretical diffusion coefficients which are compared to the experimental results.

VI. Metal hydride research

NMR STUDIES. 43

Studies of TiCuH Measurements of the proton relaxation times for TiCuH yield an activation energy of 0.79 eV for hydrogen diffusion. This result strongly suggests that the hydrogen atoms in TiCuH jump directly between the tetrahedral sites rather than through the vacant octahedral sites as proposed for hydrogen atom jumps in f.c.c. TiH_x . In addition, the Korringa constant and hydrogen diffusion rate for TiCuH are compared with similar parameters for TiH_x and several ternary titanium hydrides.

Isotope Effects for Diffusion in Vanadium Hydride Comparative NMR studies of the nuclear relaxation times T_1 and T_2 have been performed for $VH_{0.50}$ and $VT_{0.50}$. Diffusion is the primary T_1 relaxation mechanism below the phase transitions at 470 K and 375 K for $VH_{0.50}$ and $VT_{0.50}$, respectively. Below the T_1 minima, diffusion activation energies of 0.41 eV for $VH_{0.50}$ and 0.31 eV for $VT_{0.50}$ indicate a more rapid diffusion rate throughout the β -phase temperature region. Furthermore, nonexponential T_1 and T_2 magnetization recoveries were observed in two temperature ranges for $VT_{0.50}$ and only exponential recoveries were found for $VH_{0.50}$ between 100 K and 520 K.

ELECTRON PARAMAGNETIC RESONANCE (EPR) STUDIES. 54

EPR spectra have been used to derive structural information about dilute octahedral metal hydride complexes. EPR spectral data also measure the extent of deviation from strictly ionic electronic bonding within the complex; in this sense it is a measure of covalency. This observation is related to the properties of metal hydride compounds, in particular for the complexes $[\text{RhH}_6]^{4-}$ and $[\text{NiH}_6]^{5-}$ in a LiH matrix.

THEORETICAL STUDIES OF HYDROGEN IN METALS. 57

The interaction of hydrogen with metal clusters is being studied using Hartree-Fock molecular orbital theory to determine the electronic factors involved in hydrogen solubility and hydride formation. Using a pseudo-potential to replace the atomic cores, preliminary calculations on the hydrogen interaction with clusters of four, five, and six magnesium atoms reveal that hydrogen binds strongly to the surface of the clusters but that there is a potential barrier to penetration into the bulk.

I. Computer operations

Automation in HH building

R. E. Eppley

MICROCOMPUTER DEVELOPMENT FACILITY

There are a number of functions in HH Building which can benefit from some type of automation providing it can be accomplished in a cost effective manner. The adaptability of small computers make them attractive for such applications. Each application (e.g., lab instrument control, monitoring of small conversion systems) could be controlled from the MODCOMP IV computer system with proper interfacing and software development. However, for small applications which do not need extensive software, higher reliability and easier implementation can be afforded by a stand-alone microprocessor operating with a high-level software language. It was determined that it would be far less expensive to standardize on a commercially available system rather than develop hardware from the "chip" level. Available products from various manufacturers of microprocessor products were, therefore, analyzed. A system was sought that could provide a wide range of PC card-level components as well as complete development systems. Equally important was the choice of a company that supported their hardware with extensive software for rapid development of the applications programs.

The decision was to use the MCZ series of cards manufactured by Zilog Corporation [1], which are designed for their Z-80 8-bit microprocessor. In addition, the Zilog MCZ microcomputer system with dual floppy disk drives can be used for program

development. The heart of each dedicated system is the Zilog MCB card. This card, 7.7 in. x 7.5 in. with a 122-pin edge connector, implements a complete 8-bit computer system. It includes the Z-80 CPU, four programmable clock/timer circuits, a full-duplex asynchronous I/O channel, 16-bits of digital I/O, 8K bytes of EPROM memory, and 16K bytes of RAM memory. Additional cards are used to extend the memory, digital I/O, and analog I/O channels. These cards are mounted in a card cage which has a wire-wrap back plane for inter-card communication. These systems are easy to implement, are low in cost, and deliver powerful control and computational capabilities for small applications.

Future plans call for developing the capability to interface these microcomputers to the central MODCOMP system via asynchronous channels. With this capability, any microprocessor controller which needs computational power beyond its own capabilities will be able to call upon the MODCOMP for help.

BASIC IMPLEMENTATION FOR REAL-TIME CONTROL

Programming microcomputers in assembly language is difficult and time consuming. A more effective way to use microcomputers for monitoring and control purposes in one-of-a-kind applications, and with very limited manhours available for software development, is to do the bulk of the programming in a high-level language. The only problem with this approach is that very few languages have been developed for small systems which can operate with (a) limited memory; (b) little, if any, peripheral support; and (c) rapid response to system "interrupts".

Lawrence Livermore Laboratory was confronted with this problem and solved it by contracting to have such a language developed [2]. The result is a BASIC interpreter which is a small subset of the usual BASIC commands. This BASIC, which is optimized for real-time operation, includes GET and PUT statements for directly addressing all I/O ports and also provides multiple-parameter calls to assembly language subroutines. Additionally, floating point arithmetic is used for all computations [3]. The published source code, in the public domain, was written for the MCS-8080 microprocessor with LLL I/O configurations. We have modified it somewhat for our Z-80 microprocessors, I/O access, and monitor support. The interpreter resides in 5K bytes of EPROM (including our own assembly routines), and the floating-point package uses another 2-3K bytes. With this software we are able to develop the application software in the computer which will be used on the project. It can be done rapidly with all of the advantages that interpretive languages offer.

After the application software is developed and debugged, it can be loaded into EPROMS for permanent, nonvolatile storage. A further step in this software development would be to develop a BASIC compiler. The application program, after being debugged with the interpreter, would be compiled and then loaded in EPROM for execution in the microcomputer. This procedure would improve the speed of the application program by a factor of 3-4. This is an area being explored for future development. BASIC, while not the last word in computer languages, is easy to learn and can be used by laboratory personnel (i.e., scientists and technicians)

to develop their own application programs. This greatly decreases the dependence on a professional programming staff.

REBUILDING OF THE "620" MASS SPECTROMETER

The Isotope Separation Section relies heavily on the CEC "620" cycloidal mass spectrometer for process control analyses of both gaseous and liquid samples. This mass spectrometer has been upgraded over the past couple of years and now runs under computer control [4], including computer control of a complex inlet system [5].

For some time there have been problems with the reproducibility of peak intensities. This was caused primarily by electronics drifts in the 20-year-old, tube-type electronics. Problems in maintenance were also increasing for the same reason. For these reasons, as well as others, the decision was made to replace the old electronics with a completely redesigned, solid-state electronics package. This project has recently been completed, and now the mass spectrometer is in operation with only the cycloid tube and magnet assembly retained from the original instrument. Modified or completely rebuilt components include the filament emission circuit, the sweep-voltage power supply, the voltage divider circuit, and a computer-controlled circuit for local control functions.

The filament emission control circuit was designed and built at Mound by the Electronics Group. It provides an AC current to the filament which is adjustable from 0-50 mA. The filament is presently being run at $37.5 \text{ mA} \pm 0.02\%$ (which compares to a 5-10% variation with the old regulator). This closer control means that a standard

peak-intensity calibration remains valid for a longer period of time. Also, the need for frequent emission current adjustments has been eliminated.

The sweep-voltage power supply, previously installed for control via the MODCOMP computer, was modified to allow digital control from a local source as well as from the MODCOMP. This control mode (remote/local) is chosen by a switch on the power supply.

The supply has been described previously [3] and provides a 0-500 VDC output at a maximum of 5 mA. This voltage range, or a fraction of this range, can be controlled to a resolution of 1 part in 8000. A $(1/V)$ function is built into the sweep circuit to provide a linear mass-voltage relationship for simplified mass calibrations.

These changes to the mass spectrometer electronics have resulted both in improved ion sensitivity and in improved mass resolution. For the first time, with this instrument, there is virtually unit mass resolution in the xenon mass region. For example, xenon-132 exhibits at least a 100:1 peak-to-valley ratio. The resolution calculated using $M/\Delta M$ is about 300.

Local control functions have been implemented under the control of a Zilog Z-80 microcomputer. This microcomputer provides control for the mass spectrometer when the MODCOMP system is not available. Basically, it provides a mass sweep at operator-defined rates and allows operator definition of the mass range. The mass spectrum is traced on a strip-chart recorder. The computer was chosen for local control as one of the early applications of microcomputers in HH Building. The control functions were provided at a

lower cost than would have been the case for the design and construction of all hard-wired circuits. In addition, new functions can be added easily, with little or no modification to current ones. Also, hardware maintenance problems are minimized. The control software is written in assembly language, which is adequate for the present application. For the future, it is planned that the software will be rewritten in a high-level language for easier maintenance and expansion of the control/acquisition functions.

³He ANALYZER

An analyzer for helium-3 has been installed on the helium separation system in an effort to reduce both the cost and turn-around time for process analyses of helium-3 in the bottom stream of helium-4. These analyses are used for controlling helium-3 production rates.

The analyzer operates on the principle of a gas chromatograph and uses matched 3 ft x 1/8 in. columns of 110/120 mesh charcoal, which are operated at room temperature. Helium-4 is used as the carrier gas, with operation at atmospheric pressure. Ratios of helium-3 to helium-4 are detected with a Carle microdetector consisting of a dual thermistor detector and a bridge-type control circuit which presents the thermal conductivity ratio between the two cells for display on a strip-chart recorder. Samples, 1 cm³ in size, are analyzed against helium-3/helium-4 standards having a helium-3 component in the same ppm range. Gas is taken directly from the helium separation system and admitted into the analyzer sample loop in a batch mode. This eliminates any extra handling of the sample. Under the current operating conditions the helium-3 sensitivity is 5 ppm,

which far exceeds the cycloidal mass spectrometer sensitivity of about 1000 ppm. The entire analysis, including both the standard and process analyses, takes less than 10 min to perform.

At this time, it is not clear whether this technique should be adopted for analyses of the top stream on the helium separation system. Such a system would necessitate the use of helium-3 for the carrier gas and would need to be operated in a closed loop fashion so that all carrier gas could be reclaimed. This would greatly increase the complexity of the system and would make it more difficult to operate. For now, the top-stream samples will continue to be analyzed via the mass spectrometer.

II. Isotope separation

Argon

W. J. Roos

The 13-column argon system continued to produce argon-38 at an intermediate enrichment of 7%. This material is being collected for later enrichment to 95%. The system also produced argon-36 at 99.5% enrichment as a by-product.

Carbon

W. J. Roos and G. E. Stuber, Jr.

During this period 128 g of carbon-13 at an enrichment of 90+% was converted from carbon monoxide to elemental carbon. Also, 445 g of 90+% carbon-13 was converted from carbon monoxide and carbon dioxide to methane.

During this period, enrichment of carbon-13 by thermal diffusion of methane was resumed. Two batches of material, totaling approximately 125 g of 99+% carbon-13 methane, were produced. Enrichment of a third batch is currently in progress. Of this methane, 102 g of carbon-13 was converted to elemental carbon at 99+% enrichment, and the remainder was converted to carbon dioxide.

Helium-3

T. F. Walburg

During this period approximately 3350 STP liters of 99.9% helium-3 and 100 STP liters of 99.9995% helium-3 were produced.

Krypton

G. E. Stuber, Jr.

The nine-column and 19-column double cascade thermal diffusion system has continued producing 99% krypton-86. The raffinate stream from the first cascade is being used as feed for the enrichment of krypton-82 in a 10-column cascade.

The 10-column cascade has continued producing 70% krypton-82 as a side stream. The material from the top raffinate stream is being collected for later enrichment of krypton-80 to 90%. The bottom stream will be used for enrichment of krypton-83 to 70%.

Neon

G. E. Stuber, Jr.

Two batches of neon-22, totaling approximately 100 liters, have been enriched to

greater than 99.9% neon-22. The feed for this process is material that has been collected as raffinate from neon-21 enrichment in the past and is slightly below product specifications.

Xenon

W. J. Roos

During this period a 19-column thermal diffusion system produced approximately 0.4 STP liter of 40% xenon-124; a 22-column system produced approximately 0.3 STP liter of 5% xenon-124 and approximately 0.2 STP liter of 20% xenon-124; and an eight-column system produced approximately 8.5 STP liters of 80% xenon-136.

III. Low temperature research

Helium potential function

G. T. McConville and W. L. Taylor

In the past decade many potential functions have been introduced to describe the properties of helium. They have met with less success than those proposed for the heavier inert gases. In cooperation with R. A. Aziz, J. S. Carley, and V. Nain of the University of Waterloo, we have proposed a new potential for helium which has two appealing characteristics. It relies on recent ab initio calculations for the short range exponential and long range dispersion parameters, hence it has a Hartree Fock-Dispersion (HFD) designation. One disposable parameter describes the overlap region. The second characteristic is that the potential produces a superior description of second virial and transport property data over the extended temperature region of 1.5 to

1200 K. The form of the HFD potential proposed as a general form by Scoles et al. [1] is a modified Buckingham with an overlap correction term multiplying the dispersion terms:

$$V(r) = Ae^{-\alpha r} - \left[\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right] F(r) \quad (1)$$

$$\text{where } F(r) = \exp \left[-D/r - 1 \right]^2 \quad r < Dr_{\min} \\ = 1 \quad r \geq Dr_{\min}$$

The accepted values of A and α for helium are taken from the self-consistent Hartree-Fock repulsion calculations of McLaughlin and Schaefer [2]. Many values of C_6 have been calculated, and at one time a value of 1.47 atomic units was accepted, but recent values cluster around the Starkshall and Gordon value [3]. The values of C_8 and C_{10} are taken from the work of Tang, Norbeck, and Certain [4]. These values are listed in Table III-1. The

Table III-1 - ATOMIC UNITS

A	2.3814
α	18.365
C_6	1.4600
C_8	14.22
C_{10}	187.2
D	1.241314

value of D is then determined to produce a fit to the recent thermal conductivity data of Haarman [5] which has a stated accuracy of 0.3%. These parameters produce a potential for helium, HFD-2, with a well depth of $\epsilon/k = 10.80$ and $r_{\min} = 2.96729$. The only reason for the excess significant figures in $r_{\min}$ and D is to keep the whole set of parameters consistent.

This potential form was used to calculate the following properties for helium: second virial (1.5 to 1000 K); viscosity (1.5 to 2000 K); and differential scattering for 20 K crossed helium beams. These calculations are compared with those using four recently proposed potentials for helium: the two beam potentials of Lee and co-workers, ESMSV II[6] and ESMMSV[7]; the second form of Bruch and McGee [8]; and Aziz parameters for the Maitland-Smith potential, AMS [9]. In Figures III-1 and III-2, the repulsive and attractive portions of these potentials are displayed. It can be seen in Figure III-2 that the Bruch-McGee form is displaced to larger radius in the bowl. It also can be seen that in the attractive region the ESMSV II, ESMMSV, and the HFD-2 are nearly identical with the AMS being slightly lower. Of these four, the ESMSV II shows the most deviation from the others in the repulsive region shown in Figure III-1.

VIRIALS

In an earlier report [10] the helium second virial data were compared to several potentials. An error in the program was discovered which produced a high value for the calculated semiclassical virial at low temperatures. Thus, the calculations for ESMSV II and ESMMSV are reproduced in Figures III-3 and III-4. The calculation marked "Aziz" in the previous report [10] is an HFD form with $C_6 = 1.47$ and $\epsilon/k = 10.9$. Comparing Figure III-3 with Figure 5 of Reference 10, one can see differences in the fit between 100 and 200 K. It can be seen in these figures that the Lennard-Jones with Mason's parameters still does not fit the modern data. At the maximum in the data, the Bruch-McGee II is too low and the Maitland-Smith, AMS, is too high. Of the two beam potentials, the ESMSV II

fits better in the 100 to 900 K region than the ESMMSV. The fit of the ESMSV II and the present HFD potential is comparable. Of all the data in Figure III-3, those of Gammon are of high accuracy and fall in the middle of the scatter of the others. Gammon's data for B are derived data from velocity of sound measurements in the region from 98 to 450 K. In this region, the HFD-2 and Lee's ESMSV II agree with the data to within $0.02 \text{ cm}^3/\text{mole}$ near 100 and 450 K. In between, the ESMSV II is about $0.06 \text{ cm}^3/\text{mole}$ higher than the data between 250 and 350 K, whereas the present HFD is about 0.06 lower between 150 and 250 K.

At temperatures below 10 K, the calculations are compared to the data in Figure III-4. The fit to the low temperature virials in Figure III-4 for the HFD-2 potential is better than any of the others including the HFD form with $C_6 = 1.47$. The improvement is particularly noticeable with respect to the helium-3 data. The ESMSV II and Bruch-McGee II fall on the same curve slightly above the present HFD calculation. Thus, the present HFD potential produces the best fit to the data between 1.5 and 900 K.

Gammon produced a functional form for B which can be used outside the range of his data. Figure III-5 shows a deviation plot of his functional form against B calculated from the HFD-2 form. There is little deviation above the experimental range, but the deviation is extreme below 100 K, where the series expansion for B in terms of h^2/m becomes inadequate to represent the quantum behavior of the gas. Gammon's Table IX becomes inaccurate below 90 K.

FIGURE III-1 - Repulsive portion of five recently proposed helium potentials: — present work, HFD-2; --- ESMSV II (Ref. 6); . . . ESMMSV (Ref. 7); -.- Bruch-McGee II (Ref. 8); --- Maitland-Smith (Aziz parameters, Ref. 9).

FIGURE III-2 - Negative portion of same five helium potentials as in Figure III-1. Below 2.8 Å, ESMSV II and Maitland-Smith are shown by the same curve.

FIGURE III-3 - Second virial coefficient for ^4He above 60 K. The experimental points are: $\circ$, Gammon (Ref. 11); $\emptyset$, White et al. (Ref. 12); $\times$, Schneider and Duffie (Ref. 13); $\bullet$, Hoover et al. (Ref. 14); $\blacksquare$, Canfield et al. (Ref. 15); $\blacktriangledown$, Briggs (Ref. 16); $\square$, Sullivan and Sonntag (Ref. 17). Potential functions are the same as in Figure III-1 with the addition of - - - - Lennard-Jones (Mason's parameters, Ref. 18).

FIGURE III-4 - Second virial coefficient for ^3He and ^4He below 10 K. The experimental points are: $\circ$, ^3He , and $\square$, ^4He , Keller (Ref. 19); $\bullet$, ^3He and ^4He , Grimsrude and Werntz (Ref. 20); $\diamond$, ^4He , Keesom et al, recalculated by Keller (Ref. 19); $+$, Berry (Ref. 21); $\circ$, Boyd et al (Ref. 22); $\times$, Levelt-Singers et al (Ref. 23). Potential functions are the same as in Figure III-1 except that ESMSV II and Bruch-McGee II fall on same curve ----.

FIGURE III-5 - Deviation plot of Gammon second virial (0) against present HFD-2 potential.

VISCOSITY

The viscosity data for helium between 1.5 and 2000 K are shown in Figures III-6 and III-7. The data are reduced by $1/(mT)^{1/2}$ to facilitate the comparison to the potential calculations and to display the data for helium-3 and helium-4 on the same graph. Potential calculations of the viscosity are shown for ESMSV II, ESMSV, AMS and HFD-2. The low temperature behavior calculated from the potentials can be seen to correlate with the attractive part of the potentials shown in Figure III-7. The lower values for AMS do not fit the low temperature viscosity data. As first proposed, HFD-2 had a value of $C_6 = 1.47$ and it displayed much the same low-temperature behavior as AMS. The adoption of $C_6 = 1.46$ produces an improved fit to the low-

temperature viscosity data. In the high-temperature region shown in Figure III-7, the relative behavior of the four potentials mirrors the repulsive parts shown in Figure III-1. The HFD-2 potential produces the best fit to the data by taking the middle ground between ESMSV and ESMSV II.

ORDINARY DIFFUSION COEFFICIENT

The isotopic diffusion coefficient, D_{34} , for helium-3/helium-4 has been measured over a relatively broad temperature range from 1.74 to 888 K. The low temperature points are due to Bendt [30], who covered the temperature range up to 296 K and who reported an experimental uncertainty of $\pm 2-6\%$. DuBro and Weissman [34], using a twin-chambered cell with no moving parts, and suitable for operation at high

FIGURE III-6 - Low temperature viscosity data for ^3He and ^4He compared with calculations for four potentials given in Figure III-1. The data are: $\circ$, ^3He , and $\blacksquare$, ^4He , Becker (Ref. 24); Δ , Becker (Ref. 25); $\square$, Coremans et al (Ref. 26); $\diamond$, Johnston and Grilly (Ref. 27); $\bullet$, Rietveld et al (Ref. 28); $\blacktriangle$, Van Itterbeck et al (Ref. 29).

FIGURE III-7 - High temperature viscosity data for ^4He compared with calculations for potentials given in Figure III-1. The data are: Δ , Johnston and Grilly (Ref. 27); $\square$, Rietveld et al (Ref. 28); $\blacksquare$, DePippo and Kestin (Ref. 30); $\circ$, Guevara et al (Ref. 31); $\bullet$, Trantz (Ref. 32).

temperature, determined D_{34} from 77 to 888 K with an estimated uncertainty on the order of $\pm 2-3\%$. In the region of overlap between these workers an absolute average deviation of $\pm 4.6\%$ exists between Bendt and the smoothed values of DuBro and Weissman. Liner and Weissman [35] used a gas chromatographic technique to obtain data with an estimated uncertainty of $\pm 3-5\%$ in the temperature range from 300 to 800 K. These results were found to be comfortably within the mutual uncertainty of the diffusion cell work.

Isotopic diffusion coefficients, D_{34} , reported by Bendt, DuBro and Weissman, and Liner and Weissman, have been fitted to a cubic equation of the form

$$\ln D = A(\ln T)^3 + B(\ln T)^2 + C \ln T + D$$

by the method of least squares. The constants determined by the fitting procedure are: $A = 6.3810 \times 10^{-3}$, $B = 6.9878 \times 10^{-2}$, $C = 1.8687$, and $D = -9.0064$. Several fitting functions were tried, including that suggested by Morrero and Mason [36]. However, the above equation produced an rms deviation in the diffusion coefficient which was smaller by at least a factor of two, than that resulting from any of the other functions. Deviations of the five potentials, along with deviations of the individual experimental points, from the above fitting function are shown in Figure III-8. The average deviation of the experimental points from the fitting function is $\pm 2\%$, considerably less than the cited experimental uncertainties for the sets of data. None of the potentials lies within the experimental uncertainties over the entire temperature range. However, the MS12G6 errs considerably on the low

FIGURE III-8 - Deviation of calculated diffusion coefficients for $^3\text{He}-^4\text{He}$ from smoothed experimental values, $\ln D_{34} = 1.6612 \ln T - 8.8761$, obtained using least squares of the following data: +, Bendt (Ref. 33); o, DuBro and Weissman (Ref. 34); and Δ , Liner and Weissman (Ref. 35). The percentage deviation of the data from the least square equations is magnified in the area near room temperature because that is where the logarithm changes signs. The theoretical curves are the same as in Figure III-1.

side below 20 K while the MDD-2, ESMBV II and ESMSV potentials err considerably on the high side at temperatures above 600 K.

THERMAL DIFFUSION

Thermal diffusion factors, α_T , for an equimolar mixture of helium-3/helium-4 are shown in Figure III-9. Experimental data shown here have been measured by two independent experimental techniques: 1) the two-bulb method, or 2) the Trennschaukel or "swing separator". The two-bulb method, although simpler experimentally, suffers from the disadvantage that measured separations with different cold-bulb temperatures must be differentiated to obtain α_T . The loss of accuracy is particularly severe at the lower end of the separation curve as appears to be the case with van der Valk [37] data (solid triangles). Van der Valk and DeVries [38]

reported a preliminary value of $\alpha_T = 0.0617$ in the range 370 to 700 K, which, within their estimated experimental uncertainty of $\pm 3\%$, appeared to be constant. Shortly thereafter, van der Valk's thesis was released and individual points from it were used to demonstrate a gradual decrease at moderate and high temperature as well as the anomalous increase at the low end. Watson et al. [39] measured α_T from below 200 K to slightly over 300 K in a Trennschaukel, and Paul et al. [40] continued the investigation in the Yale apparatus, extending the measurements to almost 600 K. (Earlier work from the Yale group has not been included because of faulty Trennschaukel design, which produced very low separations.) The single point of McInteer et al. [41] is an early two-bulb measurement on natural abundance helium. In this case, as well as the preceding, the ~ 6 to 7% theoretical

FIGURE III-9 - Thermal diffusion factor for equimolar ^3He - ^4He . The experimental points are: o, Taylor (Ref. 42); ϕ , Taylor (Ref. 43); $\bullet$, Taylor and Weissman (Ref. 44); $\blacktriangle$, van der Valk (Ref. 38); *, Watson et al (Ref. 39); +, Paul et al (Ref. 40); and $\square$, McInteer, et al (Ref. 41). The theoretical curves are the same as in Figure III-1.

composition dependence has been used to correct individual points to an equimolar mixture. The most extensive measurements have been performed by Taylor [42,43] and Taylor and Weissman [44] in the Mound Facility Trennschaukels. These measurements extend from 2 to 900 K, demonstrating a broad maximum in α_T , which gradually decreases at high temperatures and falls off rather sharply at very low temperatures.

The third Chapman-Enskog approximation to the thermal diffusion factor, $[\alpha_T]_3$, is shown for the five potentials along with the experimental data in Figure III-9. Above 10 K the theoretical curves generally possess the same qualitative behavior, except that the ESMSV II falls off too rapidly at high temperatures while the Maitland-Smith appears to be too high. The most surprising feature is the large bump in the curve below 6 K which, if real, serves as a sensitive discriminating feature for potentials. Experimental results are, however, very difficult to obtain in this region. The Trennschaukel points by Taylor [21] are lower than any of the theoretical curves, but the Maitland-Smith prediction falls within the estimated experimental uncertainty of the measurements. Certainly more experimental data are required in this very low temperature region.

DIFFERENTIAL SCATTERING CROSS SECTION

Burgmans et al. [7] have employed crossed molecular beams to measure the differential scattering cross section of a helium-3 beam scattered by a second helium-4 beam at 90° to the first. The authors have used this work to obtain the parameters in the ESMSV potential as, in an earlier publication, Farrar and Lee [6] used scattering data on helium-3/helium-4 to develop

the ESMSV II potential. No evidence of isotopic effect on the potential was observed. Because, however, unlike particles were used in the more recent work, giving use to both even and odd l partial waves, the information content of the experiment was essentially doubled, and thus presumably the ESMSV potential is a preferred form for the helium interaction.

The ESMSV potential with differential scattering intensities calculated in the center-of-mass coordinator has been used as the reference, or base line, in the deviation plot, given in Figure III-10. The differential cross sections were calculated at a relative collision energy of $E = 0.799 \times 10^{-14}$ erg, using the following expression:

$$I(\theta; E) = \frac{\chi^2}{4} \left\{ \left[\sum_{\ell} (2\ell + 1) (\sin 2\eta_{\ell}) P_{\ell}(\cos \theta) \right]^2 + \left[\sum_{\ell} (2\ell + 1) (\cos 2\eta_{\ell} - 1) P_{\ell}(\cos \theta) \right]^2 \right\}$$

where $\chi^2/4 = \hbar^2/(2\mu E)$. The various quantities are: η_{ℓ} = phase shifts obtained by numerical integration of the wave equation with a given potential; θ = center-of-mass scattering angle; $P_{\ell}(\cos \theta)$ = Legendre polynomial; ℓ = angular momentum quantum number; and χ = the reduced wave length, the expression for which contains the reduced mass and the relative energy. The deviations for both the theoretical curves and the experimental points are relative to the ESMSV potential. The deviations with associated error bars for the experimental points were read from Figure 5 in Reference 7. These results were displayed as a function of the laboratory angle so it was necessary to convert to the center-of-mass angle by numerically solving the equation:

$$\tan \theta_{\text{lab}} = \frac{\sin \theta_{\text{cm}}}{\cos \theta_{\text{cm}} + M_3/M_4}$$

FIGURE III-10 - Deviation plot for differential scattering of helium potentials in Figure III-1 against Lee's ESMMSV potential. The data are those of Burgmans et al (Ref. 7).

where M_3 and M_4 are the atomic weights of the respective isotopes. None of the potentials pass through all of the estimated uncertainty base of the experimental points, including the ESMMSV reference potential. The ESMMSV II misses only that point, and by an even smaller amount. The HFD-2 potential behaves very similarly to the ESMMSV II, but misses the uncertainty bars of two additional points at small angles. The Bruch-McGee II and the Maitland-Smith potentials both appear to yield an unsatisfactory representation for the differential scattering.

IV. Separation chemistry

Chlorine-37

W. R. Tonne

An experimental nine-column cascade (Figure IV-1) for liquid phase thermal diffusion of chlorobenzene has been used to separate 23 grams of chlorine-37 at an enrichment of 90+%. The characteristics of the columns are summarized in Table IV-1.

FIGURE IV-1 - Chlorobenzene liquid thermal diffusion cascade for separating chlorine-37. The type of each column is indicated by the letter code; the lengths of each column are shown proportionately.

Table IV-1 - CHARACTERISTICS OF LIQUID THERMAL DIFFUSION COLUMNS USED IN THE NINE-COLUMN CHLOROBENZENE CASCADE.

Column Type	Length (m)	Spacing (μ m)	Annular Diameter (mm)
A	2.4	350	25
B	2.4	300	25
C	0.75	250	25
D	0.75	200	19

The cascade is currently set up with a 500-ml reservoir at the top of the cascade. The feed is being introduced there in batches and is recharged when its concentration of chlorine-37 is depleted to ~23%. Under construction is a continuous withdrawal system to replace this

reservoir. This will allow the introduction of feed at the bottom of the second column, allowing the first two columns to work as a stripping section. This should raise the measured transport rate of 0.2 g/day of chlorine-37 to the expected value of 0.3 g/day.

The construction of a second 11-stage cascade has been completed and is soon to be put in series with the existing cascade for enrichment of 95+% chlorine-37.

Thorium-229

W. R. Deal

A total of 186 grams of uranium, in the form of UF_4 , was processed during the reporting period to produce 20.9 mg of thorium-229. Item 78-1, containing 8.3 mg of thorium-229, was assayed and found to be 48.56% thorium-229 by weight, indicating a relatively high purity. Item 78-2, containing 12.2 mg of thorium-229 is expected to produce similar results when assayed, since it was obtained from the same source of uranium-233.

Construction of the liquid uranium-233 storage facility is nearly completed, with final completion expected before the end of FY-78.

Uranium-233 inventory records have been computerized and are now maintained in the disk storage of the laboratory mini-computer.

Protactinium-231 and thorium-230

M. R. Hertz and P. E. Figgins

Mound recovers thorium-230 and protactinium-231 from a uranium mill by-product

known as "Cotter Concentrate" and ships the products to Isotope Sales at ORNL. Previous reports in this series contain detailed descriptions of the origin and character of the Cotter Concentrate, the processing facilities, and development of the current recovery and purification processes. Briefly, the process consists of leaching 20-25 liter batches of the solids with hot, concentrated HNO_3 , and then diluting and filtering off the insoluble residue. Uranium is removed from the 90-liter batches of the filtrate by liquid-liquid solvent extraction with 10% DSBPP/ CCl_4 (di-sec-butylphenylphosphonate in carbon tetrachloride) and stripped from the organic with 0.005 M HNO_3 . Thorium is next extracted by means of multiple contacts with 0.1 M TOPO/ CCl_4 (tri-n-octylphosphine oxide in carbon tetrachloride), each contact being followed by a 0.3 M H_2SO_4 strip. After the thorium has been removed, further contact with TOPO/ CCl_4 , followed by an 0.5 M oxalic acid strip, results in recovery of the protactinium. Uranium strip solutions are precipitated with ammonia and the precipitate collected for eventual return to a uranium processor. The thorium strip solutions are purified by oxalate precipitation and calcined to the oxide. Protactinium strip solutions are concentrated by evaporation and processed by the sequence of operations described below.

1) The bulk of the impurities are removed during a TOPO/DEHPA extraction from 7 M HNO_3 . The protactinium is stripped with dilute HF, and the HF removed by hydroxide precipitation. 2) Additional purification is achieved by multiple cycles of phosphate precipitation from a 2 M HCl /0.5 M oxalic acid medium [1,2]. The phosphate precipitate is dissolved easily

by treatment with hot caustic solution. 3) When the bulk of the impurities have been separated, the solids are dissolved in H_2SO_4 and HCl , and the protactinium extracted with DIBC (diisobutyl carbinol) and stripped with oxalic acid. The protactinium is further concentrated and purified by heating and hydrolyzing the oxalic strip solution. 4) Final purification and preparation of the protactinium for shipment usually includes one or more cycles of recrystallization from concentrated H_2SO_4 , followed by hydroxide precipitation, drying, calcining, and packaging.

Since the last semiannual report [3], 18 additional batches of Cotter Concentrate have been processed from drums No. 201, 207 and 206. A shipment of 35,974 mg of thorium-230 was made in partial fulfillment of the FY-78 quota. An additional 11,385 mg is on hand from recent production.

Uranium-234

P. L. Keister and P. E. Figgins

Mound has been separating and recovering uranium-234 of high isotopic purity from aged plutonium-238 for over ten years. The chemical separation steps have been described elsewhere in detail [4].

The initial separation of uranium from plutonium "cow" B10-01 by oxalate precipitation of the plutonium was completed this period. This was the second cycle of separation for B10-01, which contained 25.9 g of plutonium-238 with an estimated 0.7 g of uranium-234. The B10-01 "cow" (oxide form) was dissolved in hot, concentrated HNO_3 . The plutonium was precipitated as the oxalate, calcined to the

oxide, and returned to storage. The uranium-rich filtrate is being held for the additional purification steps.

The initial separation of uranium from plutonium "cow" A3-0 was also completed. This was the first cycle of separation for A3-0, which contained 46.5 g of plutonium-238 (oxide form) with an estimated 3.5 g of uranium-234.

Dissolution was completed for plutonium "cow" A19-0, which contained 19.9 g of plutonium-238 (oxide form) with an estimated 1.5 g of uranium-234. This solution is ready for the initial separation, which will be the first cycle of separation for A19-0.

V. Separation research

Liquid thermal diffusion

W. M. Rutherford

The last report [1] analyzed heat transfer and temperature distribution in liquid phase thermal diffusion columns similar to those used for the recent practical scale separations of chlorine and sulfur isotopes [2]. It had been found that large increases in separation at total reflux could be obtained in some columns by reducing the flow rate of the cooling water to very low values. It was postulated that the increases were the result of the positive vertical temperature gradient thereby imposed on the column. The temperature gradient was believed to inhibit large-scale parasitic circulation arising from nonuniform geometry and temperature distribution.

Experimental investigation of coolant flow effects on the behavior of liquid phase thermal diffusion columns has con-

tinued. It has been found that the postulate of a stabilizing temperature gradient is only partially true. More importantly, it has been found that large improvements in column parameters can be gained by simultaneously increasing the rate and uniformity of heat flow between the outer surface of the cold wall and the coolant.

The experiments described below fall into three categories: the first category includes the effect of coolant flow on separation behavior in columns of the standard type with 12.5 mm coolant annuli; the second category comprises separation measurements in modified columns with coolant annuli of approximately 3 mm; and the third, refers to experiments involving standard columns having 12.5 mm coolant annuli packed with spherical particles to improve the heat transfer characteristics.

STANDARD COLUMNS WITH 12.5 mm COOLANT ANNULI

Total reflux separation was measured for the $C^{32}S^{34}S-C^{32}S^{32}S$ system in four columns with 250 μ m spacing between the hot and cold walls and for the $C_6H_5^{37}Cl-C_6H_5^{35}Cl$ system in one column having a 200 μ m spacing. Dimensions and operating conditions for the columns are given in Table V-1. Results are plotted in Figure V-1. The quantity plotted is $\ln q_e/L$, where L is the length of the column and q_e is the steady-state separation factor at total reflux defined by

$$q_e = (w_1/w_2)_B / (w_1/w_2)_T, \quad (1)$$

where w_1 and w_2 are the mass fractions of the components, and the subscripts T and B refer to the top and bottom of the column.

FIGURE V-1 - Effect of coolant flow on liquid phase thermal diffusion column performance.

Table V-1 - DIMENSIONS AND OPERATING CONDITIONS FOR
EXPERIMENTAL LIQUID THERMAL DIFFUSION COLUMNS

Steam Temperature: 437 K (164°C)

Water Temperature: 288 K (15°C)

Column	Diameters of Coolant Annulus (mm)		Average Diameter of Separation Annulus (mm)	Hot-to- Cold-Wall Spacing (μ m)	Length (m)	Packing
	Inner	Outer				
PC10D	38.1	62.6	25.3	254	0.610	None
PC7B	38.1	62.6	25.3	254	0.711	None
PC7C	38.1	62.6	25.3	254	0.762	None
8SC8	25.4	50.5	19.4	203	0.764	None
PC6CN	38.1	44.3	25.3	254	0.721	None
8SC6N	25.4	32.1	19.4	203	0.760	None
PC7B-CU	38.1	62.6	25.3	254	0.71	Copper Shot
PC8C-CU	38.1	62.6	25.3	254	0.762	Copper Shot
PC8C-GB	38.1	62.6	25.3	254	0.762	Glass Beads
PC9A-GB	38.1	62.6	25.3	254	1.168	Glass Beads
8SC8-GB	25.4	50.5	19.4	203	0.76	Glass Beads

The data in Figure V-1 show very clearly the effect noted in previous work, i.e., the increase in separation at very low water flow rates. The effect is greater for column PC10D, which has two inhomogeneities in the cold wall at points where unused ports were sealed off with silver solder.

The dashed lines in Figure V-1 are the separation factors calculated from theory using temperature distributions calculated for column PC10D. (The value of $\ln q_e/L$ is, to the first approximation, unaffected by the temperature difference between the hot and cold walls.)

It should be noted that the transition from laminar to turbulent flow in the water jacket is estimated to take place

at coolant flow rates between 10 and 14 liters/min in columns PC10D, PC7B, and PC7C. The separation does not appear to exhibit any response to this transition.

COLUMNS WITH 3 mm COOLANT ANNULI

Two columns of standard construction were modified to decrease the coolant annulus from 12.5 mm to 3 mm. Pertinent dimensions and operating conditions are given in Table V-1. One of the columns had a 250 μ m spacing between the hot and cold walls; the other, somewhat smaller diameter column, had a spacing of 200 μ m. The separation in the carbon disulfide isotopic system at total reflux was measured as a function of water flow rate for column PC6CN with 250 μ m spacing.

The results, which are plotted in Figure V-1, show very poor performance at low water flow rates with a sharp transition to extremely good performance, in excess of theoretical expectations, at coolant flow rates above 20 liters/min. The transition to high values of the separation takes place in a flow rate range approximately a factor of 2 greater than the range in which the transition from laminar to turbulent flow is expected to take place. The turbulent transition should occur somewhere between 8 and 11 liters/min. As would be expected, the measured heat flow through the column increases by about 20% in the turbulent transition range.

The initial transport coefficient, H , was evaluated for column PC6CN at a coolant flow rate of 30 liters/min. The apparatus used is depicted schematically in Figure V-2. Separation was measured as a function of time with the CS_2 flow rate through the column steady at 0.242 ml/hr. The results are plotted in Figure V-3. An experimental value of H was selected such that theoretical performance calculations based on that value gave a good match between the observed separation and the calculated separation at the steady state. Column parameters derived from the total reflux and the transport experiments are given in Table V-2. The quantity Y reported in Table V-2 is defined by

$$Y = \ln q_e, \quad (2)$$

where q_e is the separation factor at total reflux. The value of Y reported in Table V-2 for column PC6N was taken from an average of measurements at coolant flow rates of 19, 20, and 41 liters/min.

The separation at total reflux for the CS_2 system was also measured using column

8SC6N, which has a hot-to-cold-wall spacing of 200 μm . At 20 liters/min the water flow in the coolant annulus had a velocity and a Reynolds number equal to those in PC6CN at 30 liters/min. The result of the separation measurement is given in Table V-2 in the form of the coefficient Y .

FIGURE V-2 - Schematic diagram of apparatus used to measure initial transport coefficients.

STANDARD COLUMNS WITH BEAD- AND SHOT-PAKED ANNULI

The literature on heat transfer suggests that heat transfer to fluids flowing at low rates can be considerably enhanced by packing the flow cross section with particles, preferably spherical ones. The packing induces fluid velocity components and mixing perpendicular to the heat transfer surface in a system which would otherwise have only laminar flow parallel to the surface. Uniform packing also eliminates instabilities and standing waves which might be expected in the tall vertical coolant cross sections that are typical of liquid phase thermal diffusion columns.

FIGURE V-3 - Performance of liquid thermal diffusion columns at a product flow rate of 0.242 ml/hr. The lines are calculated on the basis of experimental values of H and Y given in Table V-2.

Table V-2 - COLUMN PARAMETERS FROM LIQUID THERMAL DIFFUSION EXPERIMENTS

Unmodified Columns, 12.5 mm Annulus						
Column	Water Flow Rate (liters/min)	System	$10^5 H_{\text{exptl}}$ (g/sec)	$10^5 H_{\text{theoret}}^{a,b}$ (g/sec)	Y_{exptl}	Y_{theoret}^b
PC10D	1.4	CS ₂	9.4	13.4	1.22	1.01
PC7B	1.2	CS ₂	-	-	1.10	1.18
8SC8	1.1	C ₆ H ₅ Cl	-	-	1.45	1.40
Columns With 3 mm Coolant Annuli						
PC6CN	30	CS ₂	17.4	24.0	1.54	1.28
8SC6N	20	CS ₂	-	-	2.67	3.29
Columns With Packed Annuli						
PC7B-CU	7	CS ₂	12.3	20.0	1.53	1.26
PC8C-CU	7	CS ₂	12.3	20.0	1.27	1.35
PC8C-GB	7	CS ₂	12.3	20.0	1.61	1.35
PC9A-GB	7	CS ₂	11.6	20.0	2.43	2.07
8SC8-GB	5	CS ₂	-	-	2.64	3.29
8SC8-GB	5	C ₆ H ₅ Cl	-	-	1.70	1.40

^aBased on estimated hot- and cold-wall temperatures.
^bBased on thermal diffusion factors of 0.06 for CS₂ and 0.02 for C₆H₅Cl.

The work is still continuing; however, five columns with 12.5 mm coolant annuli have so far been packed and tested. Several of these were packed with 1.6 to 3.2 mm copper shot; others were packed with nominal 2 mm glass beads. The results for both materials appear to be the same; therefore, no distinction will be made in the discussion which follows. Column parameters are listed in Table V-1.

Columns having spacings of 250 μ m were tested at total reflux and at a product flow rate of 0.242 ml/hr in a system similar to that of Figure V-2. Carbon disulfide was used as the test fluid. Selected results of the flow separation measurements are plotted in Figure V-3. The parameters H and Y derived from the two sets of experiments are given in Table V-2.

One column having a spacing of 200 μ m was tested at total reflux only. Two experiments were performed, one with carbon disulfide and the other with chlorobenzene as the working fluid. The resulting values of Y are given in Table V-2.

SIGNIFICANCE OF THE MODIFIED COOLANT FLOW EXPERIMENTS

The information reported in Table V-2 and Figure V-1 leads to some very important conclusions with respect to the design and operation of liquid phase thermal diffusion columns. These are listed as follows (assuming steam or vapor heated columns):

1. If reasonable precision has been maintained in column fabrication, the separation behavior of the column is dominated by the nature of the heat transfer between the cold wall and the coolant.

2. Moderately good total reflux performance can be obtained in short columns with wide coolant channels by reducing the coolant flow to very low values. The initial transport coefficient is greatly reduced, however, by the concomitant reduction in heat flow.
3. Very good total reflux performance can be obtained even in long (1.2 m) columns by packing a wide coolant channel with spherical particles.
4. Very good total reflux performance and high initial transport can be attained by using high coolant flow rates in narrow channels.

The mechanisms which lead to these conclusions are by no means established. It is known, however, that even slight departures from nonuniform circumferential temperature lead to large parasitic circulations. The following speculations may explain some of the results:

1. Positive vertical temperature gradients tend to suppress parasitic circulation in poorly constructed columns.
2. In columns with wide coolant channels, standing waves or other types of instability occur in the combined forced and free convection flow pattern of the coolant. These are especially likely to occur in long columns. This may account for frequently observed poor performance of columns longer than 0.6 m.
3. Bead or shot packings are effective because they eliminate instabilities in coolant flow and create a much more macroscopically uniform heat transfer pattern.

4. Satisfactorily uniform heat transfer in turbulent coolant flow can only be achieved if the scale or size of the turbulent eddies is sufficiently small. This requires a combination of high Reynolds numbers and small dimensions.

ISOTOPIC SEPARATION IN SOLUTE-SOLVENT SYSTEMS

W. M. Rutherford and S. J. Evans

Many elements for which isotopic separations are of interest do not have convenient gas phase or liquid phase compounds which could be used as working fluids in thermal diffusion columns. There is a possibility that these systems can be separated as salts or other compounds dissolved in water or nonaqueous solvents. There is some evidence to indicate that isotopic effects in such solute-solvent systems are large enough to be of interest for practical-scale separations [3, 4,5].

In a solute-solvent system, the separation between the solute and solvent is much larger and proceeds faster than the separation between the components of the solute. Korsching showed how the solute-solvent separation could be offset by a counterflow of solvent [6]. The idea is illustrated in Figure V-4. Pure solvent is injected into the bottom of the column at a controlled rate. At the top of the column an equivalent amount of solvent is removed by distillation. The solute-solvent concentration gradient is thereby flattened, and separation of the solute components can proceed much more efficiently.

FIGURE V-4 - Apparatus for separation of solutes by thermal diffusion.

If we treat the system at first as a two-component system, we can find a solvent injection rate which results in a uniform solute concentration. For the conditions illustrated in Figure V-4, the solvent transport τ_1 is given by

$$\tau_1 = \sigma_1 = Hw_1 (1-w_1) - K \frac{dw_1}{dz} + \sigma_1 w_1 \quad (3)$$

where σ_1 is the solvent injection rate, H is the initial transport coefficient, K is the remixing coefficient, z is the vertical coordinate, and w_1 is the mass fraction of solvent. If we set

$$\frac{dw_1}{dz} = 0, \quad (4)$$

this leads to

$$\sigma_1 = Hw_1 \quad (5)$$

as the condition for a uniform solute-solvent concentration profile.

Existing computer programs were modified to evaluate the stability of the condition given by Equation 5. The assumptions were as follows:

$$Y_{12} = 5 \text{ for the solute-solvent pair}$$

$$w_1 = 0.75 \text{ for the initial fill concentration.}$$

The results are plotted in Figure V-5 in which the solute concentration at the steady state is given for the top and bottom ends of the column as a function of the ratio σ_1/H . The crossover point occurs, as expected on the basis of Equation 5, at $\sigma_1/H = 0.75$.

The separation of two solute components was investigated in the same set of calculations. The additional assumptions were:

$$Y_{23} = 0.5 \text{ for the solute compounds}$$

$$w_2 = 0.9982 \text{ for one solute component}$$

$$w_3 = 0.0018 \text{ for the other solute component}$$

The results showed that at the steady state

$$\ln q_{23} \approx Y_{23} \quad (6)$$

for all values of σ_1 . It may be possible to prove Equation 6 in the formal sense but this has not yet been attempted.

FIGURE V-5 - Solute concentrations as a function of relative solvent injection rate.

Molecular beam scattering

TARGET GAS CELL

R. W. York

The new, refrigerated, target gas cell was installed in the molecular beam chamber. It was aligned to the primary beam path and connected to the volumetric target feed system. This new cell was described in a previous report written during its construction [7]. The resultant change in the target cell feed system flow characteristics made it necessary to perform new flow calibrations for accurate

FIGURE V-6 - Calibration curves for $T_{\text{cell}} = 300 \text{ K}$ and $T_{\text{feed}} = 298 \text{ K}$ for the target gas cell feed system. P_{cell} is the target cell pressure; P_{feed} is the cell feed pressure.

determinations of the target gas densities in the cell. These calibrations were completed for helium, neon, argon, and krypton at a target temperature of 300 K. The data were normalized to a constant room temperature of 298 K because of large room temperature changes during the calibration measurements.

The results of these calibrations are shown in Figure V-6. The target cell gas pressure is shown as a function of feed pressure. During an experiment, the curve value must be corrected for both room temperature and cell temperature where these differ from 298 K and 300 K, respectively. The details of this target feed system and of the calibration procedures have been described in an earlier report [8]. Both the nozzle beam source and the target cell should now be continuously variable in operating temperature from 40 K to 375 K. This will allow measurements to be made over a much wider range of relative energies than before.

The molecular beam system is currently being evacuated for adjustments to the quadrupole detector. Total scattering cross section measurements of pair collisions of the above mentioned gases will then commence.

VELOCITY SELECTOR

R. E. Miers

A drive mounting system was constructed for one of the two velocity-selector rotors [7]. The rotor design and fabrication have been described in earlier reports [8,9]. Figure V-7 is a sketch of the mounting system. The position of the rotor can be adjusted from outside the

vacuum system by means of two micrometer height-adjusting stages and their stainless steel bellows. This adjusting system allows precise alignment of the rotor with the beam-defining apertures, and also allows the rotor to be moved completely out of the beam.

Figure V-8 is a sketch showing the method used to monitor the angular speed of the rotor. The edge of the rotor is painted a matte black except for a 3/8-inch long unpainted section. A light-emitting diode is located to shine on the painted stripe. A PIN diode detector monitors the light reflected from the rotor. The light reflected from the unpainted section appears to the detector as a light pulse each time the rotor makes a revolution. The output from the PIN diode is measured with a high-speed pulse amplifier and a digital counter.

The rotor wheel is powered by an AC, hysteresis, synchronous motor manufactured by TRW Globe Motors of Dayton, Ohio. This motor is designed to be operated from a single phase, variable frequency power supply. The speed of the motor can be continuously varied from 5000 rpm to 30,000 rpm.

A special, stainless steel bell jar was constructed to be used as a vacuum test system. The rotor mounting system was installed in the bell jar and operated with a dummy rotor. This rotor is identical to the actual velocity-selector rotor except that it lacks the specially machined spiral paths which select the beam velocities. Since this wheel was not dynamically balanced, it was operated only to 10,000 rpm. The rotor system including the pulse-counting apparatus worked well with no apparent problems. A thermocouple

FIGURE V-7 - Velocity-selector drive mounting system.

FIGURE V-8 - Angular-speed monitoring system.

attached to the motor was used to measure the temperature of the motor. The temperature rose to above 100°C during extended high-speed operation, possibly indicating the need for more thermal conduction from the motor to the vacuum wall. The design of the motor mounting system will allow such a modification to be relatively simple, if needed.

An effusive beam source for permanent gases and an ion gauge detector were mounted in the bell jar. Figure V-9 shows the relative arrangement of these components. A gas-handling system allows the source to be filled with any permanent gas. Source pressures are monitored with an MKS Baratron gauge.

The next step will be to measure a beam in the bell jar with the velocity-selector

rotor mounted and dynamically balanced. Velocity distribution profiles of an effusive beam will be measured to ascertain the characteristics of the velocity selector.

Mutual diffusion coefficients of krypton-noble gas mixtures

D. Cain and W. L. Taylor

Knowledge of gaseous diffusion coefficients gives rather direct information on the pair interaction potential between unlike molecules. However, for mixtures of krypton with other noble gases, few data exist. Most of these studies have been confined to a relatively small temperature range, with only two previous studies of the diffusion coefficients of these systems above 500 K.

FIGURE V-9 - Diagram of component arrangement for testing velocity selector in bell jar.

As mentioned in a previous report [10], the diffusion coefficients of krypton-noble gas mixtures are being measured from approximately 300 to 1200 K. The apparatus, procedures, and theory have been described in some detail in the aforementioned report. Briefly, a new diffusion cell has been constructed for the experiments. The apparatus has no moving parts, allowing it to be used at elevated temperatures without fear of mechanical failure. A multiple sampling technique is used which makes these experiments independent of the initial concentrations of the feed gases. A vertical orientation of the diffusion cell is maintained to prevent spillage effects. The feed gases are simultaneously expanded from ballast tanks into the diffusion chambers, with the more massive component being introduced into the lower chamber to avoid convective effects. Small samples are drawn simultaneously from each chamber at intervals throughout the experiment and set aside for analysis.

Pertinent cell dimensions are:

$$\begin{aligned} V_1 &= 1120.1 \text{ cm}^3 \\ V_2 &= 1121.1 \text{ cm}^3 \\ L &= 10.08 \text{ cm} \\ r &= 0.1831 \text{ cm} \end{aligned}$$

Here V_1 and V_2 are the volumes of the different diffusion chambers, and L and r are the length and radius, respectively, of the connecting tube.

The equations describing the diffusion process are an adaptation of those first worked out by Ney and Armistead [11], and read as follows:

$$\ln [\chi_2(t_n) - \chi_1(t_n)] = -D_{12} P_{\text{atm}} f(G) \beta_n + \ln [\chi_2(0) - \chi_1(0)] \quad (1)$$

$$\beta_n = t_n/P_n + \sum_{i=1}^n t_{i-1} (P_i - P_{i-1})/P_i P_{i-1} \quad (2)$$

In these equations, $\chi_2(t_n)$ and $\chi_1(t_n)$ are the molar concentrations of a particular gas component in volumes V_2 at t_n , and V_1 at t_n , respectively. $\chi_2(0)$ and $\chi_1(0)$ are the initial concentrations of the gases ($t = 0$), P_{atm} is atmospheric pressure, and D_{12} is the diffusion coefficient at one standard atmosphere. The parameter $f(G)$ is a constant which depends only upon the four geometrical factors, V_1 , V_2 , L , and r , and is given explicitly elsewhere [10]. The term β_n accounts for the multiple sampling where the t_i and P_i are the times and pressures, respectively, at which the i^{th} samples are drawn.

In the equation above, the logarithm of the concentration differences is linearly related to the time/pressure variable, β_n . The intercept of that line is determined by the initial concentration difference. The diffusion coefficient, however, is extracted from the slope of the line, which can be determined without knowledge of the intercept by the method of least squares.

Table V-3 shows all the data from the present study, including those which were reported earlier [10]. Figure V-10 shows the present results along with those of other experimenters in a plot of $\ln D_{12}$ as a function of $\ln T$, which, according to theory, should be approximately linear over a wide temperature range [12]. The

Table V-3 - DIFFUSION COEFFICIENT MEASUREMENTS
CORRECTED TO 1 ATMOSPHERE PRESSURE

System	Temperature (K)	D ₁₂ (cm ² /sec)	System	Temperature (K)	D ₁₂ (cm ² /sec)
He-Kr	358.1	0.879	Ar-Kr	339.0	0.184
	497.9	1.54		458.5	0.318
	647.9	2.42		599.8	0.503
	798.4	3.39		821.3	0.882
	998.2	4.94		1008.0	1.26
	1194.2	6.89		1116.9	1.47
Ne-Kr	350.2	0.362	Kr-Xe	1216.9	1.78
	497.1	0.633		333.5	0.099
	652.1	1.010		394.0	0.136
	796.4	1.446		505.8	0.223
	911.5	1.78		599.7	0.293
	1222.4	2.998		715.3	0.401
				813.0	0.507
				911.6	0.621
				1010.2	0.752
				1199.2	0.992

experimental data shown are given in References 13-20. It should be noted, however, that additional data exist for argon, neon, and helium, with krypton. The points not shown are confined to the narrow region between 270 and 400 K and do not exhibit any significant scatter. For the sake of clarity, they have been omitted, but can be found in References 21-28.

While high temperature data are still scarce, the data of Hogervorst [16] seem to be consistently lower than both the data of Loiko et al. [13] and the present data, as can be seen in Figure V-10. Hogervorst used the method of cataphoresis in his determination of the diffusion coefficients; Loiko et al. used a twin-tank method similar to the one described here. The figure also shows that the present data have extended the temperature range for which diffusion coefficients are available by approximately 100 and 400 K, respectively, for the helium-krypton and krypton-xenon systems. The theoretical expression for the diffu-

sion coefficient is given by the following equation [29].

$$D_{12} = \frac{2.6280 \times 10^{-3} [T^3 (M_1 + M_2) / 2M_1 M_2]^{\frac{1}{2}}}{P \sigma_{12}^2 \Omega_{12}^{(1,1)*} (T_{12}^*)} \quad (3)$$

In this equation T is the absolute temperature, M₁ and M₂ are the molar masses of the species, and P is the pressure measured in atmospheres. The remaining quantities are related to the interaction forces between the opposing particles. $\Omega_{12}^{(1,1)*}$ is the dimensionless, reduced collision integral. It is obtained from the intermolecular potential by a series of integral relations and is an effective cross section for the collisions between the particles which are diffusing. The collision integrals are functions of $T^* = kT/\epsilon_{12}$, the reduced temperature. The quantity k is Boltzmann's constant, while ϵ_{12} and σ_{12} are characteristic parameters of the intermolecular potential, giving the depth and location of the potential minimum, respectively.

Collision integrals have been calculated numerically using several intermolecular

FIGURE V-10 - Diffusion coefficient, D_{12} , as a function of temperature for all krypton noble gas systems. The experimental points are: ●, present work; ○, Loiko et al (13); □, Malinauskas (17,18); ◇, Hogervorst (16); ▽, Srivastava et al (19, 20); Δ, van Heijningen et al (14); ◐, Watts (15).

potential functions. Theoretical diffusion coefficients were then calculated using the above equation. Details of the numerical techniques used to arrive at values for the collision integrals are given elsewhere [30]. The potentials under consideration are the Lennard-Jones 6-12 (LJ), the Dymond Alder potential (DA) [31], and a variety of multiparameter potentials recently proposed specifically for the krypton-noble gas mixtures.

In addition to the LJ and DA potentials which are common to all systems, the exponential-spline-Morse-spline-van der Waals potential (ESMSV) is being considered for helium-krypton and the Morse-spline-van der Waals potential (MSV) for neon-krypton. Both of these latter potentials have been fitted to differential cross section data and second virial coefficients [32,33]; in addition, the MSV potential has been fitted to diffusion coefficient data [33]. Gough et al. [34] have fitted argon-krypton viscosity measurements to the single-parameter Maitland-Smith (MS) potential. Finally, Lee and co-workers [35] used the excess thermodynamic properties of argon-krypton and krypton-xenon to arrive at potentials of the form proposed by Barker, Fisher, and Watts (BFW) [36]. The parameters for the LJ potential were determined by van Heijningen et al. [14] to fit his own diffusion coefficient data, whereas those for the DA were determined by Lin and Robinson [37] using the principle of corresponding states.

The experimental diffusion coefficient data for each system have been smoothed by fitting them to the following form:

$$\ln D_{12} = A \ln T + B. \quad (4)$$

The constants A and B are determined by the method of least squares. The values of $D_{12}(T)$ determined from this procedure are used as a basis for gauging the effectiveness of a proposed potential in terms of its ability to predict diffusion coefficients from 100 to 1500 K.

The LJ is able to predict the smoothed values of D_{12} for krypton-xenon to within 5% (the approximate experimental spread of all experimenters from the least squares value) for only a short, low temperature interval; outside this interval the agreement is poor. For helium, neon, and argon with krypton, the LJ fares much better, yielding values to within 3.5% over the entire temperature range. This result is not surprising since the parameters for this potential were determined by fitting to diffusion data which extend to only 400 K.

The DA fits neon and argon with krypton, and xenon with krypton up to 1000 K, to within 5%. Above 1000 K, DA was inadequate for krypton-xenon; it cannot satisfactorily predict diffusion coefficients for helium-krypton at any temperature. The fit for the MSV is excellent; it is able to predict D_{12} for neon-krypton to within 1% at all temperatures. Similarly, the MS and BFW deviate by less than 2% for argon-krypton. ESMSV for helium-krypton is within 3% up to about 1000 K where it gets slightly worse. BFW is more successful for krypton-xenon than are LJ and DA, but exhibits a similar, high-temperature deviation.

These results are depicted graphically for helium, neon, argon, and xenon with krypton in Figures V-11 - V-14, respectively. The zero line on each plot represents the smoothed experimental results found in the

FIGURE V-11 - Percentage deviation of calculated diffusion coefficient for He-Kr from smoothed experimental values. The theoretical curves are: —, LJ; ---, DA (31,37);, ESMSV (32).

FIGURE V-12 - Percentage deviation of calculated diffusion coefficient for Ne-Kr from smoothed experimental values. The theoretical curves are: —, LJ; ----, DA (31,37);, MSV (33).

FIGURE V-13 - Percentage of calculated diffusion coefficient for Ar-Kr from smoothed experimental values. The theoretical curves are: —, LJ; ----, DA(31,37); -.-., BFW (35,36); MS (34).

FIGURE V-14 - Percentage deviation of calculated diffusion coefficient for Kr-Xe from smoothed experimental values. The theoretical curves are: —, LJ; ----, DA (31,37); -.-., BFW (35,36).

literature. The various curves are percentage deviations of the potentials from the smoothed values. The general agreement between the potentials and the experimental data is readily seen, particularly for neon and argon with krypton.

VI. Metal hydride research

NMR studies

STUDIES OF TiCuH

R. C. Bowman, Jr.

Preliminary results for the proton relaxation times of nominal TiCuH were presented in the preceding report [1] of this series. More extensive NMR measurements, along with interpretative analyses have since been performed on a second TiCuH sample provided by Dr. A. Maeland of Allied Chemicals Research Center. Consequently, some significant new evidence on the hydrogen diffusion mechanisms in titanium-based hydrides has been obtained.

The reaction between hydrogen gas and the b.c. tetragonal γ -phase TiCu intermetallic yields two different hydrides depending upon the reaction conditions. Yamanaka et al. [2] observed the reversible reaction

However, Maeland [3,4] was able to prepare a ternary monohydride from the reaction

Heating TiCuH_x samples above ~200°C for an extended period of time produces [3,4] TiH₂ and copper metal, which indicates that the ternary monohydride is thermodynamically unstable relative to TiH₂ and copper. Neutron diffraction measurements [5] on TiCuD yielded a tetragonal structure with space group P4/nmm, Z = 2, and the deuterium atoms located in positions 2(b) which are centers of distorted tetrahedra of titanium atoms. Furthermore, space group symmetry requires the deuterium atoms to occupy positions with z-coordinates at the c-parameter midpoint which results in a two-dimensional planar arrangement of deuterium atoms. Since the Ti-Ti, Ti-D, and D-D distances [5] in TiCuD are nearly identical to the corresponding interatomic separations in TiD_{1.97} [6], the TiCuD structure can be described as alternating slices of tetragonally distorted TiD₂ and copper atoms. The present NMR studies verify that TiCuH has the same structure as TiCuD. The proton relaxation times also indicate that the hydrogen diffusion behavior in TiCuH differs significantly from the hydrogen-atom jump mechanism previously reported [7-10] for f.c.c. γ -phase TiH_x. Since the hydrogen atoms in γ -TiH_x are believed [8, 10] to jump along $\langle 111 \rangle$ -body diagonals through vacant octahedral sites, this difference is caused by restricting the hydrogen-atom jumps within the planes of the TiCuH structure.

Two samples with compositions TiCuH_{0.92} and TiCuH_{0.94} were investigated in the temperature region between 90 K and 560 K using pulse NMR techniques. The proton lineshapes were obtained from solid echoes [11]. The spin-lattice relaxation times (T₁) were measured with either the π - τ - $\pi/2$ or π - τ - $\pi/2$ -15 μ s-($\pi/2$)90° pulse

sequences, where the subscript "90°" indicates a 90-degree phase shift of the third rf pulse. The dipolar relaxation time (T_{1D}) was monitored with the $\pi/2$ -15 μ s-($\pi/4$)90°- τ -($\pi/4$)90° sequence described by Jeener and Broekaert [12]. Proton linewidths, spin echo decays, and Carr-Purcell-Meiboom-Gill pulse sequences [13] were used to determine the spin-spin relaxation times (T_2) over the appropriate temperature intervals. The T_1 , T_{1D} , and T_2 (after the onset of motional narrowing) recoveries were exponential, indicating that the TiCuH_x samples were essentially single phase.

The TiCuH_x proton linewidths are constant below ~450 K. A typical plot of the proton lineshape is shown in Figure VI-1 and obeys a Gaussian dependence over ~95% of its decay. The proton second magnetic moments (M_{2D}) can be readily obtained from these lineshapes and the average experimental $M_{2D} = 17.8 \pm 0.8 \text{ G}^2$ for room temperature. The theoretical expression for the dipolar moment M_{2D} of TiCuH is

$$M_{2D}(\text{calc}) = M_{2D}(\text{H}) + M_{2D}(\text{Cu}) + M_{2D}(\text{Ti}) \quad (3)$$

where

$$M_{2D}(\text{H}) = \frac{3}{5} \hbar^2 \gamma_H^2 I(I+1) f_H \sum_i r_i^{-6} \quad (4)$$

$$M_{2D}(\text{Cu}) = \frac{4}{15} \hbar^2 \left\{ S_{\text{Cu}}(S_{\text{Cu}}+1) \gamma_{\text{Cu}}^2 f_{\text{Cu}} + S'_{\text{Cu}}(S'_{\text{Cu}}+1) \gamma_{\text{Cu}}^2 f'_{\text{Cu}} \right\} \sum_j r_j^{-6} \quad (5)$$

and

$$M_{2D}(\text{Ti}) = \frac{4}{15} \hbar^2 \left\{ S_{\text{Ti}}(S_{\text{Ti}}+1) \gamma_{\text{Ti}}^2 f_{\text{Ti}} + S'_{\text{Ti}}(S'_{\text{Ti}}+1) \gamma_{\text{Ti}}^2 f'_{\text{Ti}} \right\} \sum_k r_k^{-6} \quad (6)$$

I , γ_H , and f_H are, respectively, the known spin quantum number, the gyromagnetic

FIGURE VI-1 - Room temperature proton lineshape for $\text{TiCuH}_{0.94}$ from solid echo at 34.5 MHz.

moment, and the atom ratio of protons. Similarly, S_{Cu} , γ_{Cu} , and f_{Cu} correspond to ^{63}Cu ; S'_{Cu} , γ'_{Cu} , and f'_{Cu} correspond to ^{65}Cu ; S_{Ti} , γ_{Ti} , and f_{Ti} correspond to ^{47}Ti ; and S'_{Ti} , γ'_{Ti} , and f'_{Ti} correspond to ^{49}Ti . The lattice sums in Equations 4-6 are between protons with the other proton, copper, and titanium nuclei and contain the structural information relating to the location of the hydrogen atoms in TiCuH . Using the P4/nmm space group atomic coordinates and the $\text{TiCuH}_{0.97}$ lattice parameters [4] $a = 3.04\text{\AA}$ and $c = 6.85\text{\AA}$, the dipolar M_{2D} has been calculated yielding

$$M_{2D}(\text{calc}) = 17.3\text{G}^2 + 0.4\text{G}^2 + 0.1\text{G}^2 = 17.8\text{G}^2 \quad (7)$$

The excellent agreement between the experimental and calculated M_{2D} indicates TiCuH and TiCuD are isomorphic and confirms the P4/nmm tetragonal structure deduced from

the powder neutron diffraction measurements. Hence, the hydrogen atoms which are located at the centers of distorted tetrahedra of titanium atoms (Ti-H distance is $1.934\text{\AA}$ with a shortest Cu-H distance of $3.171\text{\AA}$) form a planar array between the two layers of titanium atoms. This particular structure has two significant consequences: 1) the easy decomposition of TiCuH into TiH_2 and copper during heating to relatively low temperatures ($>200^\circ\text{C}$) since phase segregation can readily occur [2-4], and 2) the inhibition of hydrogen-atom jumps between different hydrogen planes, caused by the presence of the nonbonding copper layer. Hence, TiCuH corresponds to a two-dimensional lattice for hydrogen-atom diffusion.

The proton T_1 temperature dependence for the two TiCuH_x samples is summarized in Figure VI-2. When interactions with conduction electrons is the relaxation mechanism, T_1 obeys the Korringa relation [9,10]

$$(T_1 T)^{-1} = C_K N_e (E_f)^2 \quad (8)$$

where C_K is approximately constant and $N_e(E_f)$ is the density of electronic states at the Fermi surface, as sampled at the hydrogen sites. In Figure VI-2 the values of T_1^{-1} increase linearly with temperature for both TiCuH_x samples below 320 K; conduction electrons clearly dominate proton spin-lattice relaxation below this temperature. Although the difference in the $\text{TiCuH}_{0.92}$ and $\text{TiCuH}_{0.94}$ Korringa constants $T_1 T$ may reflect a concentration dependence of the electronic densities, the average $T_1 T = 40 \text{ sK}$ is taken to be representative of the TiCuH monohydride. In Table VI-1 this value is compared to

FIGURE VI-2 - Inverse proton spin-lattice relaxation times as measured for TiCuH .

similar Korringa parameters for TiH_x [7, 9,10] and several other ternary titanium hydrides [9,14-16]. The crystal structures are also included in Table VI-1. With the exception of octahedral hydrogen in orthorhombic [17] β -phase $\text{TiFeH}_{1.0}$, the hydrogen atoms occupy tetrahedral interstitial sites of the f.c.c. or slightly tetragonally distorted structures. Although the Korringa parameters may correspond to electronic structure differences among these hydrides, the relative contributions of crystal structure and metal atom substitution cannot be reliably determined from the $T_1 T$ data alone. Furthermore, Table VI-1 shows the $T_1 T$ values for TiH_x to be very concentration dependent and Korn finds $(T_1 T)^{-1/2}$ for γ - TiH_x to be generally temperature dependent as well [18]. Although Korn has related these complexities to a VanHove singularity and to shifts in the electronic density of states, as well as to a tetragonal phase transition when $x > 1.8$, the presence of similar

Table VI-1 - SUMMARY OF KORRINGA AND HYDROGEN DIFFUSION PARAMETERS
IN TiCuH , TiH_x , AND SEVERAL TERNARY TITANIUM HYDRIDES

Hydride	Crystal Structure	Preferred Hydrogen Lattice Sites	T_1T (sK)	E_a (eV)	$D(300 \text{ K})$ (cm^2/s)	Reference
$\text{TiCuH}_{0.94}$	tetragonal	tetrahedral	40 ± 2	0.79 ± 0.03	9.9×10^{-16}	Present work
$\text{TiH}_{1.55}$	f.c.c.	tetrahedral	190 ± 4	0.51 ± 0.02	--	Korn & Zamir ⁷
$\text{TiH}_{1.90}$	f.c.c.	tetrahedral	62.5 ± 2	0.51 ± 0.02	--	Korn & Zamir ⁷
$\text{TiH}_{1.90}$	f.c.c.	tetrahedral	55 ± 2	0.49 ± 0.02	5.4×10^{-13}	Schmolz & Noack ¹⁰
$\text{TiH}_{1.96}$	f.c.c.	tetrahedral	41 ± 2	0.50 ± 0.02	2.1×10^{-13}	Schmolz & Noack ¹⁰
$\text{TiH}_{1.79}$	f.c.c.	tetrahedral	18.3 ± 1.5	0.49 ± 0.03	--	Khodosov & Shepilov ^{9, 16}
TiNbH_x	f.c.c.	tetrahedral	--	~ 1.1	--	Malutchov et al. ²⁰
$\text{TiNbH}_{3.88}$	f.c.c.	tetrahedral	108(2)	0.32	--	Nowak et al. ¹⁴
$\text{TiFeH}_{1.0}$	ortho-rhombic	octahedral	3.0 ± 0.3	0.26 ± 0.02	$\sim 2 \times 10^{-12}$	Bowman et al. ¹⁵
$\text{TiZr}_{0.525}\text{H}_{2.86}$	f.c.t.	tetrahedral	24 ± 2	0.86(9)	1.5×10^{-14}	Khodosov et al. ^{16,21}
$\text{TiZr}_{1.32}\text{H}_{4.65}$	f.c.t.	tetrahedral	40 ± 4	1.00(9)	1.4×10^{-16}	Khodosov et al. ^{16,21}

effects in TiCuH and the other ternary titanium hydrides is unclear. However, the T_1 data in Figure VI-2 for TiCuH_x appear to be rather well behaved and reflect a nearly constant density of states approximately equal to $\text{TiH}_{1.96}$ from the measurements of Schmolz and Noack [10]. Although similar electronic structures are expected since the local environment for hydrogen atoms in TiCuH correspond to a distorted TiH_2 phase, further comparisons are deferred until additional investigations are completed.

The hydrogen diffusion behavior in metal hydrides can be conveniently determined by NMR techniques when the proton relaxation rates have significant diffusion contributions [19]. Consequently, the protons T_1 , T_{1D} and T_2 for $\text{TiCuH}_{0.94}$ have been measured to above 560 K and are presented in Figure VI-3. The hydrogen diffusion rate in TiCuH is apparently too slow to be a major contributor to T_1 relaxation until ~520 K; hence, hydrogen diffusion parameters for TiCuH cannot be determined from the T_1 values. However, the T_2 measurements indicate that motional narrowing [19] begins near 450 K and the T_2 increase begins, according to the Arrhenius relation, with a diffusion activation energy (E_a) of 0.80 eV. Furthermore, between ~350 K and ~420 K the decreasing dipolar T_{1D} relaxation times also exhibit an Arrhenius temperature dependence with $E_a = 0.78$ eV. Since nearly identical E_a values have been obtained from the independent T_2 and T_{1D} relaxation times, the average 0.79 eV is regarded as the best E_a value for TiCuH over the entire temperature range below 560 K. It is also possible to specify the hydrogen diffusion constant, D , from the relation [19]

$$D = \langle \lambda^2 \rangle / 6\tau_c \quad (9)$$

FIGURE VI-3 - Temperature dependence of proton relaxation times for $\text{TiCuH}_{0.94}$.

where

$$\tau_c^{-1} = \gamma_H^2 M_{2D}^2 T_2 \quad (10)$$

$\langle \lambda^2 \rangle$ is the mean-squared jump distance (assumed to be the hydrogen separation distance of 2.144 Å for TiCuH), τ_c is the diffusion correlation time, and $\tau_c \ll M_{2D}^{-1/2}$. In Table VI-1, the E_a and D (at 300 K) values for $\text{TiCuH}_{0.94}$ are compared with similar parameters for γ -phase TiH_x [7,9,10] and several other ternary titanium hydrides [14,15,20,21]. Hydrogen diffusion in TiCuH is clearly more difficult

than in TiH_x or $\text{TiFeH}_{1.0}$, but larger E_a values are reported [21] for the TiZr_y hydrides. The very large and unexplained discrepancy between the TiNbH_x E_a values of Nowak et al. [14] and Malutchov et al. [20] prevents a meaningful comparison until the correct activation energy is established. The rather low E_a and relatively rapid hydrogen diffusion rate for $\text{TiFeH}_{1.0}$ probably reflect the occupancy of octahedral sites [17] rather than tetrahedral sites as in TiH_x and the other titanium hydrides.

Although the local structures for the hydrogen-atoms in TiCuH and γ -phase TiH_x are nearly identical, a substantial difference between their E_a values is observed in Table VI-1. As mentioned previously, several earlier NMR studies [7-10] clearly demonstrate a concentration-independent E_a of 0.50 eV in γ -phase TiH_x , which Korn and Zamir [8] associate with hydrogen-atom jumps through octahedral saddle points to third nearest neighbor tetrahedral sites. This model is supported by the first-principles calculations of Bisson and Wilson [22] as well as the more recent, quantum chemical cluster calculations of Melius and Upton [23]. Both calculations predict that hydrogen-atom jumps through vacant octahedral sites give the lowest activation energy. Furthermore, Melius [23] calculates a value for E_a , larger by 0.2 eV, for direct tetrahedral-tetrahedral jumps relative to the tetrahedral-octahedral-tetrahedral jump process. Since the planar hydrogen-atom layer of TiCuH does not permit jumps through octahedral sites, the E_a of 0.79 eV for TiCuH_x is consistent with the direct tetrahedral-tetrahedral jumps that would occur between nearest neighbors in γ -phase TiH_x . Thus, the present NMR measurements on $\text{TiCuH}_{0.94}$

provide independent experimental support of the Korn-Zamir model for hydrogen diffusion in f.c.c. dihydrides. Whether similar explanations can account for the different E_a values in other ternary titanium hydrides with tetrahedral hydrogen atoms will require further investigations.

After the T_2 measurements between 500 K and 560 K had been completed on both TiCuH_x samples, irreversible changes in the NMR parameters were observed. Although subsequent gas analyses indicated that the total hydrogen content remained constant after heating to ~560 K, the proton signal amplitudes were drastically reduced and probe circuit tuning was impaired. Furthermore, the proton line-shape and T_1 at room temperature were significantly different from the initial values and from those after heating to ~500 K. X-ray diffraction studies showed that this heated material no longer contained TiCuH , but consisted of TiCu , TiH_x and copper. The decomposition observed during the high temperature NMR measurements is consequently very similar to the reactions occurring during previous [3,4] thermal analysis studies. However, the proton relaxation times obtained above ~500 K are still believed to be representative of the TiCuH_x phase, since decomposition was probably most extensive during the last measurements at the highest temperature near 560 K.

ISOTOPE EFFECTS FOR DIFFUSION IN VANADIUM HYDRIDE

*R. C. Bowman, Jr., A. Attalla and
B. D. Craft*

The nonclassical diffusion processes for hydrogen isotopes in metals and other

solids remain unresolved [24]. Recent NMR studies [25-27] of the proton relaxation times for the b.c.t. β -phase of VH_x have indicated anomalous diffusion behavior. Since the complexity of the observed hydrogen mobility precludes a completely satisfactory explanation [28], measurements of isotope effects are being used to help clarify the fundamental processes responsible for hydrogen atom mobility in this system and structurally related metal hydrides. The magnetic properties of the tritium nucleus (i.e., $I = \frac{1}{2}$ with a magnetic moment only 6.7% larger than the proton moment) make NMR studies of the tritium relaxation times in VT_x extremely favorable for quantitative comparisons with the previous [25-28] VH_x NMR results.

$\text{VH}_{0.50}$ and $\text{VT}_{0.50}$ powder samples with measured hydrogen and tritium contents being equal within the experimental uncertainty of ± 0.005 have been prepared from high purity MARZ-grade vanadium metal. X-ray diffraction measurements [28] indicate that $\text{VH}_{0.50}$ and $\text{VT}_{0.50}$ are isomorphic, at least near room temperature. Samples of approximately 0.6 g of each material were sealed in evacuated 7 mm o.d. glass tubes. The nuclear relaxation times were measured by conventional pulse techniques: spin-lattice relaxation times (T_1) using the π - τ - $\pi/2$ inversion-recovery sequence; T_2' from the spin echo $\pi/2$ - τ - π sequence, and T_{2m} using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [29] with 200 μs spacing between the π -pulses. The NMR measurements were all performed at a resonance frequency of 34.5 MHz.

The proton relaxation times for $\text{VH}_{0.50}$ were measured between 90 K and 520 K while the tritium relaxation times were

measured between 90 K and 450 K. The proton results are presented in Figure VI-4 along with the $\text{VH}_{0.50}$ phase boundaries reported by Schober and Carl [30]. The b.c.t. ϵ -phase has hydrogen atoms partially disordered on octahedral lattice sites and is similar to the more ordered β -phase. In the b.c.c. α -phase, hydrogen atoms are believed for the most part to occupy tetrahedral sites in a random manner [26,30]. The tritium relaxation times are shown in Figure VI-5 where the phase boundaries are deduced from the present NMR data. Table VI-2 summarizes several of the unusual differences in the nuclear relaxation time behavior between protium in $\text{VH}_{0.50}$ and tritium in $\text{VT}_{0.50}$. Furthermore, the proton T_1 values in the $\beta \rightarrow \epsilon \rightarrow \alpha$ transition region of $\text{VH}_{0.50}$ are essentially identical during both heating and cooling cycles. However, a large hysteresis in the tritium T_1 values obtained during heating and cooling cycles is indicated in Figure VI-5. Previous NMR studies of isotope effects of diffusion in $\text{TiH}_{1.55}$ [31], $\text{TiT}_{1.50}$ [32], and $\text{NbH}_{0.78}$ [33], and $\text{NbD}_{0.78}$ [33] yielded qualitatively similar temperature dependences for the relaxation times. Although the magnitudes of the nuclear relaxation times in $\text{VH}_{0.50}$ and $\text{VT}_{0.50}$ are close and the minimum T_1 values occur in the higher temperature β -phase region for both materials, the very different relaxation time behavior exhibited in Figures VI-4 and VI-5 was completely unexpected. Consequently, the diffusion mechanisms in $\text{VT}_{0.50}$, as reflected by the tritium relaxation times, do not closely resemble the mechanisms for $\text{VH}_{0.50}$.

Nuclei in equivalent lattice sites or experiencing homogeneous magnetic interactions generally exhibit exponential recoveries for relaxation times. Hence, the

FIGURE VI-4 - Temperature dependence of proton relaxation times for $\text{VH}_{0.50}$. Circular data points (o) in T_1 plot were obtained during cooling while square symbols ($\square$) represent data in the heating cycle.

FIGURE VI-5 - Temperature dependence of tritium relaxation times for $\text{VT}_{0.5}$. Open and closed symbols give the two relaxation times extracted from non-exponential recoveries in two temperature regions.

Table VI-2 - DIFFERENCES BETWEEN $VH_{0.50}$ AND $VT_{0.50}$ OBTAINED FROM NUCLEAR RELAXATION TIME MEASUREMENTS

Parameter or Property	$VH_{0.50}$	$VT_{0.50}$
Temperature for phase transition to the b.c.c. α -phase	470 K	375 K
Temperature where T_1 minimum (34.5 MHz) occurs	382 K	347 K
Regions with non-exponential T_1 relaxation recoveries during heating cycle	None	Two: 140 K-250 K 345 K-370 K
Regions with simultaneous short and long T_2' values	None	170 K-290K

nonexponential behavior in $VT_{0.50}$ can arise from the presence of multiple phases or tritium atoms occupying different lattice sites in a single phase. The two values for T_1 and T_2' below 290 K are interpreted as follows: the tritium atoms occupy two distinct interstitial sites, with the dominant site being the ordered octahedral positions of the V_4D_2 monoclinic superstructure deduced from neutron diffraction studies [34]. The other tritium atoms (i.e., about $5 \pm 1\%$ between 170 K and 240 K) are more randomly located on either octahedral or tetrahedral sites, and have sufficient mobility to reduce their dipolar interactions, thus resulting in the long T_2' and short T_1 values shown in Figure VI-5. Furthermore, there is an exchange of tritium atoms between the two sublattices, the rate of which is relatively slow below ~ 240 K and increases rapidly at higher temperatures until nearly exponential recoveries are obtained near 300 K. A qualitatively similar behavior has been reported for two types of fluorine atoms in LaF_3 [35]. Because tritium mobility is rapid above 345 K (i.e., T_1 minimum is 347 K and $T_{2m} > 1ms$), the two T_1 and T_{2m} values between 345 K and 370 K probably reflect the simultaneous presence of the α and β

phases rather than the occupancy of two distinct sublattices in a single phase. Since exponential recoveries are observed throughout the investigated temperature range for $VH_{0.50}$, either all protons occupy equivalent sites or there are no regions which have slow exchange rates between different sublattices. The latter possibility is believed to be more likely since $VH_{0.50}$ passes through at least two major phase transitions below 500 K.

The diffusion correlation time τ_c (i.e., reciprocal of the atomic jump rate) can be determined from the T_1 values near the T_1 minimum using the BPP model, which has been previously described [27]. The temperature dependences of τ_c for $VH_{0.50}$ and $VT_{0.50}$ are compared in Figure VI-6. Only tritium T_1 values obtained from the nearly exponential recoveries were used to calculate the plotted τ_c values. Although τ_c values for $VH_{0.50}$ yielded a non-Arrhenius temperature dependence over the entire range, a diffusion activation energy, E_a , of 0.41 eV is obtained between 320 K and 390 K. An Arrhenius plot of the tritium τ_c values over the more limited temperature range between 290 K and 345 K gave an E_a of 0.31 eV. Furthermore, throughout the β -phase regions the

FIGURE VI-6 - Diffusion correlation times for $VH_{0.50}$ and $VT_{0.50}$ derived using BPP model with T_1 data.

absolute values of τ_c^{-1} are larger for VT_{0.50} than for VH_{0.50}. Since the hydrogen diffusion constant, D , is directly proportional [27] to τ_c^{-1} , the larger τ_c^{-1} and the smaller E_a for VT_{0.50} imply that the tritium atoms diffuse more rapidly than the hydrogen atoms in VH_{0.50}. This is an inverse isotope effect compared to the classical diffusion ratio $D_T/D_H \approx \sqrt{M_H/M_T} \approx 0.58$. Although inverse isotope effects have been found [36] previously for diffusion in PdH_{0.7} and PdD_{0.7}, it is much larger in the present case. The heavier hydrogen isotope diffuses more slowly in both TiH(T)_{1.5} [32] and NbH(D)_{0.78} [33]. Hence, the vanadium-hydrogen system has been found to provide another anomalous characteristic--a remarkably large inverse isotope for diffusion in the β -phase.

More extensive theoretical analyses are currently in progress to unravel the various contributions to the VH_{0.5} and VT_{0.5} diffusion mechanisms. In particular, calculations which include atomic exchange rate dependences are being performed to determine their roles in the T_1 and T_2' non-exponential regions. Similar NMR experiments will be started on a nominal VT_{0.75} as soon as it is prepared.

Electron paramagnetic resonance (EPR) studies

G. C. Abell

Structural information, detailed both as to symmetry and dimension, can be obtained from EPR spectra of dilute octahedral metal hydride complexes. We start with a general spin Hamiltonian for the rhodium and nickel complexes.

$$H = H \cdot g \cdot S + S \cdot A_M \cdot I_M$$

$$+ \sum_{i=1}^6 (S \cdot A_{L,i} + g_N H) \cdot I_{L,i} \quad (11)$$

This expression has been discussed in detail elsewhere [37]. Briefly, the first term on the RHS is the electron Zeeman term (interaction of the electron magnetic moment with the external magnetic field). This term is by far the largest for our particular problem and determines the qualitative aspects of the spectra. The second term is the hyperfine interaction of the nuclear magnetic moment of the central ion (M) with the electron magnetic moment. The remaining terms are due to the magnetic moments of the nearest-neighbor H- ligands (L). The $A_{L,i}$ are tensors describing the interaction of the ligand nuclear magnetic moments with the electronic magnetic moment of the central metal ion. We have also included the proton Zeeman term ($g_N H$) because in this case it has a bearing on the observed spectra.

The quantities of greatest interest here are the $A_{L,i}$, but first we will consider the g -tensor since this reveals the local symmetry of the complex as well as the electronic state of the paramagnetic electron. It also gives an indication of covalency.

For the rhodium complex, we have observed two paramagnetic species which we call {A} and {0}. One of these, {A}, shows an axial distortion with tetragonal symmetry while the other, {0}, shows orthorhombic symmetry. We assume these two species to have only a slight deviation from the octahedral symmetry about any site of the LiH matrix. The symmetries are derived from the observed principal values of the

g-tensor. The relative magnitude of these principal values reveal the electronic state of the complex. Thus, we find a $4d^7$ low-spin state with the $4d_{x^2-y^2}$ orbital singly occupied for {A}, while for {0} the $4d_{3z^2-r^2}$ orbital is singly occupied. (By low-spin state, we mean that the coupling of the central metal ion with the ligand field dominates the spin-orbit coupling so that Hund's rule does not apply.)

For the nickel complex, we again observe two species. One of these, {A}_{Ni}, shows tetragonal symmetry with the $3d_{x^2-y^2}$ orbital singly occupied. The other complex, {I}_{Ni} has an isotropic g-tensor but the ligand hyperfine effects are anisotropic. This is probably a John-Teller ion with motional averaging among the three equivalent, axially distorted configurations.

Table VI-3 compares the isotropic components of the g-tensors found for Rh⁺² and Ni⁺¹ in LiH with those measured for the same ions in other host materials. In general, for a given transition metal ion in different hosts, the closeness of the g-value to 2.00 (the free electron value) measures the relative importance of ligand covalency effects. Using this criterion, we see from Table VI-3 that the H⁻ anion (i.e., the LiH host) shows the greatest extent of covalency with both Ni⁺¹ and Rh⁺².

Turning now to the ligand hyperfine effects, which are of primary concern, we proceed by considering the interaction of a single proton with the paramagnetic electron. In an octahedral complex the ligand hyperfine tensor, A_L , consists of isotropic and anisotropic components as follows:

Table VI-3 - EFFECT OF LIGAND ON ISOTROPIC G-FACTOR. CLOSENESS OF $\langle g \rangle$ TO 2.0 INDICATES EXTENT OF COVALENT BONDING

Complex	Host	$\langle g \rangle$
Rh ⁺² H ₆	LiH	2.06
Rh ⁺² O ₆	MgO	2.17
Rh ⁺² Cl ₆	AgCl	2.29
Rh ⁺² (CN) ₄	KCl	2.20
Ni ⁺¹ H ₆	LiH	2.10
Ni ⁺¹ O ₆	MgO	2.24
Ni ⁺¹ (CN) ₄	NaCl	2.08
Ni ⁺¹ F ₆	LiF	2.25

$$A_L = A_S \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + A_d \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (12)$$

with the proton along the z-axis. Analysis of the extra resonances due to the ligands (obtained, for example, by comparing the EPR spectra of the fully deuterated species with that of the protonated species) gives both A_S and A_d . From more basic considerations of the ground electronic state of the complex, expressions can be derived relating the quantities to certain atomistic properties of the complex. Thus, A_S is proportional to a quantity λ^2 , which is the spin density transferred from the central metal cation to the 1s-orbital of the H-ligand. To better understand this quantity and its relation to covalency, we briefly look at a molecular orbital treatment of the complex in terms of the central ion d-orbital, ϕ_d , and the ligand s-orbital χ_s . In general, there will be a symmetric and an antisymmetric combination of these atomic orbitals corresponding to bonding (ψ_b) and antibonding (ψ_a) molecular orbitals, i.e.,

$$\psi_a = N_a^{-1/2} (\phi_d - \lambda \chi_s), \quad (13)$$

$$\psi_b = N_b^{-1/2} (\chi_s + \gamma \phi_d), \quad (14)$$

where N_a and N_b are normalization constants. These expressions make no assumptions about the relative magnitudes of λ and γ . For instance, $\lambda = \gamma = 1$ corresponds to a complete sharing of the electron between the atomic orbitals ϕ and χ . But we expect the octahedral metal hydride complexes of Rh^{+2} and Ni^{+1} to be mainly ionic, in which case the electrons center mainly about the central ion or the ligands. In this approximation, it can be shown that

$$\lambda = S + \gamma$$

where S is the overlap integral between ϕ and χ . In this picture, a purely ionic complex is defined by $\gamma = 0$. Thus, it is not λ but γ which measures the extent of covalency, since S will be appreciable even in the absence of covalency. Thus, we must determine S if we are going to relate the observed spin density λ^2 to covalency. Using Hartree-Fock orbitals obtained for the Rh^{+2} free ion and a Slater-type $1s$ -orbital for the ligand, and varying the internuclear separation and the $|1s\rangle$ exponential parameter, it has been determined that S is probably less than 0.1 for the Rh^{+2} complex. From the observed spin densities, $\lambda^2 = 0.068$ for {A} and 0.159 for {O}, we find $\gamma = 0.1 - 0.2$ for Rh^{+2} . In the same way we find $\gamma = 0.2 - 0.3$ for Ni^{+1} . This represents an appreciable amount of covalent bonding and is consistent with the strongly suppressed g -values described earlier.

The anisotropic component, A_d , of the ligand hyperfine tensor, is determined by two fundamental effects--transfer of spin density to a ligand valence p -orbital and interaction of the ligand nuclear moment with the distribution of magnetization carried by the central ion d -orbital. The latter contribution, called the dipolar term, can be precisely determined for a purely ionic complex if the central ion-ligand internuclear separation, R , is known. In fact, this is seldom the case and R is usually assumed to be the same as the corresponding internuclear separation of the host lattice. With this assumption it is possible to obtain the spin density on the ligand p -orbital from a measurement of A_d .

For the H^- anion, however, there is no valence p -orbital to take part in the bonding; significant participation of the $2p$ -orbital is unlikely on energetic grounds. Given this circumstance, we can derive a value for the central ion-ligand internuclear separation R from the measured value of A_d . And since A_d varies as R^{-3} , we have a sensitive yardstick for the determination of this quantity. Using this approach, we find that for Rh^{+2} species {A}, the planar ligands have expanded away from the central ion by about 10%, while for Rh^{+2} species {O}, the axial ligands show a 2% expansion relative to the LiH equilibrium separation. On the other hand, both Ni^{+1} complexes show a 5-10% relaxation of the H^- anions toward the central ion. This trend is consistent with the considerably greater radial extent of Rh^{+2} vs. Ni^{+1} d -orbitals.

In summary, we have shown how information obtained from single crystal EPR studies of dilute metal-hydride complexes bound in a diamagnetic host has been used to deduce the symmetry and electronic state of each complex. This information has also given a quantitative measure of the internuclear separation within the various complexes. Finally, and perhaps most important, we have obtained a quantitative measure of the extent of covalent bonding between the metal d-orbital and the hydride s-orbital. We have learned that covalent bonding effects are substantial in these metal-hydride complexes.

These results raise an interesting question. What is the relation between metal-hydrogen bonds observed in these dilute metal-hydride complexes and metal-hydrogen bonding in the corresponding metal-hydride compound? Perhaps there is no connection. On the other hand, the compound NiH has an fcc structure with hydrogen atoms occupying octahedral sites so that the local symmetry (i.e., nearest-neighbors only) about the nickel atom is that of our dilute nickel complex. Moreover, the Ni-H internuclear separation is $1.86\text{\AA}$ for the compound vs. $1.9\text{\AA}$ measured for the dilute complex.

It is also interesting to note that all the first- and second-row transition metal dihydrides have a metal-hydrogen internuclear separation of $1.8 - 2.2\text{\AA}$ with cubic coordination of nearest-neighbor protons to the metal atom. It would surely be fruitful to study a series of dilute paramagnetic metal hydrides using first- and second-row transition metals. Any correlation between bonding parameters in these complexes and properties of the corresponding metal hydride compounds would be highly informative.

Theoretical studies of hydrogen in metals

M. P. Guse

We are using Hartree-Fock molecular orbital calculations to study the electronic structure and energetics of hydrogen interacting with clusters of metal atoms representing a solid. These calculations give detailed information about the effect of hydrogen on the electronic structure of the cluster and the binding energy of hydrogen at various positions in the cluster and on the surface. Ultimately, by studying the factors determining hydrogen solubility and the capability of some materials to form hydrides, we expect to define the guidelines for good hydrogen storage materials.

We treat a cluster of metal and hydrogen atoms as a single, large molecule and calculate the quantum mechanical ground state energy and electronic wave function self-consistently in the Hartree-Fock approximation. The approach is a "first-principles", i.e., *ab initio*, unrestricted Hartree-Fock (UHF) calculation, with basis function integrals evaluated using the Bigmoli computer code and the self-consistent field calculation performed by a UHF code developed by Frank Bobrowicz of Mound Facility. The molecular cluster method has been used previously by others to study hydrogen chemisorption on lithium [38,39] and beryllium [40]. Recently, the theory of pseudopotentials has been developed to such a point that it may be used reliably in molecular orbital calculations [41,42]. Using a pseudopotential to replace the atomic cores of the metal atoms reduces the calculation to one involving only the valence electrons. This allows us to treat heavier atoms than in previous

work and to consider technologically interesting materials, such as magnesium hydride and transition metal hydrides.

Magnesium hydride has been studied as hydrogen interacting with several small clusters:

- Mg₄ - A cluster of four magnesium atoms forming a tetrahedron.
- Mg₅ - An atom is added to Mg₄ to form a cluster of two tetrahedra back to back (hexahedron).
- Mg₆ - A cluster of six magnesium atoms forming an octahedron.

Magnesium metal has a hexagonal, close-packed structure with lattice constants, $a = 3.21\text{\AA}$, and $c = 5.21\text{\AA}$. In these clusters the atoms were placed as though they occupied positions in a magnesium lattice.

A measure of hydrogen solubility in a metal is the energy required to dissociate molecular hydrogen, H₂, minus the binding energy of each hydrogen atom to the metal. This value is 0.25 electron volts for magnesium [43]. The binding energy of H₂ was found to be -0.126 Hartree or -3.4272 eV in the Hartree-Fock approximation. Therefore, in order to dissociate H₂ and absorb the atomic hydrogen the metal must bind each hydrogen atom by -0.063 Hartree or -1.7136 eV.

We calculated the binding energy of hydrogen in the center of Mg₄, in the center of the top tetrahedron of Mg₅, and in the center of Mg₆. These energies were -0.503 eV, -1.499 eV, and -1.931 eV, respectively. Assuming that hydrogen dissolves into octahedral sites in magnesium and binds with -1.931 eV, we obtained a value for

the solubility of 0.217 eV which compares well with the experimental value of 0.25 eV. The fact that the binding energy of hydrogen in a tetrahedral site increases by a factor of 3 with the addition of one magnesium atom warns us that size effects are very important for such small clusters. However, the solubility calculated from the Mg₆ cluster is close enough to the experimental value that the size effects may decrease rapidly, as expected, with increasing cluster size.

Figure VI-7 gives the potential energy curve for a hydrogen atom moving into the center of the Mg₆ octahedron along a line passing through the center of one of the triangular faces. It shows that hydrogen is bound about 1.5 bohr outside the surface of the cluster by 2.3 eV. The hydrogen must pass through a 1/2 eV potential barrier before it is bound in a metastable state inside the cluster. It is not known at this time whether the hydrogen atom is actually bound off center or if this is an artifact of the calculation. This potential barrier may reflect the known difficulty of "hydriding" magnesium.

Figure VI-8 shows the change in the orbital energy levels of the magnesium cluster as it binds hydrogen. The lowest cluster orbital interacts strongly with the hydrogen potential taking on more and more hydrogen character and lowering in energy. As hydrogen approaches the cluster the Mg₆ orbital degeneracy is broken and all orbitals are lowered in energy. On the other hand, the atomic hydrogen orbital level disappears as the hydrogen electron goes into a new state at the top of the Mg₆ "band".

FIGURE VI-7 - Mg_6H potential energy curve.

In the future we intend to study magnesium hydride by treating larger magnesium clusters and introducing more hydrogen atoms. Our study of Mg_6 suggests that surface effects are important in the initial stages of hydride formation and we will explore this more fully. In addition, we

will study other metal hydrides such as LiH , BeH , AlH , and NaH in order to determine the role of the metallic electronic structure on hydride formation. Eventually we will consider the much more complicated transition metal hydrides such as iron titanium hydride.

FIGURE VI-8 - Electronic structure of Mg_6H .

References

I. Computer operations

1. Zilog, 10340 Bubb Road, Cupertino, Calif. 15014.
2. R. Eckard and J. Barber, User's Guide to the LLL-BASIC Interpreter, UCID-17090, Lawrence Livermore Laboratory, Livermore, Calif. (April 1976).
3. M. D. Maples, Floating-Point Package for Intel 8008 and 8080 Microprocessors, UCRL-51940, Lawrence Livermore Laboratory, Livermore, Calif. (October 1975).
4. Mound Laboratory Activities for the Division of Physical Research: January-June 1976, MLM-2354 (September 30, 1976), p. 8.
5. Mound Laboratory Activities in Chemical and Physical Research: January-June 1977, MLM-2450 (October 4, 1977), pp. 8-9.

III. Low temperature research

1. R. Ahlrichs, P. Penco and G. Scoles, Chem. Phys., **19**, 119 (1976).
2. D. R. McLaughlin and H. F. Schaefer, III, Chem. Phys. Lett., **12**, 244 (1971).
3. G. Starkschall and R. G. Gordon, J. Chem. Phys., **54**, 663 (1971).
4. K. T. Tang, J. M. Norbeck and P. R. Certain, J. Chem. Phys., **64**, 3063 (1976).
5. J. W. Haarman, AIP Conf. Proc., **11**, 193 (1973).
6. J. M. Farrar and Y. T. Lee, J. Chem. Phys., **56**, 5801 (1972).
7. A. L. J. Burgmans, J. M. Farrar and Y. T. Lee, J. Chem. Phys., **64**, 1345 (1975).
8. L. W. Bruch and I. J. McGee, J. Chem. Phys., **52**, 5884 (1970).
9. R. A. Aziz (private communication 1978).
10. Mound Laboratory Activities in Chemical and Physical Research, January-June 1977, MLM-2450 (Oct. 4, 1977), pp. 14-20.
11. B. E. Gammon, J. Chem. Phys., **64**, 2556 (1976).
12. D. White, T. Rubin, P. Camky and H. L. Johnston, J. Phys. Chem., **64**, 1607 (1960).
13. W. G. Schneider and J. A. H. Duffie, J. Chem. Phys., **17**, 751 (1949).
14. A. E. Hoover, F. B. Canfield, R. Kobayashi and T. W. Leland, J. Chem. Eng. Data, **9**, 568 (1964).
15. F. B. Canfield, T. W. Leland and R. Kobayashi, Adv. Cryog. Eng., **8**, 146 (1963).
16. T. C. Briggs, Bureau of Mines Report of Inv., 7352 (March 1970).
17. J. A. Sullivan and R. E. Sonntag, Cryogenics, **7**, 13 (1967).

18. J. O. Herschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, 3rd Edition, John Wiley and Sons, Inc., New York, 1977.
19. W. E. Keller, Phys. Rev., 97, 1 (1955) and 98, 1571 (1955).
20. D. T. Grimsrude and J. H. Werntz, Jr., Phys. Rev., 157, 181 (1967).
21. K. H. Berry, Metrologia, 8, 125 (1972).
22. M. E. Boyd, S. Y. Larsen and H. Plumb, J. Res. Nat. Bur. Stand., 72A, 155 (1968).
23. J. M. H. Levelt Sengers, Max Klein and J. S. Gallagher, Am. Inst. of Phys. Handbook.
24. E. W. Becker, R. Misenta and E. Schmeissner, Z. Physik, 137, 126 (1954).
25. E. W. Becker and R. Misenta, Z. Physik, 140, 535 (1955).
26. J. M. J. Coremans, A. Van Itterbeck, J. J. M. Beenakker, H. F. P. Knapp, and P. Zondbergen, Physica, 24, 557 (1968).
27. H. L. Johnston and E. R. Grilly, J. Phys. Chem., 46, 948 (1942).
28. A. O. Rietveld, A. Van Itterbeck and C. A. Velds, Physica, 25, 205 (1959).
29. A. Van Itterbeck, F. W. Schapink and G. J. Vandenberg, Physica, 19, 1158 (1953).
30. R. DePippo and J. Kestin, Proceedings of the Fourth Symposium on Thermal Physical Properties, American Society of Mechanical Engineers, New York, 1968, p. 304.
31. F. A. Guevara, B. B. McInteer and W. E. Wageman, Phys. Fluids, 12, 2493 (1969).
32. M. Trautz and R. Zink, Ann. Physik, 7, 427 (1930).
33. P. J. Bendt, Phys. Rev., 110, 85 (1958).
34. G. A. DuBro and S. Weissman, Phys. Fluids, 13, 2682 (1970).
35. J. C. Liner and S. Weissman, J. Chem. Phys., 56, 2288 (1972).
36. T. R. Morrero and E. A. Mason, J. Chem. Phys. Ref. Data, 1, 3 (1972).
37. F. van der Valk, Thesis, Amsterdam University, 1963.
38. F. van der Valk and A. E. DeVries, J. Chem. Phys., 34, 345 (1961).
39. W. W. Watson, A. J. Howard, N. E. Miller and R. M. Shiffrin, Z. Naturforsch, 18a, 242 (1963).
40. R. Paul, A. J. Howard and W. W. Watson, J. Chem. Phys., 43, 1622 (1965).
41. B. B. McInteer, L. T. Aldrich, and A. O. Nier, Phys. Rev., 72, 510 (1947).

42. W. L. Taylor, Low Temperature Physics - LT14, Vol. 4, M. Krusius and M. Vuorio (eds.), North-Holland Publishing Co., Amsterdam, 1975, pp. 433-436 (Proceedings of the 14th International Conference on Low Temperature Physics, Helsinki, Finland, Aug. 14-20, 1975).
43. W. L. Taylor, J. Chem. Phys., **58**, 834 (1973).
44. W. L. Taylor and S. Weissman, J. Chem. Phys., **55**, 4000 (1971).
3. P. H. Abelson, N. Rosen, and J. I. Hoover, Liquid Thermal Diffusion, USAEC Technical Information Service, Oak Ridge, Tennessee, 1951.
4. G. Panson and T. I. Taylor, USAEC Report NYO-625, July 1952.
5. P. Varga-Manyi, Acta Biochim, et Biophys. Acad. Sci. Hung., **1**, 197 (1966).
6. H. Korsching as cited by H. J. V. Tyrrell, Diffusion and Heat Flow in Liquids, Butterworths, London, 1961, p. 223.

IV. Separation chemistry

1. Mound Laboratory Activities for the Division of Physical Research: July-December 1975, MLM-2296 (May 14, 1976), pp. 25-29.
2. Mound Laboratory Activities for the Division of Physical Research: January-June 1976, MLM-2354 (September 30, 1976), pp. 32-35.
3. Mound Facility Activities in Chemical and Physical Research: July-December 1977, MLM-2506 (May 1, 1978), pp. 21 and 22.
4. P. L. Keister, P. E. Figgins and R. M. Watrous, Recovery and Purification of Uranium-234 from Aged Plutonium-238, MLM-2490 (January 20, 1978).
7. Mound Laboratory Activities in Chemical and Physical Research: July-December 1976, MLM-2414 (May 4, 1977), pp. 26-29.
8. Stable Gaseous Isotope Separation and Purification: April-June 1972, MLM-1943 (Aug. 18, 1972), pp. 11-15.
9. Mound Laboratory Progress Report for August 1965, MLM-1287.
10. Mound Facility Activities in Chemical and Physical Research: July-December 1977, MLM-2506 (May 1, 1978), p. 35.
11. E. P. Ney and F. C. Armistead, Phys. Rev., **71**, 14 (1947).
12. T. R. Marrero and E. A. Mason, J. Phys. Chem. Ref. Data, **1**, 3 (1972).

V. Separation research

1. Mound Facility Activities in Chemical and Physical Research: July-December 1977, MLM-2506 (May 1, 1978), p. 27.
2. W. M. Rutherford, I&EC Process Design and Development, **17**, 77 (1978).
13. A. E. Loiko, B. A. Ivakin and P. E. Seutin, Sov. Phys. - Tech. Phys., **18**, 266 (1973); also Sov. Phys. - Tech. Phys., **19**, 434 (1974).
14. R. J. J. van Heijningen, J. P. Harpe and J. J. M. Beenakker, Physica, **38**, 1 (1968).

15. H. Watts, Trans. Faraday Soc., **60**, 1745 (1964).
 16. W. Hogervorst, Physica, **51**, 59 (1971).
 17. A. P. Malinanskas, J. Chem. Phys., **45**, 4704 (1966).
 18. A. P. Malinanskas and M. D. Silverman, J. Chem. Phys., **50**, 3263 (1969).
 19. B. N. Srivastava and K. P. Srivastava, J. Chem. Phys., **30**, 984 (1959).
 20. K. C. Srivastava and A. K. Barua, Ind. J. Phys., **33**, 229 (1959).
 21. K. Schafer and K. Schuhman, Z. Elektrochemie, **61**, 246 (1957).
 22. L. Durban and R. Kobayashi, J. Chem. Phys., **37**, 1643 (1962).
 23. B. P. Mathur and S. C. Saxena, Appl. Sci. Res., **18**, 325 (1968).
 24. R. Paul, Ind. J. Phys., **34**, 141 (1960); Ind. J. Phys., **36**, 464 (1962).
 25. B. N. Srivastava and R. Paul, Physica, **28**, 646 (1962).
 26. S. P. Wasik and K. E. McCulloh, J. Res. Nat. Bur. Stand., **73A**, 207 (1969).
 27. B. R. Annis, A. E. Humphreys and A. E. Mason, Phys. Fluids, **11**, 2122 (1968).
 28. E. B. Federov, B. A. Ivakin and P. E. Seutin, Sov. Phys. Tech. Phys., **11**, 424 (1966).
 29. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, Inc., New York, 1954.
 30. Mound Laboratory Progress Report for August 1965, MLM-1287, p. 17.
 31. J. H. Dymond and B. J. Alder, J. Chem. Phys., **51**, 309 (1969).
 32. C. H. Chen, P. E. Siska, and Y. T. Lee, J. Chem. Phys., **59**, 601 (1973).
 33. C. Y. Ng, Y. T. Lee and J. A. Barker, J. Chem. Phys., **61**, 1996 (1974).
 34. D. W. Gough, G. P. Matthews, E. B. Smith, and G. C. Maitland, Molec. Phys., **29**, 1759 (1975).
 35. J. K. Lee, D. Henderson and J. A. Barker, Molec. Phys., **29**, 429 (1975).
 36. J. A. Barker, R. A. Fisher and R. O. Watts, Molec. Phys., **21**, 657 (1971).
 37. H. M. Lin and R. L. Robinson, J. Chem. Phys., **54**, 52 (1971).
- ## VI. Metal hydride research
1. Mound Facility Activities in Chemical and Physical Research: July-December 1977, MLM-2506 (May 1, 1978), pp. 11-12.
 2. K. Yamanaka, H. Saito and M. Someno, J. Chem. Soc. Japan, **8**, 1267 (1975).
 3. A. J. Maeland, Advances in Chemistry, (In press).

4. A. J. Maeland, in Proceedings of the International Symposium on Hydrides for Energy Storage, Geilo, Norway, August 1977 (to be published).
5. A. Santoro, A. J. Maeland and J. J. Rush, presented at the Winter Meeting of the American Crystallographic Association, Asilomar, California, February 1977, and Acta Cryst. (in press).
6. S. S. Shidhu, L. Heaton and D. D. Zauberis, Acta Cryst., 9, 607 (1956).
7. C. Korn and D. Zamir, J. Phys. Chem. Solids, 31, 489 (1969).
8. C. Korn and D. Zamir, J. Phys. Chem. Solids, 34, 725 (1973).
9. E. F. Khodosov and N. A. Shepilov, Phys. Stat. Sol. (b), 47, 693 (1971).
10. A. Schmolz and F. Noack, Ber. Bunsenges. Phys. Chem., 78, 339 (1974).
11. J. G. Powles and J. H. Strange, Proc. Phys. Soc., 82, 6 (1963).
12. J. Jeener and P. Broekaert, Phys. Rev., 157, 232 (1967).
13. H. Y. Carr and E. M. Purcell, Phys. Rev., 94, 630 (1954); S. Meiboom and D. Gill, Rev. Sci. Instrum., 29, 688 (1958).
14. B. Nowak, N. Piślewski and W. Leszczyński, Phys. Stat. Sol.(a), 37, 669 (1976).
15. R. C. Bowman, Jr., A. Attalla, G. C. Carter and Y. Chabre, in Proceedings of the International Symposium on Hydrides for Energy Storage, Geilo, Norway, August 1977 (to be published).
16. E. F. Khodosov and N. A. Shepilov, Phys. Stat. Sol.(b), 49, K83 (1972).
17. P. Thompson, M. A. Pick, F. Reidinger, L. M. Corliss, J. M. Hastings, and J. J. Reilly, J. Phys. F: Metal Phys., 8, L75 (1978).
18. C. Korn, Phys. Rev. B, 17, 1707 (1978).
19. R. M. Cotts, Ber. Bunsenges. Phys. Chem., 76, 760 (1972).
20. O. T. Malutchov, J. J. Lileeva and A. A. Tchertkov, Proceedings of the International Congress on Hydrogen in Metals, Paris, 1972, p. 261.
21. E. F. Khodosov, A. K. Prokopenko and A. E. Linnik, Fiz. Metal. Metalloved., 38, 746 (1974).
22. C. L. Bisson and W. D. Wilson, in Effects of Hydrogen Behavior on Materials: Proceedings of the International Conference, 1975, A. W. Thompson and I. M. Bernstein (eds.), AIME, 1976, p. 416.
23. C. F. Melius and T. H. Upton, Bull. Am. Phys. Soc., 23, 234 (1978) and to be published.
24. A. M. Stoneham, J. Nucl. Mater., 69 and 70, 109 (1978).

25. R. C. Bowman, Jr., A. Attalla and W. E. Tadlock, Int. J. Hydrogen Energy, 1, 421 (1977).
26. Y. Fukai and S. Kamama, Acta. Met., 25, 59 (1977).
27. Mound Laboratory Activities in Chemical and Physical Research: January-June 1977, MLM-2450 (Oct. 4, 1977), pp. 22-26.
28. Mound Facility Activities in Chemical and Physical Research: July-December 1977, MLM-2506 (May 1, 1977), pp. 12-17.
29. S. Meiboom and D. Gill, Rev. Sci. Instrum., 29, 1688 (1958).
30. T. Schober and A. Carl, Phys. Stat. Sol.(a), 43, 443 (1977).
31. C. Korn and D. Zamir, J. Phys. Chem. Solids, 31, 489 (1969).
32. H. T. Weaver, Phys. Lett., 35A, 417 (1971).
33. H. G. Bohn, Kernresonanzuntersuchungen an den Systemen Niob-Wasserstoff und Niob-Deuterium, Jülich Report Jül-853-FF (May 1972).
34. H. Asano and M. Hirabayashi, Phys. Stat. Sol.(a), 15, 267 (1973).
35. M. Goldman and L. Shen, Phys. Rev., 144, 321 (1966).
36. G. Bohmholdt and E. Wicke, Z. Phys. Chem. N.F., 56, 133 (1967).
37. Mound Laboratory Activities in Chemical and Physical Research: July-December 1976, MLM-2414 (May 4, 1977), pp. 16-17.
38. H. Stoll and H. Preuss, Surface Science, 65, 229 (1977).
39. R. F. Marshall, R. J. Blint, and A. B. Kunz, Phys. Rev. B13, 3333 (1976).
40. C. W. Bauschlicher, D. H. Liskow, C. F. Bender and H. F. Schaefer, III, J. Chem. Phys., 62, 4815 (1975).
41. L. R. Kahn, P. Baybutt and D. G. Truhlar, J. Chem. Phys., 65, 3826 (1976).
42. S. Topiol, J. W. Moskowitz, C. F. Melius, M. D. Newton and J. Jafri, ERDA Research and Development Report, COO-3077-105.
43. P. Jena and F. S. Singui, Phys. Rev. B17, 1592 (1978).

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