

phosphorus, sulfur, germanium, and arsenic, among others, can be developed into disciplines covering about as much ground as organic chemistry. However, each one of these subjects will have somewhat different rules of the game.

Another contribution to come from the renaissance in inorganic chemistry may well be a better understanding of the underlying principles of chemistry. I am firmly convinced that certain types of chemical behavior, which are not considered as general phenomena, are specific to the compounds of carbon. Likewise, there are probably a number of examples of chemical behavior which either are not found in the area of organic chemistry or are curiosities therein but which will prove to be of general applicability to a number of other elements. An example of this is the type of behavior which organic chemists call "redistribution reactions."

At present it seems that there are two broad and basic challenges facing chemists. One is biochemistry, which

consists of the elucidation of the physical-chemical basis of life. The other is inorganic chemistry, the mission of which is to prepare and understand the behavior of a myriad of potential new compounds which are not found in nature. The title of a film concerned with organic plastics, shown by the Monsanto Chemical Company several years ago, is "The World that Nature Forgot."³ The part of this world dealing with the compounds of carbon has been rather well studied by organic chemists. The challenge of inorganic chemistry is to explore the part of the world that nature forgot which deals with the hundred odd other elements!

- (3) "The World That Nature Forgot," Modern Talking Picture Service, Inc., 45 Rockefeller Plaza, New York, N. Y., or any of the M.T.P.S. film-distributing centers in 28 principal cities; or from Monsanto Chemical Company, Public Relations Department, Film Library, St. Louis 4, Mo.

CREATIVITY IN PHYSICAL CHEMISTRY BASED ON THE LITERATURE*

By HILTON A. SMITH

University of Tennessee, Knoxville, Tennessee

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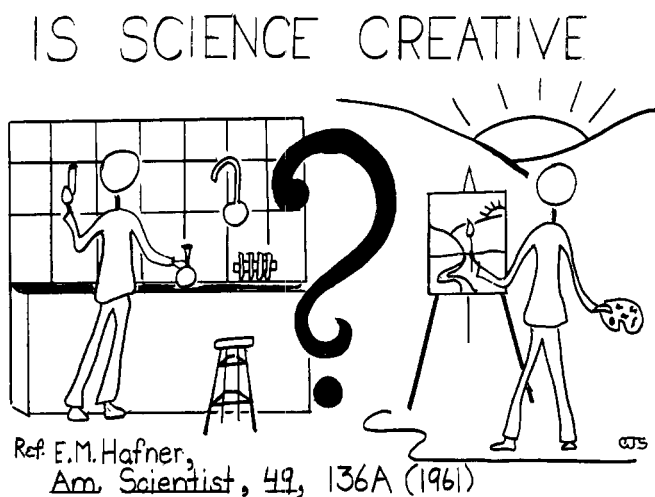
In a recent article dealing with creativity in science, E. M. Hafner, Professor of Physics at the University of Rochester, suggested that, "It is easy to suspect that the observational sciences cannot be truly creative. The natural scientist discovers things by looking keenly at the world. He does not—or at least should not—invent his data. He may construct ingenious experiments, but he designs them in order to bring into the laboratory whatever small part of the world he wishes to observe more precisely."¹ Dr. Hafner goes on to say that "if we define an act as creative only if it brings something new into existence, scientific activity can be regarded as uncreative"

when compared with literary, graphic or musical arts. He does point out, however, that in any scientific system, "laws can be derived from abstract principles, but the truth of the principles themselves cannot be proved." Thus one can regard science as a framework for creative work of the highest calibre. The scientist is attempting to create a true picture within the framework of science itself.

Chemists may well challenge Professor Hafner on the basis of the fact that molecules which are not only unknown, but may never have existed, are created by both organic and inorganic chemists. These are, however, created not by chance, but in the light of hypotheses such as those referred to by Dr. Hafner and which in themselves are creations. If, then, one considers physical or theoretical chemistry in reference to creativity, he must recognize the fact that it is, to a large measure, a creative field in the sense used by Dr. Hafner; one must also recognize that it is virtually impossible to separate it from the other branches of chemistry or from physics.

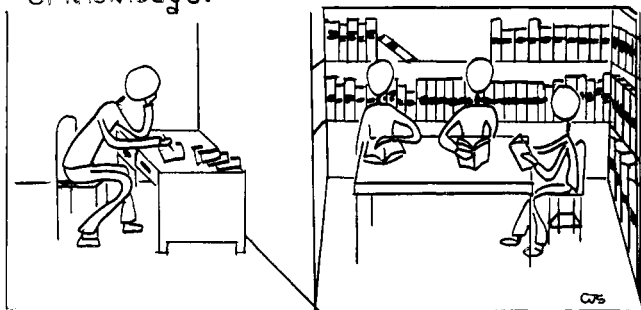
No individual physical chemist can divorce himself from the literature which of course contains the experimental findings and theoretical deductions of his predecessors and colleagues, for science has become too complex to allow any worker to ignore the efforts of others. The subject of this article deals with the actual creative aspects of physical chemistry which are based on such literature. This has been rather arbitrarily divided into three phases:

1. The introduction of new instruments and continued improvement of those types already available make possible measurements of physical properties with ever greater precision, and often allows measurements of a type not hitherto possible.



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Scientific literature is a medium through which all scientists work together for the creation of new laws and the advancement of knowledge.



2. The theoretical physical chemist depends largely on the literature for experimental information which will confirm or deny the results of his calculations and the models on which his calculations are based. Conversely, the experimental physical chemist often finds in the literature work of the theoretical researchers which suggests problems of particular importance.

3. The literature of other fields, particularly organic and inorganic chemistry, describes new compounds and new reactions, some of which are ideally suited for experimentation designed to answer specific questions of interest to the physical chemist.

It may not be too easy to cite examples of creativity in physical chemistry based on the literature without crossing into the areas of organic, inorganic, and analytical chemistry, for, as has been stated, previously, it is virtually impossible to make a sharp distinction between these areas. The examples chosen are picked primarily from the author's own studies dealing with hydrogen and hydrogenation, but could be paralleled in numerous research projects of others.

1. The introduction of new instruments, their construction, application, and availability are reported in the chemical literature, both that of the pure research variety and that of the practical and trade organ type. One instrument which has been available commercially for the past several years is the vibrating reed electrometer.² A problem which has considerable interest is the separation and analysis of mixtures of hydrogen and tritium when the tritium is present in tracer quantities. A logical method for accomplishing this is by gas chromatography, but the usual katharometer (thermal conductivity cell) will not detect tritium in tracer quantities. However, the vibrating reed electrometer can be modified by use of a suitable high resistance leak³ so that one may use it as a detector. With this instrument, the separation of tritium, tritium hydride, and hydrogen in mixtures where only tracer quantities are present has been recorded.⁴ As an extra dividend, it has been found that the continuously recording vibrating reed electrometer can detect non-radioactive substances including hydrogen and its spin forms, ortho- and parahydrogen. The availability in the literature not only of the description of this instrument but of the means of its modification to make it continuously recording, together with the gas chromatographic column so abundantly described in recent literature,⁵ has led to the creation of a method of isotope

separation and of a new detecting device for non-radioactive materials which will undoubtedly have many applications in the future.

2. The intermingling of the literature provided by the experimental and theoretical physical chemist and its application to creativity in physical chemistry may be well illustrated by the discovery and isolation of the spin isomers and isotopic forms of hydrogen and the theories concerning them. Heisenberg⁶ and Hund⁷ postulated on theoretical grounds the existence of two isomeric forms of hydrogen with paired and unpaired nuclear spins. Abnormalities in the spectrum of molecular hydrogen,⁸ plus discrepancies in the measured heat capacity when compared with that calculated on the basis of quantum statistics, led to the postulation of ortho- and parahydrogen and the explanation by Dennison⁹ based on the assumption that the nuclear spins of the atoms in the hydrogen molecule are not readily reversed. Giauque and Johnston showed that there was a change from the high temperature statistical ratio of three parts ortho- to one part parahydrogen when the gas was maintained at liquid air temperatures for some time as evidenced by a change in the triple point,¹⁰ while Eucken and Hiller¹¹ measured the change in the heat capacity of hydrogen maintained at low temperatures. Bonhoeffer and Harteck¹² found that the attainment of statistical equilibrium could be accelerated by adsorption on charcoal. Since statistical theory predicts that equilibrated hydrogen is virtually pure parahydrogen (paired nuclear spins) at temperatures near absolute zero, it has been possible to prepare this spin isomer in the pure form. On the other hand, statistical theory indicates that the equilibrium ratio of ortho- to parahydrogen is a maximum of 3 to 1, and so until recently it has been impossible to obtain a sample of hydrogen with greater than 75 per cent in the *ortho* form.

In 1958, Cunningham and Johnston¹³ showed that a separation coefficient for orthohydrogen on alumina at liquid hydrogen temperatures (20.4° K.) was 16 ± 3 while the rate of interconversion of the two forms was very small. By means of a 3-stage adsorption separator, they were able to prepare orthohydrogen of greater than 99 per cent purity.¹⁴ This information led almost immediately to the separation of orthohydrogen and parahydrogen by means of gas chromatography on an alumina column at 77° K. with helium as a carrier.¹⁵

In 1931, Birge and Menzel concluded that atomic weight measurements of hydrogen and oxygen indicated the possible presence of a heavier isotope of hydrogen in the ordinary hydrogen gas. The same year, faint lines in the Balmer series of hydrogen, in addition to those due to hydrogen of mass one, were noted¹⁷ and attributed to hydrogen of mass two. Within two years, essentially pure deuterium had been isolated by electrolysis of water.^{18,19} The importance of this work to both theory and practice is indicated by the great number of articles dealing with deuterium labelling and deuterium isotope effect.

One area of particular interest to the author has been gas chromatography of hydrogen isotopes. The separation of hydrogen spin isomers¹⁵ and of hydrogen, tritium, and tritium hydride⁴ by gas chromatography has been mentioned already. The research with hydrogen, deuterium, and hydrogen deuteride by this method was

complicated by the fact that the chromatographic peaks of orthohydrogen and hydrogen deuteride overlap,²⁰ and hence simple separation and analysis were not possible on an alumina column with helium carrier at -195° . The separation and analysis were accomplished by coating the alumina with a substance which catalyzes the ortho-para-hydrogen conversion.^{21,22,23} Finally, by employing a column of activated alumina followed by a column of ferric oxide-coated alumina with helium carrier at -195° , it has been possible to separate the spin forms of hydrogen plus hydrogen deuteride and deuterium in a single sample.²⁴

The literature of the past thirty years which deals with research on isotopic forms of hydrogen is an excellent example of the intermingling of theory and practice in such a manner as to lead to creativity in a very real sense.

3. The interdependence of the various fields of chemistry and the creative use which the physical chemist may make of literature in other fields may again be illustrated from the author's interests in hydrogen, in this case catalytic hydrogenation of aromatic compounds and catalytic hydrogen exchange. In 1923, Adams and Shriner reported the preparation of an unusually active platinum catalyst.²⁵ This platinum oxide preparation, now known as Adams catalyst, probably has been used in laboratory organic preparations more than any other hydrogenation catalyst. Several years later, the over-all times necessary to reduce given quantities of some aromatic compounds were reported.²⁶ To the physical chemist, the reporting of such over-all reduction times leaves much to be desired. No information is procured concerning the kinetic characteristics of the reaction, and the phenomenon of catalyst poisoning causes large variations in such over-all times. In the hope of obtaining fundamental information about what really happens on a catalyst surface when such compounds undergo hydrogenation, a study of the kinetic variables involved was undertaken. It was shown that, under carefully controlled conditions, the reaction was independent of the concentration of the organic compound undergoing reduction, but directly proportional to the hydrogen pressure, and that specific reaction rate constants could be determined which were characteristic of the reaction involved.²⁷

The rate constants for hydrogenation of all of the methylbenzenes were determined, and it was noted that while, in general, the rate constants for reduction of substituted benzenes decreased as substitution increased, the values within a set of isomers also varied, the largest "*k*" being characteristic of the most symmetrical molecule.²⁸ By making similar studies with methyl-substituted benzoic acids, it was demonstrated that this was the influence of symmetrical substitution rather than molecular symmetry itself.²⁹ Incidentally, new methods of preparation of many of these organic compounds were devised,^{30,31} and new compounds were produced in the hydrogenation process which were isolated and characterized. Further, some of the compounds prepared for and resulting from the hydrogenation reactions were used in the synthesis of more complex chemicals of potential physiological activity.^{32,33,34} Thus these studies in kinetics of catalytic hydrogenation resulted more or less directly in creativity in the area of organic chemistry.

To return to the field of hydrogenation kinetics, the similarity between the rate of catalytic reduction of benzoic acid, in which the benzene ring and carboxyl

group are conjugated, and that of phenylacetic acid, in which the same groups are insulated by a methylene group, suggested that resonance in the benzene ring is destroyed when it is adsorbed on the surface of the platinum catalyst.²⁷ Comparison of the heats of activation for the hydrogenation of benzene, cyclohexene, and the cyclohexadienes with the thermodynamic enthalpies of the same reactions confirmed that resonance of the benzene ring must indeed be destroyed when it undergoes such adsorption.³⁵

The kinetic characteristics of reduction of the methylbenzenes have been mentioned already. The question arose as to whether symmetrically-substituted molecules are reduced more rapidly than their unsymmetrical isomers because of fundamental differences in kinetic phenomena, or because the symmetrical molecules are more strongly adsorbed and activated. In order to answer this question, experiments in catalytic hydrogenation of mixtures of methylbenzenes have been carried out. It has now been shown that the more symmetrical isomers are less strongly adsorbed than their unsymmetrical counterparts.³⁶ In fact, certain such mixtures may show increasing hydrogenation rates during the course of a reduction, since the slower reacting hydrocarbon in the mixture is adsorbed the more strongly of the two and displaces the faster reacting isomer from the active catalytic surface in the early stages of the reaction. As the reaction proceeds, the more strongly adsorbed, but slower reacting, isomer is reduced at the expense of the more rapidly reacting isomer. An increasing fraction of the latter covers the catalyst surface as the reaction proceeds, and the rate of reduction increases.³⁷

Finally, studies of the catalytic exchange reaction between deuterium gas and the active hydrogen in acetic acid or methanol are influenced by the presence of unsaturated organic compounds in a manner which is clearly related to the kinetic behavior of the hydrogenation of the same unsaturated compound on the same catalyst.^{38,39,40}

In the past few years, it has become of great interest to label certain organic molecules with tritium, which serves as a tracer in organic chemical and biochemical studies. The usual method is that of Wilzbach.⁴¹ However, this method has certain drawbacks, since curie amounts of tritium are required, and the presence of by-products requires careful product purification procedures.⁴² Catalytic exchange of tritium gas with organic acids followed by decarboxylation is an effective method of labelling without some of the difficulties inherent in Wilzbach's method.⁴³

The hydrogenation studies which have been described are contributing to fundamental knowledge of the mechanism of the catalytic reduction of aromatic compounds. However, there are many questions still to be answered. In fact, it sometimes seems as though such research creates more questions than it answers. It is hoped that the presence of such research reports in the literature will stir creativity in others and that in this manner some of the many problems concerning catalytic hydrogenation may be solved.

The discussion of these examples of creativity in physical chemistry based on the literature hardly answers the questions as to how one may systematically use the literature to become creative in a broad sense. There

is surely no single answer to this question. An article which leads one individual into a creative research enterprise may be quite unexciting to another. This is, of course, fortunate, for it results in research chemists undertaking problems along many different lines. It is certain that unless a chemist browses through the literature both with regularity and with perception, he has little chance of using this vast storehouse of knowledge in a creative manner. With the tremendous advances in all areas of science now being reported in our chemical periodicals, it seems almost unimaginable that creativity in modern science can have any firm basis except through the theories and experiments which are described in the scientific literature.

Of course, it should always be remembered that individual scientists and groups of scientists create the chemical literature. Creativity based on the literature can only be creativity based on the work of others; the scientific literature represents a medium through which all scientists work together for the advancement of knowledge.

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Creativity in Organic Chemistry Based on the Literature*

By. ROBERT C. ELDERFIELD

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

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When one approaches the subject of creativity in organic chemistry, or for that matter in any science, it seems to me that at least two distinct aspects of the subject must be recognized. One is essentially that based on a chance or purely empirical observation, proper interpretation and exploitation of which results in creativeness of high order. Roughly speaking it can be said the spectacular developments in organic chemistry in the latter half of the nineteenth century for the most part

fall into this class. If the state of evolution of this discipline at about 1850 be considered, the reasons for this situation become abundantly clear. Organic chemistry in 1850 was a relatively new science and its literature was both scanty and frequently of debatable quality. It must be remembered that it was only in 1828 that Wöhler's synthesis of urea without the intervention of a "vital force" disproved the theory held until that time that synthesis of what are regarded as organic compounds without application of such a force was impossible. A few examples of such empirical creativeness may not be out of order.

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