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THE CATHOLIC UNIVERSITY OF AMERICA

Department of Chemistry
Washington, D.C. 20064

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The Catholic University of America
Washington, D.C. 20064

Progress Report

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Studies of Elementary Reactions of Chemical Importance in the Atmospheres of Planets

Fred L. Nesbitt, Principal Investigator

Submitted to

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Greenbelt, Maryland 20771

Period of Report: 5/1/00 to 4/30/01

Progress Report

Fred L. Nesbitt
$CH_3 + CH_3$ Kinetics.

The methyl self-reaction was studied at T = 298 K and 202 K and at three different pressures, P = 0.5, 1.0 and 2.1 Torr.

$CH_3 + CH_3 + M \rightarrow C_2H_6$

The experimental measurements were performed in our discharge flow-mass spectrometer
(DF-MS) apparatus. The methyl radicals were generated by the reaction of F with methane.

$CH_4 + F \rightarrow CH_3 + HF$

Passing a mixture of molecular fluorine, F_2, in helium through a microwave cavity generated the
atomic fluorine reagent. The atomic F enters the flow tube through a rear port on the flow tube.
The methane reagent enters the flow tube through a movable injector located coaxial in the
flow tube. The decay of methyl radical signal was monitored at a mass/charge ratio (m/z) of 15 as a function of the injector distance. To minimize secondary chemistry from the reaction

$CH_3 + F \rightarrow CH_2 + HF$

the initial $[CH_4]_0/[F]_0$ was above 37.0 and typically 100. This ensures a 1:1 relationship betweenititial [F] and $[CH_3]$. A titration of F with excess Cl_2 yields the initial $[F]_0$.

Our experimental methodology to accurately measure the mass spectrometer scaling factor, i.e. the relationship between initial signal and $[CH_3]_0$, has been improved. Now we measure the CH_3 signal decay under exponental decay conditions at low initial $[F]_0$, 3×10^{11} molecule cm^{-3}, in the presence of Cl_2. This minimizes the second-order decay contributed by the CH_3 self-reaction and a simple extrapolation of the ln(signal) vs time plot to t = 0 gives the initial signal. This provides the desired relationship between initial signal at 15 amu and $[CH_3]_0$. The resulting calibration is then applied to the observed
decay of the CH_3 signal at high concentrations of CH_3 assuming linearity of this scaling factor.

The rate constant was determined by a one parameter fitting of the net signal decays to a numerical model (FACSIMILE program). This was required to correct the methyl radical
decay curves for two additional loss processes of the methyl radical:

$CH_3 + F_2 \rightarrow CH_3F + F$

$CH_3 \rightarrow$ first-order wall loss

Although analysis and parameter fitting of the data is continuing, we tentatively report a coefficients at T = 298 K and P = 1.0 Torr of $k_1 = 4.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} with

$5 < [CH_3]_0 < 10x10^{12}$ molecule cm^{-3} . This is consistent with the range of previous measurements once account is taken for extrapolation to lower pressure and bath gas composition. Experiments are in progress to complete our study of the $CH_3 + CH_3 + M$ reaction by examining the effect of pressure at T = 298 K.

Our latest experiments involved the following:
1. Changes to the flow tube
Redesigned the flow tube to reach temperatures of 156 K.
Liquid N_2 vapors was used maintain the temperature.

2. Experimental conditions
Range of pressures:0.6,1.0,1.5 Torr
Temperature: 156 K
CH_3 $(4.13 - 9.8)x10^{13}$ molecules/cm^3
3. Rate constant: $k = 6.77(\pm 0.54)x10^{-11}$ cm^3/molecule s

Summary of Research
1 May, 2000 to 1 May, 2001

Frank T. Ferguson

During the past year, our research has focused on topics related to nucleation and condensation phenomena. There are many unanswered questions as to the origin of cosmic dust grains, but it is generally believed that a significant fraction of these grains are refractory species such as silicates and graphite that condense in the outflows of stars. The exact conditions under which these refractory vapors condense are unknown and there is very little experimental data on the condensation of such species. We are currently performing experiments with a gas evaporation apparatus to provide such data. In the fall of 2000 we published results from a series of experiments with lithium and have just completed experimental work on sodium. We are currently interpreting the sodium experimental results and preparing these for publication.

In the past we have had some success comparing our experimental refractory nucleation data with a formalism of classical nucleation theory called scaled nucleation theory. During a recent review of this theory, we discovered that some of the generalizations made for more volatile species do not hold for metallic species. If more appropriate terms are used, (based on the physical properties of these metallic species), there tends to be better agreement between existing refractory experimental data and the scaled theory. This includes both data taken using our gas evaporation apparatus as well as data taken using other experimental techniques. Results of this re-analysis are scheduled to be published during the summer of 2001.

Finally, roughly half of the nucleation data for lower-temperature, volatile species have been collected using a device known as the thermal diffusion cloud chamber. To a lesser extent, this apparatus has also been used to study the nucleation of some refractory species. There is currently quite a lot of interest in determining the limits of stable operation for this device. In addition, the experimental results from this chamber seem to be pressure dependent whereas no pressure dependence is seen with other types of nucleation chambers. We have continued to study the role that convection plays in affecting the experimental results gathered from these chambers. Our recent results seem to indicate that both the pressure and sidewall heating induce a convective flow in the chamber which tends to suppress the maximum attainable supersaturation within the interior of the chamber. This can result in an "apparent" change in the supersaturation with pressure. Our recent work suggests that these problems may be circumvented by using smaller chamber sizes, thereby reducing the magnitude of these buoyancy-induced flows.

Papers Completed During the Period

"Experimental Studies on the Condensation of Refractory Materials V. The Condensation of Lithium," Frank T. Ferguson and Joseph A. Nuth, III, *Journal of Chemical Physics*, 113, 4093 (2000).

"Vapor Transport Within the Thermal Diffusion Cloud Chamber," Frank T. Ferguson, Richard H. Heist, and Joseph A. Nuth, III, *Journal of Chemical Physics*, 113, 7393 (2000).

"Application of Scaled Nucleation Theory to metallic vapor condensation," Daniel M. Martinez, Frank T. Ferguson, Richard H. Heist, Joseph A. Nuth, III, *Journal of Chemical Physics*, in press.

"The effect of carrier gas pressure and wall heating on the operation of the thermal diffusion cloud chamber," Frank T. Ferguson, Richard H. Hesist, Joseph A. Nuth, III, *Journal of Chemical Physics*, submitted.

"The impact of convective flow on thermal diffusion cloud chamber operation," Frank T. Ferguson and Richard H. Heist, *Journal of Physical Chemistry*, submitted.

"A Note on the Phenomena of Diffusive Slip," Frank T. Ferguson, *Physics of Fluids*, submitted.

Summary of research
1 November, 2000 to 1 May, 2001

Gunther Kletetschka

During the past year I have been involved in several projects.

I measured magnetism of various meteorites with focus on their magnetization origin. I considered mainly the Space to Earth transit issue with resultant exposure to temperature change and general aspects of residence in the geomagnetic field. This work was presented in one extended abstract at LPSC in Houston, Texas, this spring in March 11 –16 where I gave a poster presentation on magnetization of chondrules

I have been involved in excavating of Jurassic age dinosaurs (May 25 – May 28) in NW Colorado where I participated on WEB cast presentation and explained geophysical approach when excavating these fossils.

I participated on expedition North Pole 2001 as a geologist. Gave 3 WEB cast presentations (coolspace.gsfc.nasa.gov/northpole); April 22 - climate change, April 23 - glaciers, April 25 - ore deposits. And one presentation at Polaris mine facility (northern Canada) on magnetization of bodies in our solar system

I gave a seminar (April 5) at GSFC/NASA, bldg 2, on magnetic nature of EROS asteroid where I summarized my findings on magnetism of meteorites

I accepted a role of a field geologist explaining geology of Grand Canyon, Meteor and Sunset craters in Arizona for the purpose of building high school educational package (Feb 8 - Feb 12, see coolspace.gsfc.nasa.gov/grandcanyon).

I actively participated on expedition to Belize with objectives to get samples of ejecta blanket from Chixculub impact event (Jan 16 - Jan 29). The subsequent work resulted in one oral presentation in Boston, at American Geophysical Union 2001 spring meeting.

I traveled to San Francisco, California, American Geophysical Union, December 16 -19, 2000, where I gave four poster presentations (magnetism of reduced basalt, sequoia trees, vector analysis of data, magnetic contamination near highway), one oral presentation (magnetism of large meteorites).
I accepted invitation to participate on WEB cast event (coolspace.gsfc.nasa.gov/deathvalley/webcast.html) "Field Science in Geology and Hydrology" in Death Valley, Ca, Dec 12-Dec 15, 2000.

I participated on poster presentation to NASA director and presented two posters (Electric discharge in meteorites and Magnetism of Banded Iron Formations) at GSFC/NASA, Bldg. 28, Dec 7, 2000.

I accepted mentoring Catie Carter, grade school female student, project on magnetism of petrified wood.

I participated on Window on the Universe Team (Nov 24, 2000) and interacted with 6th graders from two schools in the District of Columbia.

Submitted for Publication:

Connerney, J.E., M.H. Acuna, P.J. Wasilewski, G. Kletetschka, N.F. Ness, H. Reme, R.P. Lin, and D.L. Mitchell, The Global Magnetic Field of Mars and Implication for Crustal Evolution, *Geophysical Research Letters, submitted,* 2001s.

Dunlop, D.J., and G. Kletetschka, Why Does Multidomain Hematite Acquire Intense TRM?, *submitted to GRL*, 2001s.
Kletetschka, G., and P.J. Wasilewski, Grain size dependent magnetic susceptibility of hematite, *Physics of the Earth and Planetary Interiors*, 2001s.
Kletetschka, G., P.J. Wasilewski, and P.T. Taylor, The role of hematite - ilmenite solid solution in the production of magnetic anomalies in ground and satellite based data, *Tectonophysics*, 2001s.

Published in Refereed Journals:

Kletetschka, G., P.T. Taylor, P.J. Wasilewski, and H.G.M. Hill, The magnetic properties of aggregate polycrystalline diamond: Implication for carbonado petrogenesis, *Earth and Planetary Science Letters, 181* (3), 279-290, 2000.
Kletetschka, G., P.J. Wasilewski, and P.T. Taylor, Hematite vs. magnetite as the signature for planetary magnetic anomalies?, *Physics of the Earth and Planetary Interiors, 119* (3-4), 259-267, 2000.
Kletetschka, G., P.J. Wasilewski, and P.T. Taylor, Mineralogy of the sources for magnetic anomalies on Mars, *Meteoritics and Planetary Science, 35* (5), 895-899, 2000.
Kletetschka, G., P.J. Wasilewski, and P.T. Taylor, Unique thermoremanent magnetization of multidomain sized hematite: Implications for magnetic anomalies, *Earth and Planetary Science Letters, 176* (3-4), 469-479, 2000.
Nuth, J.A., H.G.M. Hill, and G. Kletetschka, Determining the ages of comets from the fraction of crystalline dust, *Nature, 406* (20 July), 275-276, 2000.
Wasilewski, P.J., G. Kletetschka, and T. Dickinson, Magnetic characterization of reduction in Mount Fuji basaltic tree mold, *Geophysical Research Letters, 27* (10), 1543-1547, 2000.

Published Abstracts from Meetings:

G. Kletetschka, P.L. Zitzelberger, P.J. Wasilewski, A. Ocampo and K. Pope, Magnetic properties of the ejecta blanket from the Chicxulub impact crater: Analog for robotic exploration of similar deposits on Mars, EOS, transactions, American Geophysical Union, (supplement (abstract)), 2001-.
G. Kletetschka, P.J. Wasilewski, M.H. Acuna and T.L. Dickinson, Why is EROS, "non-magnetic"?, EOS, transactions, American Geophysical Union, (supplement (abstract)), 2001-.
M.H. Acuna, P.J. Wasilewski, G. Kletetschka, B.J. Anderson and C.T. Russell, The Magnetization of 433 Eros as Measured from its Surface, EOS, transactions, American Geophysical Union,(supplement (abstract)), 2001-.
J. Connerney, M.H. Acuna, P.J. Wasilewski, G. Kletetschka, N. Ness, H. Reme, B. Lin and D. Mitchell, The Global Magnetic Field of Mars and Implications for Crustal Evolution, EOS, transactions,American Geophysical Union, (supplement (abstract)), 2001-.
J.E.P. Connerney, M.H. Acuna, P.J. Wasilewski, G. Kletetschka, N.F. Ness and H. Reme, Mars crustal magnetism: models, minerals, mysteries, XXV EGS, 2000-.
G. Kletetschka, Intense remanence of hematite-ilmenite solid solution, Geologica Carpathica 51(3), 187-187, 2000-.
G. Kletetschka and P.J. Wasilewski, Remanent magnetism of rocks containing hematite - ilmenite solid solution, EOS, transactions, American Geophysical Union, (supplement (abstract)), 2000-.

G. Kletetschka, Grain size limit for SD hematite, EOS Transactions, American Geophysical Union, (Supplement (abstract)), 2000-.
G. Kletetschka and P.J. Wasilewski, Remanent Magnetism Record in a Recent Basaltic Tree Mold, EOS Transactions, American Geophysical Union, (Fall Supplement (abstract)), 2000-.
P.J. Wasilewski, G. Kletetschka and M. Acuna, Magnetic Properties of Large Meteorites: Analogy to Asteroid Signatures, EOS Transactions, American Geophysical Union, (Fall Supplement(abstract)), 2000-.
S. Ibsen, G. Kletetschka and P. Wasilewski, New method for presentation of the vector magnetic data from layered sequences, EOS Transactions, American Geophysical Union, (Fall Supplement(abstract)), 2000-.
G. Kletetschka and P.J. Wasilewski, Evidence for electric discharge in carbonaceous meteorites, Chemical Evolution - abstract, 2000-.
J.A. NuthIII, H.G.M. Hill and G. Kletetschka, The Formation Age of Comets: Predicted Physical and Chemical trends, Chemical Evolution - abstract, 2000-.
P. Pruner, G. Kletetschka and P. Wasilewski, Magnetic record associated with tree ring density: possible climate proxies, EOS Transactions, American Geophysical Union, (Fall Supplement(abstract)), 2000-.
V. Zila, G. Kletetschka and P. Wasilewski, Magnetic Contamination of Soil and Flora Proximate to a Busy Highway, EOS Transactions, American Geophysical Union, (Fall Supplement (abstract)),2000-.
P.J. Wasilewski and G. Kletetschka, Nanoscale Exchange Anisotropy in Basaltic Rocks, XXV EGS abstract, 2000-.

Summary of Research
1 September 2000 to 1 May 2001

Robert N. Nelson, Ph.D.

During the past year, our research has focussed on two projects.
1. Completion of the measurements of the vapor pressure of ethane (C_2H_6) below its triple point (90 K).

2. The design and construction of a 2-channel sunphotometer to replace our older 1-channel unit.

Vapor Pressure Project:
The latest gas for which I have been studying is ethane. I completed detailed measurements in the temperature range from the triple point (90.3 K, 8.5×10^{-3} torr) down to 72 K where the vapor pressure is about 6×10^{-6} torr. Previous measurements extended only to about 80 K and 3×10^{-4} torr and Ire only available at two temperatures below the triple point. Thus I have extended the measured range by nearly three orders of magnitude in pressure and nearly 20 K in temperature. Previous extrapolations from data taken above the triple point turned out to be as much as 2 orders of magnitude too high. I presented these results at the meeting of the Division for Planetary Sciences of the

American Astronomical Society in Pasadena, California in November 2000. (Nelson, R. N. and Allen, J. E., Jr., *Low-Temperature Vapor-Pressure measurements of Ethane).*

Sunphotometer Project:
I have been working on the design and construction of a two-channel sunphotometer. This instrument will be used to make measurements of the trace gases in the atmosphere by determining the absorption of solar radiation in the wavelength range from roughly 390 nm to 4.5 μm. A previous single channel instrument covering the wavelength range 1.2 - 4.5 μm was the basis for our new design but I decided to carry out a complete redesign rather than try and adapt the older instrument. This design process involved extensive discussions with Mr. Cheyenne Harris, an instrument maker at GSFC and resulted in the design of a compact and versatile instrument. I did extensive computer aided drafting (CAD) work to produce the drawings and refine the design. More recently I have been involved in calibrating the circular variable filters which are the wavelength selection devices. This involved making measurements of the bandpass frequency vs. angle and measurements of sensitivity using a precision blackbody light source. This work in continuing. The mechanical design is nearly complete and it is hoped that we can field-test the instrument in early Fall.

Summary of Research

16 Dec 2000 to 1 May 2001

Benjamin P. Michael

Vibrational-to-translation (V-T) transfer rates for light hydrocarbons at low temperatures are important parameters in thermal-structure models of the upper atmospheres of the outer planets and their satellites. However, the required data are either simply not available or do not extend to the low temperatures found in those systems. Because methane is such an important constituent in outer planet atmospheres, we have initiated a program to measure the temperature dependence of (V-T) rates for its relaxation by appropriate collision partners. These rates are in turn used for the engineering development of, planning of, and the interpretation of data from a variety of planetary missions: Cassini/Huygens, Galileo Orbiter/Probe and Pluto-Kuiper Express.

To properly treat relaxation data it is necessary to first know the self-relaxation rate for methane over the temperature range of interest. Therefore, we have first determined the self-relaxation of methane from 90 to 300 K in approximately 10 K increments using a photoacoustic technique. This data represents the first ever-direct experimental results over this temperature range and extends the lowest temperature data point by over 60 K. The results from this data reveals that theoretical methods such as Landau-Teller and Schwartz, Slawsky and Herzfeld (SSH) can have significant deviations, especially at lower temperatures, where their results can deviate by over an order of magnitude at room temperature and even larger at lower temperatures. These results were recently presented at the 32nd Annual Meeting of the American Astronomical Society (AAS) Division for Planetary Sciences in Pasadena, CA. A manuscript describing the experimental setup, operation and results is currently being completed and will be submitted to *Review of Scientific Instruments*.

Relaxation data for methane with helium and hydrogen is currently underway using the same technique and over the same temperature range. In addition, for hydrogen the effects of both ortho and para are being examined. This analysis will allow the determination of any changes in rate due to deviation from the normal 3:1 otho/para ratio.