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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT

NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

ANNUAL REPORT

March 15, 1970 to September 14, 1970

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Report Prepared by

A. L. Ducoffe, Chairman

Georgia Tech Space Sciences Technology Board

October 15, 1970

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GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

Office of
The Vice President for
Academic Affairs

October 15, 1970

Dr. Francis B. Smith
Assistant Administrator for
University Affairs
National Aeronautics and Space
Administration
Washington, D. C. 20546

SUBJECT: Annual Report
March 15, 1970 to September 14, 1970
Multidisciplinary Research Grant NGL 11-002-018

Dear Dr. Smith:

The Georgia Institute of Technology Space Sciences and Technology Board is pleased to submit herewith thirty (30) copies of an annual report for Multidisciplinary Research Grant NGL 11-002-018.

We shall be pleased to provide any additional information that you find necessary.

Sincerely yours,

Vernon Crawford

V. Crawford
Vice President for
Academic Affairs

VC/mjs

Enclosures

cc: Mr. H. L. Baker
Members of the Space Sciences and Technology Board

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ANNUAL REPORT

March 15, 1970 to September 14, 1970

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

I. SUMMARY

The National Aeronautics and Space Administration granted the Georgia Institute of Technology $600,000 on June 15, 1964, $300,000 on June 15, 1965, $300,000 on March 15, 1966, $300,000 on March 15, 1967, and $100,000 on March 15, 1968 for the support over six years and nine months of basic scientific research entitled "Multidisciplinary Research in the Space Sciences and Technology."

The grant funds have been used to support an expansion of multidisciplinary research programs in materials and materials processing, transport phenomena, energy conversion, systems, and nuclear processes.

The grant has been administered by the Space Sciences and Technology Board established at the Georgia Institute of Technology. The Chairman of the Board is Dr. A. L. Ducoffe, Director of the School of Aerospace Engineering. The other Board members are H. F. Bauer, Engineering Mechanics; C. H. Braden, Physics; W. O. Carlson, Acting Dean of Engineering; J. W. Hooper, Electrical Engineering; R. H. Kasriel, Mathematics; P. Kelly, Social Sciences; H. A. McGee, Jr.,

Chemical Engineering; and W. M. Spicer, Director, School of Chemistry.

The last grant period runs from March 15, 1970 through March 14, 1971. The present document reports the research results obtained during the first six months of this period.

An indication of the research activity stimulated by the grant during this reporting period is the publication in recognized journals of 4 papers and the submission of 4 additional. Three papers have been read at scientific meetings. During the present grant period 2 Undergraduate students, 1 Masters student, 10 Ph.D. students and 1 Post Doctoral participated in the research effort.

II. RESEARCH RESULTS

1. Complex Metal Hydrides. High I_{sp} Fuel Components - E. C. Ashby

During this report period, efforts have been directed towards the preparation of complex metal hydrides of the type $M_nM'_{n'}H_{n + 2n'}$, where M is an alkali metal or a cation such as NR_4^+, M' is a group II metal like Be, Mg, Zn, Cd, Hg and n or n' = 1, 2, 3. Using different combinations of the alkali metal and the group II metal it should be possible, in principle, to prepare a whole series of new hydrides. The first major breakthrough in this direction was made earlier in our laboratories with the successful preparation of $KMgH_3$, $NaMgH_3$ and $Na_2Mg_2H_5$. These compounds were prepared by the hydrogenolysis or pyrolysis of complexes of KH and NaH with $(s\text{-}C_4H_9)_2Mg$ in benzene.

$$KH + R_2Mg \rightarrow KMgR_2H \xrightarrow{H_2} KMgH_3 + 2\ RH \qquad (1)$$

Due to the unique solubility in benzene of $MM'R_2H$ compounds where R = s-butyl, the necessity of hydrogenolysis in more basic solvents such as ether can be avoided. The competition between solvent and hydride ion for coordination sites in the expected product is thus eliminated; in addition, secondary butyl groups bonded to relatively electropositive metals are known to undergo hydrogenolysis under mild conditions.

It was decided to attempt first the preparation of trihydridomagnesiate complexes of lithium and NR_4^+, in order to complete the $NMgH_3$ series where M = Li, Na, K, NR_4^+.

When KH is added to a solution of $(s\text{-}C_4H_9)_2Mg$ in benzene, the KH dissolves giving the compound $KMg(s\text{-}C_4H_9)_2H$. Similarly, NaH dissolves in a benzene solution of $(s\text{-}C_4H_9)_2Mg$ to form $Na[(s\text{-}C_4H_9)_2Mg]_2H$. However, when LiH was added to a benzene solution of disecondary butylmagnesium, no dissolution of LiH took place even after several days at higher temperatures.

When to a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in benzene, trioctylpropyl ammonium bromide was added, a precipitate formed after overnight stirring producing a solution light orange to purple in color.

$$KMg(s\text{-}C_4H_9)_2H + N(C_8H_{17})_3(C_3H_7)Br \xrightarrow[\text{Benzene}]{25^\circ}$$

$$\underset{\text{I}}{N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H} + KBr\downarrow \qquad (2)$$

The precipitate was determined to be potassium bromide. The filtrate upon analysis showed potassium and bromide to be absent. Upon removal of solvent an oily orange product resulted. This oil (I) reacted with water slowly and incompletely and quantitative hydrolysis even with concentrated hydrochloric acid at 80° could not be achieved. The yield of active hydrogen and butane was about 60% of the theoretically required value.

Although the direct reaction of KH with $(s\text{-}C_4H_9)_2Mg$ did not proceed in tetrahydrofuran, the compound $KMg(s\text{-}C_4H_9)_2H$ prepared from benzene dissolved readily in THF. The solution was not very stable at room temperature. At low temperatures, however, it was stable up to five days and no THF cleavage was observed.

When a tetrahydrofuran solution of $KMg(s\text{-}C_4H_9)_2H$ was added to trioctylpropyl ammonium bromide in THF, quantitative precipitation of KBr took place and the filtrate upon solvent removal produced the oily orange $N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H$ (I). Analysis of the THF solution of this compound was not quite as difficult as that of the benzene solution. The Mg:Butyl:H ratios were found to be 1:1.90:0.92. The infrared spectrum of the neat material was similar to that of $KMg(s\text{-}C_4H_9)_2H$ with the characteristic broad absorption envelope between 1300 and 600 cm^{-1} (ν Mg-H).

A solution of (I) in benzene when hydrogenolyzed under 3000 psi of hydrogen at 60-70° overnight produced a white gelatinous precipitate. Analysis showed about 30% magnesium to be present in solution. The dried solid gave the following analysis: Mg:H:Butyl = 1:2.7:0.2.

$$N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H \xrightarrow[H_2,\ 3000\ psi]{Benzene,\ 60\text{-}70^\circ} \underset{(II)}{N(C_8H_{17})_3(C_3H_7)MgH_3}\downarrow \quad (3)$$

Further characterization of (II) by X-ray powder pattern and DTA-TGA analysis is in progress.

When a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in tetrahydrofuran was added to an equivalent amount of lithium bromide in THF, KBr precipitated quantitatively after overnight stirring.

$$KMg(s\text{-}C_4H_9)_2H + LiBr \xrightarrow{THF,\ 25^\circ} \underset{(III)}{LiMg(s\text{-}C_4H_9)_2H} + KBr\downarrow \quad (4)$$

Analysis of the clear filtrate gave the following ratios: Li:Mg:Butyl:H = 1:1.12:2.04:0.93. Upon solvent removal under vacuum, an orange viscous material resulted. The infrared spectrum of this product was identical with the analogous potassium and tetraalkylammonium compounds. The THF solutions of (III) at room temperature are apparently more stable than those of the potassium compound.

Attempts to hydrogenolyze a THF solution of (III) have so far yielded inconclusive results. The mixture resulting from hydrogenolysis at room temperature under 3000 psi hydrogen produced a very small amount of a grey solid with negligible active hydrogen content. The supernatant solution was found to retain its original composition. Efforts are being continued to effect the hydrogenolysis of (III) under a variety of experimental conditions. With the right coice of temperature and solvent it would hopefully be possible to hydrogenolyze (III) to give $LiMgH_3$.

The fact that a tetrahydrofuran solution of $KMg(s\text{-}C_4H_9)_2H$ is stable for several days at low temperature opens up possibilities for the study of a large number of reactions in solution, such as chemical reductions with $LiAlH_4$, AlH_3, B_2H_6 to give possibly $KMgH_3$, $KMg(AlH_4)_3$ and $KMg(BH_4)_3$ respectively. Reactions of $KMg(s\text{-}C_4H_9)_2H$ with THF-soluble metal halides could give a variety of $MMg(s\text{-}C_4H_9)_2H$ type of intermediates which upon hydrogenolysis might be able to produce new and unusual $M(MgH_3)_n$ type of complex hydrides (n = 1, 2, 3 depending upon the metal M). Studies to explore these possibilities are currently in progress.

Significant Results: Preparation of R_4NMgH_3 where R_4N = trioctyl-n-propylammonium and precursors to $LiMgH_3$.

Publications:

(1) J. Dilts and E. C. Ashby, "Composition of Complex Metal Hydrides in Solution. I. Tertiary Amines," Inorg. Chem., 9, 855 (1970).

(2) S. Srivastava and E. C. Ashby, "Reaction of Aluminum Hydride with Diethylmagnesium in Tetrahydrofuran. Characterization of New Ethyl Substituted Hydridomagnesium Aluminum Hydrides," Inorg. Chem., (in press).

Graduate Students: One Postdoctoral student.

2. Vibration and Stability of Distensible Fluid Lines Carrying a Pulsating Incompressible Liquid - H. F. Bauer

Objectives of the Research:

The feedline system of liquid-propelled space vehicles

exhibits, in the problem of interaction with the combustion and pump dynamics and the longitudinally elastic structure, an oscillatory behavior. The propagation of viscous liquids in such a cylindrical elastic conduit will be investigated.

Description of the Work Performed:

The pulsating flow of an incompressible, viscous liquid in an elastic pipeline of circular cross section is investigated. The equations of motion of the liquid and structure have been derived and are given by:

The continuity equation: (because of symmetry)

$$\frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z} = 0 \tag{1}$$

The Navier-Stokes equation:

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} + w\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left\{\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} - \frac{u}{r^2} + \frac{\partial^2 u}{\partial z^2}\right\} \tag{2}$$

$$\frac{\partial w}{\partial t} + u\frac{\partial w}{\partial r} + w\frac{\partial w}{\partial z} = g - \frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left\{\frac{\partial^2 w}{\partial r^2} + \frac{1}{r}\frac{\partial w}{\partial r} + \frac{\partial^2 w}{\partial z^2}\right\} \tag{3}$$

where ν is the kinematic viscosity of the liquid and ρ is the mass density. If the pipeline has a wall thickness $\bar{h}$ and a diameter 2a, the behavior of the elastic cylindrical pipe may be approximately described by Donnell's Equations:

$$\frac{\bar{\nu}}{a}\frac{\partial \bar{w}}{\partial z} + \frac{\bar{u}}{a^2} + \frac{\bar{h}^2}{12}\nabla^4\bar{u} + \frac{(1-\bar{\nu}^2)\bar{\rho}}{E}\frac{\partial^2 \bar{u}}{\partial t^2} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\left\{p\Big|_{r=a} - 2\mu\frac{\partial u}{\partial r}\Big|_{r=a}\right\} \tag{4}$$

$$\frac{\partial^2 \bar{w}}{\partial z^2} + \frac{\bar{\nu}}{a}\frac{\partial \bar{u}}{\partial z} - \frac{(1-\bar{\nu}^2)}{E}\bar{\rho}\frac{\partial^2 \bar{w}}{\partial t^2} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\,\mu\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right)\Big|_{r=a} \tag{5}$$

where $\bar{\rho}$ is the mass density of the shell, $\bar{\nu}$ is Poisson's ratio, $\bar{u}$ the radial and $\bar{w}$ the longitudinal displacement of the shell. E is Young's modulus of elasticity, $\nabla^2 \equiv \partial^2/\partial z^2$ (because of the symmetry), and μ is the dynamic viscosity of the liquid. The equations of motion of liquid and pipeline wall are coupled by the conditions

$$(6) \qquad \begin{aligned} u &= \frac{\partial \bar{u}}{\partial t} \\ w &= \frac{\partial \bar{w}}{\partial t} \end{aligned} \qquad \text{at the wall, } r = a$$

For the solution of this hydroelastic problem, i.e. the simultaneous treatment of the equations (1) through (6), the liquid equations (2) and (3) have to be linearized. We consider a pipeline of infinite length and neglect gravity. Representing pressure and velocity as

$$(7) \qquad p = Pe^{i\omega(t-z/c)}$$

$$(8) \qquad u = U(r)e^{i\omega(t-z/c)}$$

$$(9) \qquad w = W(r)e^{i\omega(t-z/c)}$$

where ω is the circular frequency and c the speed of propagation, yields

$$(10) \qquad U' + \frac{1}{r} U = \frac{i\omega W}{c}$$

$$(11) \qquad U'' + \frac{1}{r} U' + (k^2 - 1/r^2)\, U = 0 \quad \left(k^2 = \frac{i^3\omega}{\nu} - \frac{\omega^2}{c^2}\right)$$

$$(12) \qquad W'' + \frac{1}{r} W' + k^2 W = - \frac{i\omega}{\rho c \nu} P_o$$

which are for $\omega^2 c^2 \ll 1$ satisfied by

(13) $$W(r) = AJ_o(kr) - \frac{i\omega}{\rho c \nu k^2} P_o$$

and

(14) $$U(r) = \frac{i\omega A}{ck} J_1 (kr) + \frac{\omega^2 P_o r}{2\rho\nu c^2 k^2}$$

A is an unknown integration constant. The elastic wall equations are

(15) $$\bar{u} = \bar{U} e^{i\omega(t-z/c)}$$

(16) $$\bar{w} = \bar{W} e^{i\omega(t-z/c)}$$

The resulting expressions are

(17) $$\bar{U}\left(\frac{1}{a^2} - \frac{(1-\bar{\nu})}{E}\bar{\rho}\omega^2\right) - \frac{\nu i\omega}{ac}\bar{W} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\left\{P_o - 2\mu\left[\frac{i\omega A}{c} J_1'(ka) + \frac{\omega^2 P_o}{2\rho c^2 \nu h^2}\right]\right\}$$

(18) $$-\frac{\bar{\nu} i\omega}{ac}\bar{U} + \bar{W}\left[\frac{(1-\bar{\nu}^2)\bar{\rho}\omega^2}{E} - \frac{\omega^2}{c^2}\right] = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\mu\left\{i\omega\left[\frac{i\omega A}{ck} J_1(ka) + \frac{a\omega^2 P_o}{2\rho c^2 \nu k^2}\right] + AkJ_o'(ka)\right\}$$

With the boundary conditions (6) one obtains two additional equations

(19) $$\frac{i\omega A}{ck} J_1(ka) + \frac{\omega^2 a P_o}{2\rho\nu k^2 c^2} = i\omega\bar{U}$$

(20) $$aJ_o(ka) - \frac{i\omega P_o}{\rho\nu c k^2} = i\omega\bar{W}$$

which together with (17) and (18) represent four equations for the determination of the unknowns. Introducing these into the equations (15), (16) and (7) through (9) gives the behavior of such a pulsating system.

Results:

The mathematical solution has been found for a simple pulsating system. The speed of propagation is obtained by setting the coefficient determinant obtained from equations (17) and (18) equal to zero. Thus the ratio A/P_o, $\bar{U}/P_o$ and $\bar{W}/P_o$ may be obtained from the above equations. In the next phase the arbitrary pulsating pressure gradient superimposed on a uniform flow will be treated. Additional mathematical analysis relative to the project, recently submitted by Mr. S. C. Chang and performed primarily by him, will be incorporated in the final report on this project.

Publications:

None.

Graduate Students: One Ph.D. student.

3. A Study of Helicopter Blade Slap Noise - R. B. Gray

Research Performed and Results Obtained:

The interaction under certain flight conditions of a helicopter blade with the vortex field shed from preceeding blades produces a loud repetitive noise. Other studies have shown that a realistic mathematical model of the vortex structure is required for analysis of the noise generating mechanism. Such a model is not presently available. The objective of this grant is to explore several methods of measuring the flow field associated with vortex systems. At present, the hot-wire anemometer is being used to study the flow field of vortex rings generated in air.

To date, velocity surveys across a ring diameter have

been made at the vortex generator exit and at a station twelve inches from the exit. Both the axial component and the total velocity magnitude have been measured. Although there is some scatter in the data, the results appear reasonable. However, a comparison with vortex ring models available in the literature is not good. In continuing the study, stronger rings will be generated to reduce the scatter in the data. An attempt will also be made to determine the vorticity distribution in the ring from the velocity measurements.

Publications:

(1) "Hot-Wire Velocity Surveys with Pressure-Velocity Correlation of Air Vortex Rings", John F. Betsill, Jr. Georgia Institute of Technology, School of Aerospace Engineering, Masters' Special Problem. September 4, 1970.

Graduate Students: One M. S. student.

4. Application of Mass Spectrometric and Cryogenic Methods to the Analysis and Synthesis of Highly Unstable Boron Compounds - H. A. McGhee, Jr.

As part of a multi-faceted theoretical and experimental research program in High Energy Chemistry, we have been concerned with the synthesis and chemistry of highly unstable and reactive compounds of boron. A scientifically particularly interesting and also important from an applications perspective class of compounds are ethylene-like and acetylene-like compounds of boron and nitrogen.

Non-aromatic (non-"borazine type") boron-nitrogen-hydrogen compounds such as NH_2-BH_2 and NH=BH, and their halogen derivatives

are very unstable. Classical organic or inorganic synthetic methods usually fail because of their strong tendency to fast degradation and formation of unstable polymer products of undetermined composition.

A promising route has been developed in this laboratory[1] wherein borazine is discharged in a low pressure inductive plasma followed by a rapid quench of the intermediate product NH_2-BH_2 in a liquid nitrogen cooled mass spectrometric inlet system. Slow fractional low temperature vacuum distillation directly into the ion source of the mass spectrometer led to the detection and identification of NH_2-BH_2. Also a direct mass spectrometric analysis of the gas mixture behind the plasma discharge indicated the existence of the compound. It was postulated that halogen derivatives such as NH_2BCl_2, NH=BCl, and flourine analogs also might exist as short life time intermediates. A similar way to get to those compounds would therefore be to discharge the corresponding 3 - halogeno borazines, however, the vapor pressures are too low for evaporation into the plasma-discharge because of their heteropolar character. Therefore, the alternative, but more difficult route was undertaken to primarily synthesize appropriate parent compounds as NH_3BCl_3 and NH_3BF_3 and decompose these unstable compounds in a one step process.

An apparatus has been designed whereby either the components NH_3 and BCl_3 or NH_3 and BF_3 can be discharged in a plasma directly in the mixing area or only one may be discharged with the second component introduced thereafter. The reaction products were analyzed by a Bendix time-of-flight mass spectrometer in order to determine the

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[1] C. T. Kwon and H. A. McGhee, Jr., Inorg. Chem. in press.

most favorable conditions (total pressure, residence time, composition ratio of the two initial compounds, and discharge current) for the yield of one particular compound as NH_2BCl_2. When the maximum peak height of NH_2BCl_2 (or the BHNF compound) occurred in the mass spectrum, the reaction mixture was trapped at liquid nitrogen temperature for further study. The total pressure was varied between 100 to 1000 microns of mercury. During the time when the mixture was trapped small amounts of the products were aspirated into the mass spectrometer for continuous analysis. This turned out to be very important because a change of the composition ratio had to be corrected immediately. Thereafter the liquid nitrogen was exchanged by 2 - methylpentane, at its melting point of -159°C. This refrigerant was then slowly heated up to room temperature within two to four hours and the sequentially vaporized products were analyzed with the Bendix mass spectrometer.

Roughly about one half of the reactants formed a white solid product directly at the point where they were mixed together. It was slowly soluble in water. No further analytical investigations were conducted on this product.

The gaseous part was analyzed mass spectrometrically. In general the spectra were similar with or without discharge of the reaction mixture. Therefore, if not specified otherwise, the following description applies to both cases. As mentioned above, the ratio of composition of NH_3 and BCl_3 was the most important factor for the formation of the final products. Depending on this ratio three

different products were obtained.

At excess amounts of ammonia, the only significant mass peaks belonged to ammonia (NH_3, NH_2, NH, N, N_2, H_2). Consequently a discharge of this reaction mixture gave N_2 and H_2 as decomposition products of NH_3. With excess amounts of BCl_3, only mass peaks of BCl_3 and of nitrogen were observed. HCl and N_2 are decomposition products of the unstable intermediate compound NH_3BCl_3 or its polymeric products. In the first case, HCl was not obtained because it reacts with excess NH_3 to form solid NH_4Cl.

Within a very small range of equal NH_3/BCl_3 composition, suddenly new peaks with the mass numbers 96-101 and 60-64 appeared while the mass intensities of BCl_3, BCl_2, BCl decreased. At a definite composition ratio only these new mass peaks were observed (together with HCl, Cl) while the BCl_3 peaks nearly decreased to zero. It can easily be proven that the peaks at 96-101 only belong to the compound NH_2BCl_2 because boron and chlorine are both isotopic and the natural abundances of these isotopes (B11: 80%, B10: 20%, Cl35: 75%, Cl37: 25%) are nearly ideal for a statistical analysis of the experimental mass intensity distribution. Table 1 shows the theoretical peak heights of NH_2BCl_2 of the mass numbers 96 to 101 in comparison to the experimental results.

Table 1

Theoretical and experimental mass intensity distribution for the compound NH_2BCl_2.

mass	96	97	98	99	100	101
I_{theo}	25	100	16.6	66.7	2.8	11.1
I_{exp}	26.9	100	18.7	65.6	2.5	13.1

The experimental values are averages of 11 independent measurements. The electron voltage at the ion source was in all cases 70 volts.

The close agreement between theoretical and experimental data leaves no doubt, that only NH_2BCl_2 contributes to above mass intensity distribution.

The peaks at the mass numbers 60-64 were analyzed in the same way and turned out to be superpositions of mainly NH_2BCl with small amounts of NHBCl. These are obviously fragmentation products. When the amount of NH_3 was increased, the NH_2BCl_2 peaks were dimished at once. When the amount of BCl_3 was marginally increased one could observe NH_2BCl_2, NHBCl together with BCl_3, BCl_2, BCl, but at further increase of BCl_3 the boron-nitrogen compound disappeared in the spectrum. This implies that both, excess NH_3 and BCl_3 are reacting with NH_2BCl_2 towards decomposition and/or polymerization. These results help to clarify why NH_2BCl_2 has never been observed before.

Current research here is concerned with efforts to quench-stablize NH_2BCl_2 at cryogenic temperatures. Our unique cryogenic mass spectrometric techniques will be indispensible for this investigation.

5. Energy Conversion in Reactive Collisions - T. Moran

Inelastic energy losses in the collisions of O^+ and O_2^+ ions with neutral molecules have been studied in a beam apparatus

designed to direct mass-analyzed low energy ion beams onto taget molecules and scan the mass, energy and angular distributions of charged reaction products. Elastic collisions are found to predominate in the forward scattering events, however inelastic collisions become important at large scattering angles. Maxima in the inelastically scattered ion intensities are displaced from the centroids of the elastic peaks by amounts corresponding to known vibrational energy spacings in the respective diatomic species. Vibrational transition probabilities obtained from the inelastic data show multiquantum transitions to be more important as the reactant ion kinetic energy is increased from 10 to 20eV. For a given relative energy of approach, it is found that higher vibrational transitions predominate at larger scattering angles. The velocity dependences of these transitions are in reasonable accord with calculations that employ a semiclassical impact parameter treatment to estimate collisional energy transfer and time dependent wavefunctions to evaluate vibrational transition probabilities for a forced harmonic oscillator model.

A statistical phase space model of chemical reactions has been developed and applied to the above inelastic energy loss process and it is found inferior to the forced quantum oscillator model; however, further examination of the statistical model shows that it can be extremely useful in describing chemical rearrangement channels of reaction. This statistical model has been applied to molecular and dissociative charge transfer reactions of He^+, Ne^+, Ar^+ and Kr^+ with neutral molecules in the 0.05 to 200eV energy range. Comparison between calculated and experimental cross sections for the molecular charge transfer channels have indicated an incomplete mixing of

statistically available N_2^+ product ion electronic states, however the cross sections computed for endoergic dissociative channels of reaction are in good agreement with experiment. Calculated product ion vibrational distributions are found to be in accord with those obtained from product N_2^+ kinetic energies and with vibrational distributions obtained from spontaneous radiative transitions of electronically excited N_2^+ ions produced in the respective chemical interactions.

The statistical model of energy conversion processes has been applied to experimental results obtained in the ion beam lab at Tech and recent results from the Aerospace Research Laboratories of Wright-Patterson AFB. The in-line high collection efficiency configuration of a tandem mass spectrometric beam apparatus at the latter location is unique and their data is supplementary to the results obtained with the beam apparatus at Georgia Tech. Cross sections for the collision induced dissociation of excited O_2^+ and NO^+ ions computed using the statistical model is in surprising agreement with existing experimental data. The variation of the calculated cross sections with both ion internal energy and ion kinetic energy are in good agreement with experiment. The statistical theoretical model of reaction thus appears to be a very effective tool in its predictive properties, in particular the involvement of vibrational and electronic excitation energy in the high energy dissociative reactions.

Publications:

(1) "H_3^+ Vibrational Frequencies from Ion Impact Spectroscopy,"

F. Petty and T. F. Moran, Chem. Phys. Lett. 5, 64 (1970).

(2) "Vibrational Excitation in Collisions Involving Oxygen Ion Beams," P. C. Cosby and T. F. Moran, J. Chem. Phys. 52, 6157 (1970).

(3) "Application of the Statistical Phase Space Theory to the Reactions of Rare Gas Ions with Nitrogen Molecules," D. C. Fullerton and T. F. Moran, Submitted to J. Chem. Phys.

(4) "Statistical Phase Space Model of the Collision-Induced Dissociation of Excited O_2^+ and NO^+ Ions," T. F. Moran and D. C. Fullerton, Submitted to J. Chem. Phys.

Graduate Students: Two Ph.D. students.

6. Atomic and Magnetic Ordering in Transition Metal Alloys - S. Sponner

Summary of Progress:

Neutron diffraction studies of the effects of atomic ordering on the atomic magnetic moments using the polarized neutron scattering technique have been continued at Oak Ridge National Laboratory with the cooperation of J. W. Cable of the Solid State Division. After preparing a draft of a research paper based on neutron data taken last fall, it was concluded that the findings were of sufficient importance that the existing experimental uncertainties should be removed before final publication. In review, the conclusions are as follows:

1. Changes in the atomic magnetic moments of iron in iron-50% cobalt alloys cannot be explained by short-range order effects.

2. A large negatively polarized non-local spin density is present in the FeIo in both the ordered and disorder state.
3. A spin density transfer of a non-localized nature appears to reduce the constituant moments in the alloy where the negative spin polarization may be found preferentially at the iron site.
4. The long-range order changes appear to be chiefly responsible for iron moment changes, possibly through the effects of an order induced Brillouin zone boundary pertubation of the 3d-4s bands.

A draft copy of these results was brought to the attention of Solid State physics theorists at the recent Sagamore conference on Magnetic Electron Density at Grenoble, France, by Dr. R. A. Young. The keen interest in the findings has made analysis and publication of our new neutron scattering results an immediate objective in the program.

Metallurgical studies of iron-cobalt alloys have also continued with the objective of elucidating the engineering factors in iron-cobalt alloy development and the production of mere suitable alloy samples for diffraction analysis. The limitation to grain growth appears already to be related to carbide pinning of grain boundaries. For some time it has been held that interstitial impurities have been responsible for imbrittling the iron-cobalt alloys. The role of vanadium additions in commercial alloys appears, from our studies, to act as a carbon scavenger in the iron-cobalt solid solutions. The behavior carbon in iron cobalt solutions is

under investigation with vanadium carbide formation a principle objective.

Publications: None.

Graduate Students: Two Ph.D. students.

7. A New Technique for Detection of Infrared Radiation - A. L. Stanford

Objectives of the Research:

To investigate materials and fabrication techniques for utilizing the pyroelectric effect as a thermal detector.

Description of Work Performed:

Our inability to observe the pyroelectric effect in biological samples has prompted a return of studies to the more common ferroelectric materials.

The combination of thermal (beat sinking) and electrical (rise time) problems have limited the use of $BaTiO_3$ and GASH (quanadive aluminum sulfate hexahydrate) as an infrared detector, except when sources of radiation are relatively intense. Using gold-coated crystals of $BaTiO_3$, rise times as low as 0.5 msec have been observed by sacrificing detectivity. With rise times of about 30 msec, detectivities of about 15×10^6 $cm^{1/2}$ $watt/cps^{1/2}$ have been achieved. In our samples, this corresponds to noise equivalent power of approximately 1.3×10^{-8} $watt/cps^{1/2}$.

With the normal ferroelectric materials, including triglycene sulfate (TGS), it does not appear that pyroelectric detectors will compete successfully with quantum detectors in the infrared region. However, with high intensity sources like lasers, fast rise times in pyroelectric detectors might be utilized in mode studies, calibrating output

energy, and in numerous situations where a rugged, small detector can be placed in the beam.

Publications: None.

Graduate Students: None.

8. The Physical and Functional Aspects of Integrated-Circuit Technology - K. L. Su and D. C. Ray

Research Performed:

In the circuit phase, work has been centered around the extension of synthesis techniques to the use of the generalized positive-impedance converter (GPIC) in active RC networks. The GPIC is characterized by the chain matrix in which $A = \pm k_1$, $B = 0$, $C = 0$, and $D = \pm k_2 f(s)$; where k_1 and k_2 have the same algebraic sign. If port 2 is terminated in Z_L, then the impedance looking into port 1 is $\frac{k_1}{k_2} f(s) Z_L$. In particular, it has been found advantageous to investigate the case in which $f(s) = 1/s$.

A grounded minimum-capacitor synthesis technique for a qth order arbitrary open-circuit voltage transfer function of real rational functions in the complex variables utilizing only resistors and GPIC's has been developed. It has been shown that the technique can be made compatible with hybrid integrated-circuit technology.

The coefficient, selectivity, and natural-frequency sensitivities have been examined for the second-order open-circuit voltage transfer function and found to be small. An advantage in selectivity sensitivity has been noted over a certain INIC realization of the second-order open-circuit voltage transfer function.

The range of passive elements (resistors) has been examined for the case where K_1 and k_2 of the GPIC can take on any real value. It has been found that all resistors in the synthesis can be restricted to have values of 1 ohm if so desired. This serves as a good indicator of the potential control over the range of passive element values in the synthesis technique.

A grounded minimum-capacitor synthesis technique for a qth order arbitrary driving-point admittance which is a real rational function in the complex variables utilizing only resistors and GPIC's has been developed. The driving-point function is rendered in terms of an open-circuit voltage transfer function and is synthesized accordingly.

In the devices area, the effort can be broken down into two parts. The first part deals with a continuation of the previous work on thin-film active devices for operation at microwave frequencies. The second part was concerned with establishing the goals for a Ph.D. dissertation based on the work accomplished on this grant. The details of these two parts are as follows.

An extension of the measurement of the microwave conductivity of a specimen by eddy current loss techniques was developed which includes the important case of a semiconductor film deposited on an insulating substrate. The dissipated power in terms of the dimensions and physical properties of the film and substrate has been determined using the computer. The results are such that experimentation of simple dimensions is scheduled to be carried out on germanium deposited on calcium fluoride. The selection of the

the calcium fluoride was partially dictated by the availability of backup data at microwave frequencies and the fact that germanium has been deposited epitaxially on it. The experimentation is called for because the results suggest unpublished substrate effects in the films at microwave frequencies.

The dissertation work of a graduate student will involve an investigation, analytically and experimentally, of various transport phenomena in sputtered semiconducting films as a function of film thickness and structure. Both single-crystal and polycrystalline thin-film properties will be studied to determine the fundamental factors influencing the electrical behavior. Such factors as the treatment of band edges at the surface; symmetrical versus nonsymmetrical band edges; surface scattering - specular and diffuse; impurity scattering; thermal scattering; dislocation scattering; and a complete accounting of structure sensitive properties will be considered. The fabrication of the films and useful measurement structures are a direct outgrowth of the NASA research grant. It should be noted that the Schottky microwave diode fabricated using germanium on sapphire substrates did not possess the electrical characteristics that were desired due to certain problems in the fabrication procedures. The problems encountered have been solved and a useful thin-film device will be built in the near future to demonstrate this capability.

Paper Submitted for Publication:

(1) D. R. McElroy and K. L. Su, "Admittance Matrix Synthesis with Grounded RC Network Containing Nonideal Amplifiers," submitted to the IEEE Transactions on Circuit Theory.

Papers Presented at Scientific Meetings:

(1) K. L. Su, "An All-Purpose Impedance Converter Circuit," 1970 Chiao Tung Colloquium on Circuits and Systems; Hsinchu, Taiwan, China, August 25, 1970.

(2) K. L. Su, "Synthesis of RC Active Networks Using Positive-Impedance Converters," 1970 Kyoto International Conference on Circuit and System Theory, Kyoto, Japan, September 9, 1970.

Graduate Students: Three Ph.D. students.

9. Collisional De-excitation of Atomic Particles - E. W. Thomas

Objectives of the Research:

The experiments are designed to investigate the processes of formation and destruction of excited atoms at projectile energies of 5 to 30 keV. Work is presently concentrated on the metastable state of the hydrogen atom. Hydrogen atoms and ions are responsible for certain types of auroral phenomena. Results from the study of the metastable state may be readily extrapolated to other excited states by well established theoretical rules.

The research is to determine the cross sections for the formation of the metastable state of hydrogen as protons traverse targets of helium and nitrogen. Measurements are made as a function of the distance of closest approach between the colliding atoms. Experiments are also planned using metastable beams and monitoring their destruction.

Research Performed in the Current Period:

The objective of the present experiments is to study

charge transfer reactions that can be described as follows:

$$H^+ + X \rightarrow H(2s) + X^+$$

The ultimate objective is to study the angular scattering in such processes. As an initial step in the program it was decided to measure the total cross section (i.e. the cross section integrated over all scattering angles) for the case of a Helium target. It was intended to confirm the satisfactory operation of the experiment by comparing our data with previous measurements by other groups. The versatility of our apparatus permitted this measurement with great ease. Included in this phase of the work were total cross section measurements for targets of O_2 and N_2; no data on these cases is available in the literature. The cross sections for O_2 and N_2 rose with energy in the range 5 to 30 keV; cross section magnitudes were of the order 5×10^{-17} cm^2. This phase of our work is now complete and has been submitted for publication in "The Physical Review".

At the present time considerable progress has been made in the study of angular scattering in the charge transfer process. Attention is being directed at targets of He and N_2. It appears that the proportion of neutrals formed in the metastable state is a rather sensitive function of angle and energy; excited state fractions of 10% have been recorded at large angles. This is a most unexpected result. Apart from the intrinsic interest, this phenomenon could be used as a basis for design of metastable particle sources. At present there is no obvious explanation of these observations. Work in this

area continues.

Papers Submitted for Publication:

(1) A paper entitled "Formation of Metastable Hydrogen Atoms by Charge Transfer" has been submitted to "The Physical Review" for publication.

Paper Presented to Scientific Meetings:

(1) A paper entitled "Differential Cross Section for the Formation of Metastable Hydrogen by Charge Transfer" has been accepted for presentation at the Annual Meeting of the Division of Electron and Atomic Physics, American Physical Society (November, 1970, Seattle).

Students: One Ph.D. and two undergraduate students.

10. Studies in Nitrene Chemistry - L. H. Zalkow and C. L. Liotta

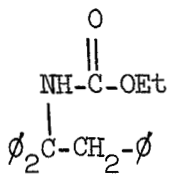
Objectives:

A study of the properties and reactions of nitrenes is proposed. Nitrenes are high energy electron-deficient nitrogen species; the parent compound, NH, has been observed to be a component of the sun, of comets, and of Jupiter; nitrenes have also been postulated as intermediates in a number of organic reactions. This study includes investigations of the electronic structure of nitrenes and investigations of the reactions of nitrenes with organic and inorganic substances. Results of this study should improve our understanding of why these species exist in space, how they may interact with man and spacecraft, and how they may be utilized in space exploration.

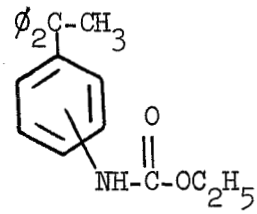
Description of Work and Results:

The Electronic Nature of Carbethoxynitrene

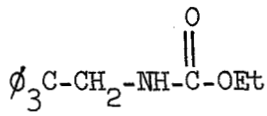
In order to distinguish between singlet and triplet carbethoxynitrene during time of reaction, a series of experiments were carried out in which carbethoxynitrene was allowed to react with 1,1,1-triphenylethane. The following products were isolated from the reaction mixture:



I



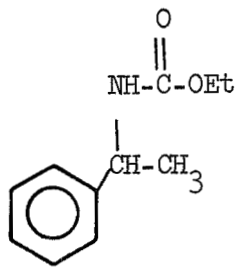
III



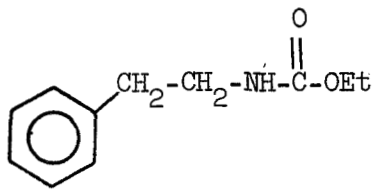
II

Product I is believed to arise from the interaction of 1,1,1-triphenylethane with triplet carbethoxynitrene, while II is believed to arise from singlet nitrene.

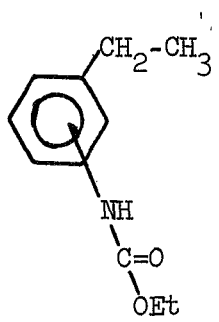
To obtain some information regarding the electrophilicity of carbethoxynitrene, a series of experiments was carried out in which carbethoxynitrene was allowed to react with ethylbenzene. The following products were obtained:



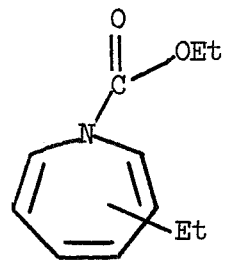
IV



V



VI



VII

The ratio of III to IV is an indication of the nucleophilicity of the attacking nitrene. This ratio was found to be much greater than one. The mechanism for the formation of VI may be explained in terms of singlet carbethoxynitrene. Compounds IV, V and the three isomeric structures of VI have been synthesized by alternate routes in order to prove the structures of the above products.

The Reaction of Various Azides with Bicyclic Olefins

The thermal reaction of methyl azidoformate and norbornene has been found to proceed via 1,3-dipolarcycloaddition yielding exo triazoline adduct. Thermal decomposition of the triazoline results in the loss of nitrogen and the formation of at least 5 products. The major products of the thermal decomposition in decalin were 3-carbomethoxy-3-azatricyclo(3.2.1.$0^{2,4}$ exo)-octane, and N-carbomethoxy-2-norbornimine. In addition, syn-2-norbornene-7-methyl carbamate, and 3-carbomethoxy-3-azatricyclo(3.2.1.$0^{2,3}$ endo)octane were isolated. The thermal decomposition of the triazoline adduct is considered to proceed by a multi-step mechanism. The first step is considered to involve heterolytic cleavage of the N_3-N_4 bond to give a zwitterion which may lead to products or rearrange via carbon-carbon bond

cleavage to give a diazoalkyl imine.

Benzenesulfonyl azide has been found to react with cis-endo and cis-exo bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride to give in both cases, predominantly the more hindered endo aziridine in addition to the exo aziridine in apparent violation of the "exo-addition rule." The stereo-chemistry of the aziridine rings was determined by nuclear magnetic resonance analysis and by conversion of the endo-aziridone-exo-anhydride to 2-endo-benzenesulfonamidobicyclo [2.2.1]heptane. The endo-aziridine-endo-anhydride has been previously converted into a lactone-N-benzenesulfonyl-lactam.

Benzenesulfonyl azide reacts with cis-endo and cis-exo-norbornene-5,6-dicarboxylic anhydrides and with the corresponding cis-exo-dimethyl ester in refluxing carbon tetrachloride to give predominantly endo aziridines. Under identical conditions the cis-endo dimethyl ester gives exclusively the exo aziridine and under photolytic conditions the cis-exo anhydrides and dimethyl esters give almost exclusively exo aziridines. At room temperature, the cis-exo dimethyl ester gives predominantly the exo aziridine, and p-methoxy-benzenesulfonyl azide reacts with the endo-anhydride Ia in refluxing carbon tetrachloride to give an even greater ratio of the endo aziridine. The exo-1,2,3-Δ^2-triazoline prepared from the exo anhydride and phenyl azide, on pyrolysis in decalin, gives an almost 1:1 ratio of the exo and endo aziridine.

A mechanism is proposed to account for the above observations which involves the conversion of exo-1,2,3-Δ^2-triazolines to endo aziridines via a 3-diazomethylcyclopentane-2-carboxaldehydeimine

intermediate.

Publications: None.

Graduate Students: Two Ph.D. students.

III. CONCLUSIONS

The NASA Multidisciplinary Grant NGL 11-002-018 continues to stimulate research on the campus and its effectiveness is demonstrated by the number of publications (4), submissions (4) and presentations (3) during the six month period, March 15, 1970 to September 14, 1970.

Through the grant graduate students are engaged in quality research activities and students in the following categories received financial support from the grant: Undergraduates - 2, M.S. - 1, Ph.D. - 10, and Post Doctorals - 1.