

CHEMISTRY

Chairman: EARL T. MCBEE, Purdue University
FRANK WELCHER, Indiana University, was elected chairman for 1959

ABSTRACTS

Turbidimetric Titrations. ROBERT B. FISCHER, MARVIN L. YATES and MARION M. BATTS, Indiana University.—The usefulness of turbidimetric measurements in quantitative analysis is limited by the irreproducibility of the physical forms of chemical precipitates. The physical form is determined largely by the first batch of precipitated particles, so titration procedures are generally preferable to measurements based upon comparisons to standards. Titration curves of optical density vs. volume of titrant have been calculated for conditions existing after the first increment of titrant and prior to the equivalence point as follows: continual new nucleation with each additional increment of titrant; no new nucleation (i.e., crystal growth only) with each addition of titrant; both nucleation and crystal growth. It is predicted from the calculated curves that any factor which enhances nucleation at the expense of crystal growth should improve the analytical usefulness of turbidimetric titrations. One such factor is the presence of a surfactant which is adsorbed on crystal surfaces, thereby preventing further crystal growth. The prediction is verified with some precipitation reactions.

A Rapid Method of Multiplication and Division. THOMAS DE VRIES, Purdue University.—In the method of multiplication and division commonly used, more digits are often obtained than the number of significant figures given by the experimental data. It is possible to eliminate unnecessary multiplications and additions, and obtain the answer to any desired number of digits by a method where the multiplier is written backwards underneath the multiplicand. The new rules of multiplication will be explained. Similarly, in division the calculation can be considerably shortened and simplified by decreasing the number of digits in the divisor stepwise. Several examples will be given.

Specialized Graduate Courses for the High School Chemistry Teacher. W. G. KESSEL, Indiana State Teachers College.—A committee of the Division of Chemical Education of the American Chemical Society, on the Teaching of Chemistry, made a study last year of 323 colleges and universities that had a Dean of Graduate School or a special Graduate Division in order to see what kinds of programs are available for the high school chemistry teacher in his unique situation.

A listing of schools that are giving "special" courses for these teachers and some comments that they have made give indications that there is:

- (1) a definite need to develop a more satisfactory program
- (2) a definite trend toward such courses

- (3) a divergent opinion on how to solve this problem
- (4) still some conflict between "Education" and Chemistry

On the Reactivity of Perhalotoluenes. EARL T. MCBEE and LAWRENCE W. FROST, Purdue University and Westinghouse Research Laboratories.—Dichlorohexafluoro- and monochloroheptafluoro toluene were prepared by chlorination of benzotrifluoride in the presence of iron at 200°C., subsequent fluorination with bromine trifluoride in bromine solution at 0°C., and final dehalogenation with zinc dust in ethanol.

The tentative structure assignment of these compounds was based on their reactivity in several nucleophilic displacement reactions:

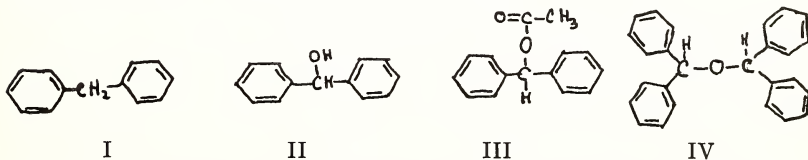
All three of the ring fluorine atoms in dichlorotrifluoro-(trifluoromethyl)-benzene reacted rapidly and exothermically with aqueous methanolic potassium hydroxide to give dichlorotrimethoxy-(trifluoromethyl) benzene. This suggests *m*-position in regard to the trifluoromethyl group for the two remaining chlorine atoms.

Reaction of chlorotetrafluoro-(trifluoromethyl)-benzene with methanolic base gave chlorotrifluoro-(trifluoromethyl)-anisole, again presenting preferential replacement of a ring fluorine atom, presumably in *p*-position.

The obtained chlorotrifluoro-(trifluoromethyl)-anisole, again present-remarkably stabilized by the trifluoromethyl group. Photochlorination and subsequent treatment with antimony (III) fluoride resulted in exclusive substitution at the methoxy group.

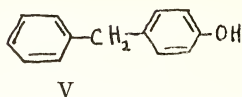
Reduction of Carbonyl Compounds with Alloys of Magnesium.¹ JOHN H. BILLMAN, LINNEAUS C. DORMAN and FOREST L. GAGER, Indiana University.—While methods, such as the Clemmensen, Wolff-Kishner, Wolfrom, or palladium-hydrogen, have proved to be very useful in the reduction of the carbonyl group to the methylene group, their individual usefulness has been limited by their reaction conditions and they, of necessity, supplement each other. Indeed, the reduction of aromatic ketones have presented some interesting problems and a study was undertaken to investigate the use of a nickel-magnesium alloy in glacial acetic acid for the reduction of such ketones.

Thus far, the reduction of two aromatic ketones, benzophenone and *p*-hydroxybenzophenone, has been investigated. The products isolated from the reaction of benzophenone and nickel-magnesium alloy were diphenylmethane I, benzhydrol II, benzhydryl acetate III, and dibenzhydryl ether IV.



The only product isolated from the reduction of *p*-hydroxybenzophenone was *p*-benzyphenol V. The analogous reduction of these ketones with magnesium metal or a homogenous mixture of nickel and magnesium

¹ Contribution No. 876.

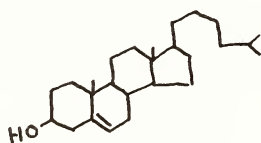


metals in glacial acetic acid yielded pinacols or resinous products demonstrating the necessity of nickel in the reaction and for its incorporation with magnesium in alloy form in order to obtain monomeric reduction.

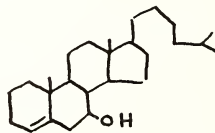
Attempted reductions with other alloys of nickel and magnesium have been studied.

Synthesis and Evaluation of Selected Mono-derivatives of Methylene Citric Acid. JOHN W. MARTIN and ROBERT W. GARDIER, Butler University and Pitman-Moore Company.—By the condensation of citric acid with formaldehyde and subsequent dehydration the anhydride of methylene citric acid was prepared. The fusion of trioxymethylene with citric acid was the most practical method for preparing the methylene citric acid while phosphorus pentachloride was found to be the best for dehydration. By the addition of the anhydride to the desired alcohol or amine the reaction proceeded to yield the desired mono-ester or mono-amide. This series was studied for biological activity. Several of the group were active, but generally none were of sufficient promise to warrant further study. Most compounds were unstable due to the rather easy hydrolysis with the liberation of formaldehyde.

The Structure and Reactions of Pseudocholesterol. QUENTIN R. PETERSEN, Wabash College.—Pseudocholesterol is a substance possessing the same function groups as cholesterol but in the former compound the positions of these groups in the A and B rings are the reverse of those found in cholesterol.



Cholesterol



Pseudocholesterol

Some of the unique reactions of cholesterol seem to be due to the specific steric environment of the functional groups and the reported studies are directed to the question of whether or not such unique reactions will take place when the steric environment of the homoallylic cholesterol system is radically changed. Reaction with positive bromine, displacement reactions, and oxidation and reduction reactions on the pseudocholesterol nucleus appear to resemble those with cholesterol. The i-steroid rearrangement, characteristic of the cholesterol system, is involved in displacement reactions on pseudocholesterol, although the i-intermediate itself cannot be isolated from the reaction mixture.

The Use of Handbooks in the Teaching of Beginning Courses in Chemistry. G. W. H. POWELL, Evansville College.—Handbooks contain essential information and present it in condensed, concise and specific forms. Handbooks are in use by all chemists and laboratories around the world, therefore they appeal to the student as being more real, alive and up-to-date than textbooks. The student in using handbooks

tends to associate himself with the scientists of the world. Slides showing arrangement of books in laboratory, mobile book case and kits of chemicals arranged for student use as well as sample pages of instructions to students. Physical properties, density, specific gravity, weights and measures, melting points, distillation vapor densities, formulae, conversion tables, and chemical factors present opportunities to correlate handbook and laboratory work. This material presented at the beginning takes up the lag between textbook and laboratory work.

One Dimensional Atomic Potential Functions. JOHN A. RICKETTS and LARRY D. NICHOLS, DePauw University.—The problem of finding a suitable one dimensional potential field which yields a one dimensional wave function that is exactly analogous in its form to that obtained by the solution of the three dimensional Schrodinger equation is applied to hydrogen-like atoms and ions. A suitable one dimensional potential function can be found for any s or p state. For the 1s state of hydrogen the potential function can be pictured as a negative Dirac delta function of unit strength in the system of atomic units.

Theory and Application of Flotation for Solids-Liquid Separation. ROBERT H. L. HOWE, Eli Lilly and Company.—The process of flotation has long been employed in many chemical and biochemical processes for solids-and-liquid and liquid-and-liquid separation. The application of the process and the design of the equipment have been more or less based on empirical data. This paper discusses the theoretical aspects of flotation process. Factors that may affect the process of flotation of a particle in the liquid are investigated. Equations showing the rising velocity of a solid particle in a liquid and the efficiency of solids removal by flotation process are derived by the author.

Dative Bonding and Polarizability. ROBERT J. POLACEK and Brother COLUMBA CURRAN, University of Notre Dame.—Previous work in this laboratory has revealed that addition compound formation involving dative bonding results in an increase or decrease in absorption of ultra-violet radiation, depending on the presence or absence of unshared valence electrons in the acceptor atom. As polarizability is related to light absorption by the Drude equation, a study has been made of the effect of dative bond formation on molar refraction. Because the low solubility of most addition compounds in inert solvents precludes a direct determination of their molar refractions, measurements have been made on solutions of the acceptor molecules in dioxane.

Indices of refraction and densities have been obtained for solutions of tin tetrachloride, arsenic trichloride and antimony trichloride in inert solvents and in dioxane, and for sulfur dioxide in triethylamine-benzene and triethylamine-butyl chloride solutions, and the refractions of the solutes were calculated. In dioxane, tin tetrachloride shows a decrease in molar refraction of 0.6 ml. and the refractions of arsenic and antimony trichloride are increased by 0.8 and 3.9 ml. respectively. The molar refraction of sulfur dioxide is 0.6 ml. higher in trimethylamine-butyl chloride solution than for the pure liquid. These changes in molar refraction have been correlated with dielectric constant measurements.

Hexacoordinate Copper(II) in Trisethylenediaminecopper(II) Sulfate. R. K. BIRDWHISTELL and GILBERT GORDON, Butler University and Michigan State University.—Evidence is offered for the existence of

hexacoordinate copper(II) in trisethylenediaminecopper(II) sulfate and the monohydrate of the trisethylenediaminecopper(II) sulfate. Studies of the infrared spectra of these and related compounds indicate that no free amine or any amine hydrochloride is present in the purified samples. Analytical data and visible absorption spectra are given. The absorption maxima of the tris complex which has not been previously reported but has been predicted by Bjerrum is given. The molar or specific extinction coefficient is not reported. Optical rotation and electron paramagnetic resonance spectra indicate that the observed properties can be used in support of an octahedral structure. Clarification in procedures for the preparation of diaquomonoethylenediaminecopper(II) sulfate, bisethylenediaminecopper(II) sulfate and its hydrates, and trisethylenediaminecopper(II) sulfate and its hydrates. A discussion is given on the existence of compounds previously reported as the bisethylenediaminecopper(II) sulfate with either four or four and one-half waters of hydration.

A Survey of Recent Studies with Hexafluorides. E. EUGENE WEAVER, Wabash College.—The author spent his recent leave from Wabash College working with Bernard Weinstock and John G. Malm at the Argonne National Laboratory. The major interest of this research group has been the study of the chemical and physical properties of the metallic hexafluorides. These unique compounds, exhibiting a volatility greater than water while having molecular weights greater than 300, readily lend themselves to the measurement of a wide range of physical properties. Among these are infrared and raman spectra, vapor pressures, molecular weights, melting points, and X-ray and electron diffraction patterns. Of the actinide elements, UF_6 was the only hexafluoride produced in gram amounts until the Argonne group produced PuF_6 and NpF_6 in specially designed reactors. The group's attention then turned to the hexafluorides of the 5d transition series. Repetition of Otto Ruff's work with osmium verified their suspicion that OsF_6 was in reality OsF_5 . Further exploration with this group of metals produced a new compound, PtF_6 . Platinum hexafluoride is a dark red solid exhibiting a vapor pressure of about 100 mm Hg at room temperature. PtF_6 is probably the least stable and most reactive of the known hexafluorides. Attempts have been made to prepare hexafluorides of Cr, Mn, Ru, Rh, Pd, Ta, Au and Gd without success. The method of preparation of the hexafluorides, their purification and determination of physical properties are reported.

The Role of the Solvent in Chemical Equilibria: Comparison of Reduction Potentials and Complex Ion Stabilities in the Solvents Ethylenediamine and Water. WARD B. SCHAAP, RICHARD E. BAYER, JOSEPH SIEFER and FREDERIC C. SCHMIDT, Indiana University.—As part of a study of the role of the solvent in the electrochemical behavior of solute ions, polarographic reduction potentials of metal ions and stability constants of metal-ion complexes were measured in the strongly coordinating solvent, anhydrous ethylenediamine. It was observed that this solvent greatly alters the relative reduction potentials of the metal ions (compared with those in aqueous solution) and causes several changes in position in the electromotive series. The transition metals become relatively more difficult to reduce in ethylenediamine while the

alkali metals become relatively more easily reduced. As a result, the oxidation-reduction potential scale is compressed in ethylenediamine as compared with aqueous solution. These relative shifts in reduction potential can be correlated with the known stability constants of the corresponding metal-ethylenediamine complexes measured in aqueous solution. The high solvation (coordination) energy of the chelate-forming ethylenediamine solvent molecules with transition metal ions would be expected to cause other complexes of the metals to be much weaker in ethylenediamine than in water. Such expectations are verified by experimental measurements of the stability constants of cadmium complexes, in ethylenediamine, with cyanide and with hydroxyethylethylenediamine-triacetate.

Teaching Undergraduate Organic Chemistry at Indiana University. C. E. KASLOW, Indiana University.—Scope of the course, method of presentation, demonstration, recitation, examination, and treatment of the laboratory instructions will be discussed.

Some Applications of Audio-Visual Aids in the Teaching of General Chemistry. FRANK D. MARTIN, Purdue University.—The following equipment has proved to be helpful in connection with the author's courses in general chemistry for first-year students in science and engineering:

1. A large magnet board with movable symbols for atoms, ions, and electrons.
2. A horizontal projector for the large scale projection of lecture experiments.
3. A simple electrical quizboard.
4. Mechanical model to illustrate effect of bond angle on dipole moment.
5. Working model of an electrochemical cell.
6. Apparatus for safe demonstration of spontaneous combustion of liquid rocket propellants.

The Utilization of Audio-Visual Devices in the Teaching of General Chemistry Laboratory Work.¹ J. M. HONIG and D. F. MOSES, Purdue University.—Closed-circuit live television broadcasts and televised film presentations have been utilized to demonstrate proper laboratory techniques required to carry out assigned experiments in the general chemistry laboratory work at Purdue University. Student reaction to these presentations was quite favorable initially, though there was some disenchantment with the program in the course of a given semester. Judging from scores received on laboratory reports, students in the experimental sections performed as well as those taught conventionally. It was found possible to operate the experimental sections in groups of 70 students assigned to 1 laboratory instructor. This compares with the conventional ratio of 25 to 1. However, there was a concomitant increase in administrative burden on the professors in charge of the laboratory work.

Several films, prepared in conjunction with this program will be briefly described; details of the experimental work and the implications of the program will also be discussed.

¹ This work was supported by a grant from The Fund for the Advancement of Education.