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Curriculum Vitae:

James L. Dye

University Distinguished Professor of Chemistry Emeritus

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Biography and

Education:

Born in Soudan, Minn., July 18, 1927; **A.B.**, 1949, Gustavus Adolphus St. Peter, Minn. (Chem. & Math.); **Ph.D.**, 1953, Iowa State U., Ames, Iowa, Physical Chemistry with F. H. Spedding (Lanthanide Electrochem.).

Employment:

Michigan State University, 1953 to 1994: Physical and Inorganic Chemistry and Solid-State Chemistry; Chairperson, Department of Chemistry, 1986-1990; Emeritus, 1994- present.

Sabbatical Leaves:

NSF Science Faculty Fellow, 1961-62, with Manfred Eigen, Max Planck Institute for Phys. Chem., Göttingen, Germany (Rate of reaction of solvated electrons with water).

Visiting Scientist, 1968-69, with Leon Dorfman, Ohio State University, Columbus, Ohio (Pulse-radiolysis studies of the solvated electron in mixed solvents).

Guggenheim Fellow and Fulbright Research Scientist, 1975-76, with Jean-Marie Lehn, University of Strasbourg, France (Use of cryptands to prepare alkalide salts).

Visiting Scientist, 1982-83, with D. W. Murphy and A. Wayda, ATT Bell Labs, Murray Hill, NJ (alkali metals in inorganic oxides and the synthesis of organo-lanthanoids).

Guggenheim Fellow and Visiting Scientist, 1990-91, with F. J. DiSalvo, Cornell University (Preparation of finely-divided metals as precursors for inorganic synthesis).

Professional Organizations:

U. S. National Academy of Sciences; American Academy of Arts and Sciences; American Chemical Society; American Physical Society; Materials Research Society; American Association for the Advancement of Science; Fulbright Alumni Association; Sigma Xi; Phi Kappa Phi; Golden Key National Honor Society; Michigan College Chemistry Teachers Association.

Awards:

Junior Sigma Xi Award, 1968; Distinguished Alumnus Award, Gustavus Adolphus College, 1969; MSU Distinguished Faculty Award, 1974; Senior Sigma Xi Award, 1987; Michigan Association of Governing Boards Award, 1990; Chemical Pioneer Award, American Institute of Chemists, 1990; Honorary Doctor of Science Degree, Northern Michigan University, 1992; American Chemical Society Award in

Inorganic Chemistry, 1997; John C. Bailar, Jr Medal (U. of Illinois) 1997; Stauffer Lecturer (USC) 1998. Spedding Lecturer, Iowa State University, 2004. Four Camille and Henry Dreyfus Senior Scientist Mentor Awards, 2000-2008.

Publications: More than 230 refereed publications have appeared in print in addition to numerous Meeting Abstracts. Invited talks have been given at many national and international meetings and at numerous universities and colleges (at a rate of about four per year).

Other: Prof. Dye has served on a number of professional committees, including service as Interim Secretary of the Physical Chemistry Division of the ACS, member, Chairperson of the Fellowship Committee of the National Research Council, member of the Editorial Board of Inorganic Chemistry, member of the Advisory Committee of the Division of Material Sciences of the NSF, member and Chairperson of the Canvassing Committee for the ACS Award in Pure Chemistry.

Commercial: Prof. Dye is a Co-Founder of SiGNa Chemistry, Inc., www.signachem.com a company developed to utilize alkali metal – porous metal oxide materials for organic reductions, hydrogen production, etc. The company received the 2008 Presidential Green Chemistry Challenge Award.

Major Research Accomplishments of James L. Dye:

For 50 years, Dye's research has focused on the species formed when alkali metals interact with solvents or complexants. It became clear in 1969 (from his work and that of others) that *alkali metal anions* are present in metal-amine solutions along with the well-known *solvated electrons*. A milestone in this research was his discovery in 1970 that crown ether and cryptand complexants for alkali metal cations *greatly* enhanced the solubility of alkali metals in amine and ether solvents. This initiated a search for solvent-free salts in which the complexed alkali metal cation has as its counter-ion either an alkali metal *anion* or a *trapped electron*. In 1974, the Dye group isolated the first crystalline salt of an alkali metal anion, $\text{Na}^+(\text{cryptand}[2.2.2])\text{Na}^-$. Thus the 100-year old dogma that the alkali metals form only cations was shattered! In the years since that discovery, the Dye group has synthesized and characterized more than 40 *alkalides*, salts that contain the complexed alkali metal cation and one of the anions, Na^- , K^- , Rb^- , or Cs^- .

From this point on, a major dream of the group was to synthesize crystalline *electrides*, salts in which the anion is a trapped electron. For twelve years, only deep blue-black powders could be made. They were clearly electrides according to their optical, magnetic and EPR properties, but the extreme difficulty in handling these reactive and thermally unstable materials frustrated efforts to crystallize them. Finally in 1986 the crystalline electride $\text{Cs}^+(\text{18-crown-6})_2\text{e}^-$ was synthesized and structurally characterized, followed over the years by seven additional crystalline electrides. The structures and properties of electrides show that the electrons are trapped in cavities and interact with one another through connecting channels. Thus, electrides

are early examples of quantum confinement, a subject of intense current interest. To first order, electrides can be viewed as *stoichiometric* F-centers in which the electrons form a complex lattice gas. Recent research by others, stimulated by the discovery of electrides by the Dye group, has resulted in at least 50 research publications about electrides from other laboratories since 2003.

Studies of these reactive species are difficult because of their thermal instability. In spite of this, the Dye group has used NMR, EPR, ENDOR, magnetic susceptibility, time-resolved fluorescence, photoelectron emission, single crystal reflectance, thin film optical spectra, conductivity, impedance spectroscopy, EXAFS, pulsed radiolysis and neutron scattering to characterize alkalides and electrides.

Although alkalides have become useful two-electron reductants for organic synthesis, the reactivity and especially the thermal instability of alkalides and electrides has, until recently, prevented the exploitation of their unique electronic, magnetic and optical properties. A major focus of Dye's research until 2004 was the synthesis of thermally stable alkalides and electrides that utilize aza- rather than oxa- crown ethers and cryptands. Thermally stable crystalline alkalides were prepared and, in 2004, a room temperature-stable crystalline electride was synthesized and structurally characterized.

A recent initiative has great potential for the development of a new class of electrides. Instead of using organic complexants to sequester the cation from reduction by trapped electrons, thermally stable 'inorganic electrides' utilize all-silica zeolites as hosts for the alkali metal. Cesium vapor can be incorporated into ITQ-4 as well as into a 3D all-silica zeolite (ITQ-7) and all-silica zeolite beta at both room temperature and 100 °C. Sodium, potassium and rubidium can also be incorporated from the vapor phase. Both experimental and theoretical studies have shown that cesium ionizes in the channels to produce Cs^+ and trapped electrons. The synthesis by others of completely new classes of "inorganic electrides" has become a topic of great interest recently.

We have recently found that liquid alkali metals and alloys can be readily incorporated into the nanoscale pores (~15 nm nominal diameter) of silica gel at loadings up to 40 wt% alkali metal. When formed at room temperature, the metal is present as small particles. Various heating protocols form other stages of included metal cations and electrons. The big advantage for chemistry is that these materials are nearly as powerful reducing agents as the parent metals and can produce clean hydrogen by reaction with water, but they are stable in dry air and easily handled. A company, SiGNa Chemistry Inc., has been formed to commercialize this material. The environmentally benign products of such reactions and the potential savings in solvents, multiple reaction steps, and hazardous wastes, resulted in the receipt by SiGNa of the 2008 Presidential Green Chemistry Challenge Award.

All of the work described here has been published.

Publications Since 2000

208. " $\text{Cs}^+(18\text{-crown-6})_2\text{e}^-$: A 1D Heisenberg Antiferromagnet with Unusual Phase Transitions"

M. J. Wagner, A. S. Ichimura, R. H. Huang, R. C. Phillips and J. L. Dye
J. Phys. Chem.B, **104**, 1078-1087 (2000).

209. "Molecular and Electronic Structure of a Reduced Schiff Base Cryptand: Characterization by X-ray Crystallography and Optical and EPR/ENDOR Spectroscopy"

- A. S. Ichimura, Q. Xie, L. P. Szajek, J. Lema, A. Burns, R. H. Huang, J. E. Jackson, J. L. Dye, F. Demol, F. X. Sauvage and M. G. DeBacker.
J. Phys. Chem.A, **104**, 3038-3047 (2000).
210. "Structure and Properties of a New Electride, $\text{Rb}^+(\text{cryptand}[2.2.2])\text{e}^-$."
Q. Xie, R. H. Huang, A. S. Ichimura, R. C. Phillips, W. P. Pratt, Jr. and J. L. Dye
J. Am. Chem. Soc., **122**, 6971-6978 (2000).
211. "Thermionic Emission from Cold Electride Films"
R. C. Phillips, W. P. Pratt, Jr. and J. L. Dye
Chem. Mater., **12**, 3642-3647 (2000).
212. "Toward Inorganic Electrdes"
A. S. Ichimura, J. L. Dye, M. A. Cambor and L. A. Villaescusa
J. Am. Chem. Soc., **124**, 1170-1171 (2002).
213. "Inverse Sodium Hydride': A Crystalline Salt that Contains H^+ and Na^- "
M. Y. Redko, M. Vlassa, J. E. Jackson, A. W. Misiolek, R. H. Huang and J. L. Dye
J. Am. Chem. Soc., **124**, 5928-5929 (2002).
214. "Structure of Intercalated Cs in Zeolite ITQ-4: An Array of Metal Ions and Correlated Electrons Confined in a Pseudo-1D Nanoporous Host"
V. Petkov, S. I. Billinge, T. Vogt, A. S. Ichimura and J. L. Dye
Phys. Rev. Lett., **89**, 075502 (2002).
215. "Synthesis and Characterization of 4,7-dimethyl-1,4,7,10,15,18-hexaazabicyclo[8.5.5]octane. Crystal Structures of the Cryptate and of the First Small Azacage Complexes with Six-Coordinate Lithium Geometry"
M. Vlassa, R. H. Huang, J. E. Jackson and J. L. Dye
Tetrahedron, **58**, 5849-5854 (2002).
216. "Anisotropic Charge Transport and Spin-Spin Interactions in $\text{K}^+(\text{cryptand}[2.2.2])$ Electride"
A. S. Ichimura, M. J. Wagner and J. L. Dye
J. Phys. Chem. B, **106**, 11196-11202 (2002).
217. "Barium Azacryptand Sodide, the First Alkalide with an Alkaline Earth Cation, Also Contains a Novel Dimer, $(\text{Na}_2)^{2-}$ "
M. Y. Redko, R. H. Huang, J. L. Jackson, J. F. Harrison and J. L. Dye
J. Am. Chem. Soc. **125**, 2259-2263 (2003).
218. "Inorganic Electrdes Formed by Alkali Metal Addition to Pure Silica Zeolites"
D. P. Wernette, A. S. Ichimura, S. A. Urbin and J. L. Dye
Chem. Mater. **15**, 1441-1448 (2003).
219. "Electrons as Anions"
J. L. Dye

Science **301**, 607-608 (2003).

220. "Alkalides and Electrides"
J. L. Dye
In *Encyclopedia of Supramolecular Chemistry*
J. L. Atwood and J. W. Steed, Editors
Marcel Dekker, Inc., New York, 2004
221. "Alkali Metals Plus Silica Gel: Powerful Reducing Agents and Convenient Hydrogen Sources"
J. L. Dye, K. D. Cram, S. A. Urbin, M. Y. Redko, J. E. Jackson and M. Lefenfeld
J. Am. Chem. Soc. **127**, 9338-9339 (2005).
222. "Design and Synthesis of a Thermally Stable Organic Electride"
M. Y. Redko, J. E. Jackson, R. H. Huang and J. L. Dye
J. Am. Chem. Soc. **127**, 12416-12422 (2005).
223. "One-Pot Synthesis of 1,4,7,10,13,16,21,24-Octaazabicyclo[8.8.8]hexacosane – The Peraza Analogue of [2.2.2]Cryptand"
M. Y. Redko, R. Huang, J. L. Dye and J. E. Jackson
Synthesis 759-761 (2006).
224. "One-Dimensional Zigzag Chains of Cs⁻: The Structures and Properties of Li⁺(Cryptand[2.1.1])Cs⁻ and Cs⁺(Cryptand[2.2.2])Cs⁻"
A. S. Ichimura, R. H. Huang, Q. Xie, P. Morganelli, A. Burns and J. L. Dye
J. Phys. Chem B **110**, 12293-12301 (2006).
225. "Role of Cation Complexants in the Synthesis of Alkalides and Electrides"
J. L. Dye, M. Y. Redko, R. H. Huang and J. E. Jackson
In *Advances in Inorganic Chemistry, Vol. 59*, R. Van Eldik and K. Bowman-James, Eds.,
Elsevier, Amsterdam, 2007.
226. "Structures of Alkali Metals in Silica Gel Nanopores: New Materials for Chemical Reduction and Hydrogen Production"
M. Shatnawi, G. Paglia, J. L. Dye, K. D. Cram, M. Lefenfeld and S. J. L. Billinge
J. Am. Chem. Soc. **129**, 1386-1392 (2007).
227. "Alkali Metals in Silica Gel (M-SG): A New Reagent for Desulfonation of Amines".
P. Nandi, M. Y. Redko, K. Petersen, J. L. Dye, M. Lefenfeld, P. F. Vogt and J. E. Jackson
Org. Lett. **10**, 5141-5144 (2008).
228. "Preparation of Diphenyl Phosphide and Substituted Phosphines using Alkali Metal in Silica Gel (M-SG)".
P. Nandi, J. L. Dye, P. Bentley and J. E. Jackson
Org. Lett. **11**, 1689-1692 (2009).
229. "Reductive Amine Deallyl- and Debenzylation with Alkali Metal in Silica Gel (M-SG)".
P. Nandi, J. L. Dye and J. E. Jackson

Tetrahedron Lett. **50**, 1364-1366 (2009).

230. "Birch Reductions at Room Temperature with Alkali Metals in Silica Gel (Na₂K-SG(I))".

P. Nandi, J. L. Dye and J. E. Jackson

J. Org. Chem. **74**, 5790-5792 (2009).

231. "Electrides: Early Examples of Quantum Confinement"

J. L. Dye

Accounts of Chemical Research. **42**, 1564-1572 (2009).