COO-3498-33

Progress Report

Contract No. EY-76-S-02-3498

Fundamental Studies in Isotope Chemistry

between

Division of Research

U.S. Energy Research and Development Administration

and

University of Rochester

Jacob Bigeleisen
Tracy H. Harris Professor

Principal Investigator

1 July 1976 - 30 June 1977

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Publications

Closed System Gas Circulating Pump, F. J. Torre, D. M. Eshelman, M. W. Lee, P. Neufeld, and W. Watson. Rev. Sci. Inst. 47, 1142-1143, (1976).

Vapor Pressures of the Isotopic Ethylenes. V. Solid and Liquid Ethylene-d_1, Ethylene-d_2, (cis, trans, and gem), Ethylene-d_3, and Ethylene-d_4, J. Bigeleisen, S. Fuks, S. V. Ribnikar and Y. Yato. J. Chem. Phys. 66, 1689 (1977).

Chemistry in a Jiffy. Chem. & Eng. News 55, No. 17, 26 (1977).

Reports Issued

COO-3498-30	Introduction to the Symposium "New Advances in Isotope Separation", Div of Nuclear Chemistry, American Chemical Society, San Francisco, California, 30-31 August 1976.
COO-3498-31	Liquid-Vapor Isotope Fractionation Factors in Argon-Krypton Binary Mixtures, M. W. Lee, P. Neufeld and J. Bigeleisen. Submitted for publication to the J. Chem. Phys.
COO-3498-32	Calculation of the Mean Force Constants of the Rare Gases and the Rectilinear Law of Mean Force. M. W. Lee and J. Bigeleisen. Submitted for publication to the J. Chem. Phys.

Lectures and Talks

1. "Isotope Chemistry and Molecular Structure" and "Vapor Pressure Isotope Effect - Past, Present and Future", Gordon Research Conference, 5 July 1976.
2. "What is NRCC?", National Resource for Computation in Chemistry Workshop, NAS-NRC, 13 July 1976.
3. "Vapor Pressures of the Isotopic Liquid Hydrogens - Effects of Symmetry", Lawrence Livermore Laboratory, 23 August 1976.
4. "New Advances in Isotope Separation", Div of Nuclear Chemistry, American Chemical Society, San Francisco, 30 August 1976.
5. "What Can Be Learned About Liquids and Solids from Isotope Effects", Physics Department, University of Rochester, 14 October 1976.
6. "What Can Be Learned About Liquids and Solids from Isotope Effects", University of North Carolina, Chapel Hill, 23 November 1976.
7. "Molecular Motion in Liquids", Session Chairman, CIC/ACS Symposium, Montreal, Canada, 29 May 1977.
8. "Liquid-Vapor Isotope Fractionation Factors in Argon-Krypton Binary Mixtures", CIC/ACS Symposium, Montreal, Canada. 29 May 1977.

Professional Activities

Visiting Committee, Carnegie-Mellon University.

Visiting Committee, AUA, Argonne National Laboratory.

Consultant, Oak Ridge Gaseous Diffusion Plant.

Consultant, Los Alamos Scientific Laboratory.

Consultant, Lawrence Livermore Laboratory.

National Research Council - National Academy of Sciences,
Chairman, Assembly of Mathematical and Physical Sciences.

Scope of Activities

The principal investigator is Professor of Chemistry and Tracy H. Harris Professor of Mathematics and Natural Philosophy in the College of Arts and Science at the University of Rochester, where he is active in undergraduate teaching, graduate instruction, research, and university affairs. During the past year he has continued as a consultant to the isotope separation programs at Oak Ridge and Los Alamos. He has extended his consulting activities to include Lawrence Livermore Laboratory.

The principal investigator is, by arrangement with the University of Rochester, a part time officer of the National Academy of Sciences - National Research Council. He is Chairman of the Assembly of Mathematical and Physical Sciences with policy and operating responsibilities in all areas of the mathematical and physical sciences, including chemistry, physics, mathematics, earth sciences, geophysics, space science, statistics, and international programs in these areas.

Abstract

Starting in 1971 USAEC and now ERDA undertook planning studies of isotope separation processes and plant capacity to meet nuclear power requirements during the period 1980-2000. The important separation processes are ^{235}U-^{238}U enrichment for light water reactors, D_2O production for heavy water moderated reactors and possibly ^{15}N-^{14}N separation for the high temperature breeder reactor. The principal investigator participated actively in the ^{235}U-^{238}U enrichment studies during 1971-'3 and organized a symposium "New Advances in Isotope Separation" for the Division of Nuclear Chemistry and Technology of the American Chemical Society in San Francisco, 30-31 August 1976. The program included laser, aerodynamic, chemical exchange and distillation processes. This investigator presented an overview summary, COO 3498-30, which is included in this report.

We have continued our basic research program in isotope chemistry. The current thrust of the program is the use of isotope effects to study the fundamental properties of matter, measurement and calculation of isotope fractionation factors of systems of potential technological importance and the correlation of isotope effects with molecular structure. The past year has seen practical realization of two isotope separation processes based on basic research carried out by this investigator. Sulzer in collaboration with the Laue-Langevin Institute (Grenoble, France) have successfully designed, constructed and

placed into operation a plant for stripping both protium and tritium from the heavy water moderator of the high flux Grenoble reactor. The process involves low temperature distillation of liquid deuterium. Separation depends on the vapor pressure differences of HD, D_2 and DT. The latter were measured by this investigator in 1956 and form the basis of the process design. As early as 1950 this investigator proposed homogeneous catalytic exchange of ammonia and/or amines with hydrogen gas for large scale heavy water production and carried out the basic experimental work necessary for process development. The first successful plant utilizing the ammonia-hydrogen process was constructed in 1967 at Mazingarbe, France. Three ammonia-hydrogen exchange plants are under construction in India. Commencing in 1973 the Canadians, AECL, and Sulzer have undertaken process design using homogeneous catalysis of methylamine and hydrogen. Prospects are good that the amine-hydrogen exchange process may be the heavy water production process of the future.

During the past year we have completed the first measurements of the isotopic fractionation factors for two components in a solution by the study of argon-krypton mixtures. The measurements cover the range from pure argon to pure krypton and extrapolate very well to our previous measurements on the pure components. The mean square force on Kr in an infinitely dilute solution of Ar has been found equal to the mean square force on Ar in an infinitely dilute solution in krypton. The latter result suggests that three body forces make a small contribution to $<\nabla^2 U>$. An equilibrium isotope effect has been studied as a continuous function of the potential field acting on the atom undergoing isotopic exchange. This has been accomplished through a study of the liquid vapor isotope fractionation factors for both $^{36}Ar/^{40}Ar$ and $^{80}Kr/^{84}Kr$ in a series of binary mixtures which span the range between the pure components at 117.5°K. The $^{36}Ar/^{40}Ar$ fractionation factor increases (linearly) from ($\ln\alpha$) 2.49×10^{-3} in pure liquid argon to 2.91×10^{-3} in an infinitely dilute solution in liquid krypton. Conversely, the $^{80}Kr/^{84}Kr$ fractionation factor decreases (linearly) from ($\ln\alpha$) 0.98×10^{-3} in pure liquid krypton to 0.64×10^{-3} in an infinitely dilute solution in pure liquid argon. The mean force constants, $<\nabla^2 U>_c$, on both argon and krypton atoms in the mixtures are derived from the respective isotope fractionation factors. It is shown that the mean force constant on argon atoms in infinitely dilute solution in krypton is equal, within experimental error, to the mean force constant on krypton atoms in infinitely dilute solution in argon. The symmetry of the mixed force constants, $<\nabla^2 U_i>_j = <\nabla^2 U_j>i$ indicates that the assumption of additive pair interactions is sufficient to treat $<\nabla^2 U>$. The latter is mainly a function of $U(r)$ in the range $0.90 r_{min} < r < 1.10\ r_{min}$.

The mean force constants for argon and krypton as a function of composition have been calculated by a modified corresponding states theory which uses the pure liquids as input parameters. The modified corresponding states theory reproduces $<\nabla^2 U>$ for Kr over the entire concentration range, but leads to values of

$<\nabla^2 U>$(Ar) which are systematically higher than experiment. The discrepancy is 8% at $X_{Ar}=0$. A systematic set of calculations has been made of $<\nabla^2 U>$(Ar) and $<\nabla^2 U>$(Kr) as a function of composition using radial distribution functions generated by the Weeks-Chandler-Anderson perturbation theory. The calculated results for $<\nabla^2 U>$(Kr) using the Lee-Henderson-Barker, Maitland-Smith, and Lennard-Jones potentials are in good agreement with experiment. None of these potentials give satisfactory agreement with the experimental values of $<\nabla^2 U>$(Ar) in dilute solution in krypton. The discrepancy is ascribed to failure of the WCA method to predict g_{Ar-Kr}, the mixed radial distribution function, with sufficient accuracy close to the triple point of a fluid.

We have now measured the vapor pressure isotope effects between solid-vapor and liquid-vapor for the rare gases neon, argon and krypton. These fractionation factor give directly the mean square force constants, $<\nabla^2 U>$, in the solid and liquid as a function of temperature. For the gas, $<\nabla^2 U>$ can be calculated by the Percus-Yevick equation from the intermolecular potential. Previous work by Klein has led to successful calculation of $<\nabla^2 U>$ for the rare gas solids based on an anharmonic lattice and reasonable intermolecular potentials. In a pioneer investigation we calculated $<\nabla^2 U>$ for liquid argon from the triple point to 0.9 TIT_c in excellent agreement with experiment using the Weeks-Chandler-Anderson perturbation theory for the liquid structure. We have now extended this method to liquid krypton using the recent potential parameters of Barker-Henderson and Maitland-Smith.

We have now found a universal relationship for $<\nabla^2U>$ and the density of a fluid of spherical particles which leads to the rectilinear law of mean force. The rational for this law, which spans the range from the triple point of the liquid to the infinitely dilute gas, has been established by a power series expansion of the radial distribution function as a function of the fluid density and the use of the WCA and PY approximations to the radial distribution functions of the liquid and gas respectively.

The method of moments has proven to be a powerful tool in equilibrium statistical mechanics. As early as 1943 Bigeleisen and Mayer introduced this method into isotope chemistry. Successive development of the method culminated in a series of papers by Bigeleisen, Ishida and Spindel who combined the method of moments with a rapidly converging finite orthogonal polynomial expansion of the isotopic reduced partition function ratio. Their development extended the first order rules of isotope chemistry established by Bigeleisen to the isotope chemistry of all compounds of all the elements at any temperature. The finite orthogonal polynomial method also provides a framework for the correlation of isotope chemistry with molecular structure. As part of that program we have undertaken a systematic study of the relationship between isotope chemistry and basis coordinates involving bending and stretching coordinates and interactions between coordinates. The work of Bigeleisen, Ishida, Lee and Bigeleisen on this problem is almost complete and is outlined in this progress report. The WIMPER method (WINIMAX coefficients for a polynomial expansion of the reduced partition function ratio) is an alternate to the perturbation method for this problem developed by Singh and Wolfsberg.