thiourea. Inhibition is prevented when zinc is added simultaneously with one of these agents.

The present data constitute a further test of the hypothesis that pyridine nucleotide linked dehydrogenases may prove to be metalloenzymes.[1] The results here presented give impetus to continued exploration in this direction.

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[9] Fellow of the National Foundation for Infantile Paralysis.

EXISTENCE OF RING PHOSPHATES HIGHER THAN THE TETRAMETAPHOSPHATE

Sir:

We have shown recently that spots attributable to pentametaphosphate and perhaps higher ring phosphate anions are obtained in the two-dimensional paper chromatography introduced by Ebel.[1] These results are part of a study of the hydrolysis of Graham's salt which has been under way in our laboratories for about three and one-half years.

A number of chromatograms have been made on a partially hydrolyzed sample of Graham's salt having a number average chain length of 117 phosphorus atoms per molecule ion, as determined by end-group titration corrected for the presence of rings. Schleicher and Schuell paper No. 589, Orange Ribbon, was employed, with over-loading by the use of 45 μg. of total P in the drop placed at the origin instead of the optimum amount of 15 μg. which we have recommended elsewhere.[2] In the series of ring phosphates on the chromatogram, there are separate and distinct spots for trimetaphosphate, tetrametaphosphate, pentametaphosphate, and perhaps hexametaphosphate.[3] The spot attributed to hexametaphosphate partially overlaps a continuous band which we attribute to unresolved higher ring phosphates. In this sample, there is also a continuous, but less intense, band which curves upward so as to form a continuum at the high-molecular-weight end of the series of chain phosphates. Since the continuum attributed to higher chains and the continuum attributed to higher rings branch apart so as to form a Y, we feel that there is relatively good evidence for ring phosphates containing as many as eight phosphorus atoms. Indeed, the appearance of the chromatogram would lead one to suspect that there are ring phosphates even larger than the octametaphosphate.

The total ring content in this partly hydrolyzed sample of Graham's salt is not large, being about 10% of the total P. Most of the phosphate applied to the chromatogram has not moved from the origin (this allows overloading of the paper).

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RECEIVED FEBRUARY 20, 1956

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[1] J. P. Ebel, *Bull. Soc. Chim. France*, **20**, 991 (1953).

[2] E. Karl-Kroupa, *Anal. Chem.*, submitted for publication.

[3] The hexametaphosphate described here bears no relation to the term "hexametaphosphate" which has been so often misused in both the technological and scientific literature as the name for vitreous sodium phosphates having Na_2O/P_2O_5 mole ratios lying between 1.0 and 1.2. The hexametaphosphate described herein is a single molecular species consisting of a 12-membered ring of alternating phosphorus and oxygen atoms; whereas the "hexametaphosphate" of commerce is a mixture consisting predominantly of long-chain phosphates.

SELF-DIFFUSION IN MOLTEN SODIUM NITRATE[1]

Sir:

We have measured the self-diffusion coefficients of both sodium ion and nitrate ion as a function of temperature in fused sodium nitrate. The method employed involved a determination of the rate at which tracer sodium or nitrate ion diffused from a *ca.* 0.65 mm. i.d. quartz capillary tube into a stirred bath of pure sodium nitrate. The method was originally used by Anderson and Saddington[2] in aqueous solution and has since been employed by others, particularly Wang.[3] Fairly detailed investigations have proved that the method is susceptible of good accuracy.[3,4] Self-diffusion coefficients of liquid sodium[5] and mercury[6] have been measured by the capillary method. The only previous published work on self-diffusion in molten salts appears to be that of Berne and Klemm,[7] who obtained the self-diffusion coefficient of thallous ion in molten thallous chloride; we know of no prior work in which diffusion has been determined for both cation and anion.

In our experiments radioactive Na^{22} was the sodium tracer which was followed by standard counting techniques. The nitrate tracer was labelled with stable O^{18} which was determined mass spectrographically on the oxygen liberated when the nitrate was decomposed quantitatively to nitrite and oxygen. Some rather severe difficulties had to be overcome in filling and calibrating the capillaries because of the elevated temperatures. The temperatures were controlled during diffusion to ±0.1 to 0.2°.

The self-diffusion coefficients, $\mathfrak{D}$, may be expressed by rate equations of the form $\mathfrak{D} = A \exp(-\Delta H^{\ddagger}/RT)$ where A is a constant, $\Delta H^{\ddagger}$ is the energy of activation for the diffusion, R is the molar gas constant and T is absolute temperature. The self-diffusion coefficient of the sodium ion in fused sodium nitrate between 315 and 375° is given by

$$\mathfrak{D}_{Na} = 12.88 \times 10^{-4} \exp(-4970/RT) \text{ cm.}^2/\text{sec.}$$

while that for the nitrate ion similarly is

$$\mathfrak{D}_{NO_3} = 8.97 \times 10^{-4} \exp(-5083/RT) \text{ cm.}^2/\text{sec.}$$

In each case the probable error in $\Delta H^{\ddagger}$ is 80 cal.

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[1] This work was performed for the Atomic Energy Commission.

[2] J. S. Anderson and K. Saddington, *J. Chem. Soc.*, S381 (1949).

[3] J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950); J. H. Wang, *ibid.*, **74**, 1182 (1952), and others.

[4] R. Mills, *ibid.*, **77**, 6116 (1955), and previous papers.

[5] R. E. Meyer and N. H. Nachtrieb, *J. Chem. Phys.*, **23**, 1851 (1955).

[6] R. E. Hoffman, *ibid.*, **20**, 1567 (1952).

[7] E. Berne and A. Klemm, *Z. Naturforsch.*, **8a**, 400 (1953).

while in the temperature range 315 to 365° the least squares probable error in $\mathfrak{D}_{Na}$ varies between 1.2 and 1.8% (40 experimental points) and that in $\mathfrak{D}_{NO_3}$ lies between 0.7 and 1.1% (18 experimental points).

The following facts appear significant. The heat of activation for self-diffusion is independent of temperature in the range studied and is the same for both anion and cation within experimental error. The ratio of the absolute rates of self-diffusion of the two ions is approximately, but not exactly, proportional to the inverse square roots of their masses, reminiscent of Graham's law of effusion. We have found that the Nernst-Einstein equation is not applicable to reliable computation of the electrical conductance of fused sodium nitrate from the self-diffusion coefficients.

Detailed information and theoretical considerations about self-diffusion in fused sodium nitrate and other molten salts will be published later.

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BOOK REVIEWS

An Introduction to Quantum Statistics. BY WILLIAM BAND, Professor of Physics, The State College of Washington, Pullman, Washington. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y. xiii + 342 pp. Price, $6.00

This book is written for physicists and specifically for post graduate students in physics and physical chemistry. In order to use it the reader should have the usual mathematical requirements for a physics degree and should be well acquainted with quantum mechanics. However most post graduate students in physical chemistry have also studied these disciplines and it is well worth their while to possess this volume. Especially is this true because many examples throughout this book are taken from the fields of physical chemistry, chemical thermodynamics and statistics. The arrangement of the material contained in this volume is carried out in a most satisfactory manner. The simpler cases precede the more complex topics and the latter are built closely on the earlier material presented.

Another and most valuable feature of the book is the set of problems outlined at the end of each chapter. The student who works these exercises will indeed gain most definite knowledge of the subject matter. Also located at the end of each chapter is a list of references for further study for the use of those students who wish to pursue this science in even greater detail than is portrayed in this book. The fifteen chapters carry the following titles: I, Review of Quantum Mechanics; II, The Formalism of Statistical Mechanics; III, Statistical Interpretation of Thermodynamics; IV, The Partition Function in Classical Statistics; V, Equilibrium between Phases; VI, Chemical and Dissociative Equilibrium; VII, Assemblies of Dependent Systems; VIII, Independent Systems with Quantum Degeneracy; IX, Phase Equilibria Among Quantum Degenerate Systems; X, Dissociative Equilibrium Among Quantum Degenerate Systems; XI, Quantum Degenerate Assemblies of Dependent Systems; XII, The Grand Partition Function and Its Applications; XIII, General Theory of the Liquid Phase; XIV, Some Solid State Problems; XV, Fluctuations and Nonequilibrium Phenomena.

Anyone interested in these highly theoretical and therefore most important aspects of physics and chemistry must know and possess this book. The individual who already has acquaintance with this field will be delighted by the very careful presentation of a complex subject.

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GEORGE GLOCKLER

Advances in Cancer Research. Volume III. Edited by JESSE P. GREENSTEIN, National Cancer Institute, National Institutes of Health, U. S. Public Health Service, Bethesda, Maryland, and ALEXANDER HADDOW, Chester Beatty Research Institute, Royal Cancer Hospital, London, England. Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1955. viii + 369 pp. 16 × 23.5 cm. Price, $8.50.

The third volume contains a particularly lucid review by Doll of the epidemiology of lung cancer. In it appears an excellent analysis of the etiological factors including tobacco, industrial hazards and atmospheric pollution. In his concluding remarks on the carefully presented arguments concerning the role of smoking he says:

> "In the author's opinion, taking into consideration the philosophical principle of Occam's razor which has already been referred to, the facts are such that the hypothesis that cigarette smoking is a cause of the main histological types of lung cancer should be accepted. They also, in his opinion, justify a strong presumption that the smoking of pipes and cigars is, in this respect, relatively innocuous. The discovery that a known and powerful carcinogen is present in tobacco smoke in significant quantity strengthens the credibility of the conclusion, but it has yet to be shown experimentally that the substance concerned has a direct action on the bronchial mucosa."
>
> "The great majority of the observed facts accord with the hypothesis, but the picture is not yet complete. We need to know, in particular, why the mortality from the disease in the United States is so low relative to the past consumption of cigarettes; and why the association which appears to exist between cancer of the larynx and cigarette smoking has not been reflected in an increase in the incidence of cancer of the larynx comparable to that believed to have occurred with cancer of the lung. The data on the significance of inhaling are also conflicting, and it is uncertain whether the difference between the effects of smoking tobacco in the form of cigarettes and in a pipe can be attributed to differences in the extent to which the smoke is usually inhaled or whether it is necessary to postulate some other mechanism. These fields of uncertainty are, however, small in relation to the extent of established knowledge and do not justify throwing doubt on the main conclusion."

In a very comprehensive review by Morris of the experimental development and metabolism of thyroid gland tumors,