

THE NUCLEUS

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Northeastern Section of the American Chemical Society
with the cooperation of
The Connecticut Valley Section
and
The Rhode Island Section

VOL. I

FEBRUARY, 1924

No. 1



**Report of the Intersectional Symposium
on Catalysis**

Notices of February Meetings

News of the Sections

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FEBRUARY MEETINGS OF THE SECTIONS

The Northeastern Section

The one hundred and ninety-first meeting of the Section will be held **Friday, February 8, at 8:00 p.m.** at the **Wedgewood Restaurant**, 531 Washington Street. The Executive Committee and Council will meet at 5:15 p.m., in Dr. Esselen's Office, 276 Stuart Street. Dinner will be served at **6:30 p.m.** at the Wedgewood Restaurant for those who make reservation by the enclosed card before February 6. Dinner, \$1.25 per plate.

Prof. Lyman C. Newell of Boston University will speak on "The Founders of Chemistry in America." The address will be illustrated with lantern-slides, portraits, documents, etc.

On **February 29**, the First Quadrennial Leap Year Party of the Section will be perpetrated at the American House. Entertainment and buffet lunch. Tickets at \$1.50 will be on sale at the February meeting and elsewhere. Further details will be divulged later by mail.

More detailed information about both meetings will be found on page 11.

The Connecticut Valley Section

The February meeting at **Hartford, Saturday, February 9**, will include an excursion to two stations of the Hartford Electric Light Company scheduled for 3:00 p.m., dinner at the University Club at **6:00**, and address by Prof. Harry A. Curtis of Yale University at **7:30** on "The Application of the Nitrogen Problem to Agriculture." Further information will be found on page 12.

The Rhode Island Section

On **Tuesday, February 19, 1924**, a joint meeting with the Providence Engineering Society will be held at the Jesse Metcalf Chemical Laboratory of **Brown University**, at **8:15 p.m.** Speaker: Dr. Marston T. Bogert of Columbia University. Topic: "Science and Art in the Perfume Industry." (Illustrated.) This will be an open meeting, and ladies are invited. There will be an informal dinner before the meeting. Further details on page 12.

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Vol. I

BOSTON, MASS., FEBRUARY, 1924

No. 1

THE NUCLEUS EXPLAINS ITSELF

In an age like this when the presses, like volcanoes, are pouring out appalling floods of printed matter, a new publication, however modest in size, is under obligation to justify its existence and its right to ask for the attention of busy people. To the chemist especially, whose mountainous annual accumulation of journals is an embarrassment of wealth for him and a *casus belli* to his wife, another periodical may appear superfluous. Nevertheless the NUCLEUS opens its career with confidence that it is going to prove of genuine value.

Although the Northeastern Section of the Society carries the responsibility of editing and publishing the monthly, other New England Sections, as the cover proclaims, are cooperating in the undertaking. Not only does this bulletin plan to notify us of meetings to come, summarize the addresses delivered to our Section and print other matters of local interest, but it will acquaint us also with the activities of the other Sections with whom we are cooperating.

We hope, therefore, that the NUCLEUS, living up to the suggestion in its name, may bring the New England Sections into closer affiliation than heretofore, and furnish a convenient vehicle transmitting information and news to their members.

THE INTERSECTIONAL SYMPOSIUM

The symposium on "Catalysis" held at Technology, January 12th, proved pretty conclusively the value of coöperative effort. The North-eastern Section with its large membership had to play the major role in making arrangements, but the Connecticut Valley, the Rhode Island and the New Haven Sections joined in the project with a will. The weather was balmy, contrary to the best Boston traditions of the season, and the speakers on the program were men of such authority in the field chosen that chemists were naturally attracted from all directions.

More than five hundred were present at some or all of the meetings and there was a noticeable proportion of out-of-town visitors. The Rhode Island Section alone had eighteen members registered, to say nothing of those who may have escaped the card-index. The Editors of our Journals and many other well-known members of the A. C. S. attended the sessions.

Considerable time was reserved on the program for the discussion of the papers and it was well utilized. Under the witty and stimulating comments of Professor Bancroft, who served as Chairman, every paper called forth many questions and remarks and even verbal battles from the audience, and the discussion periods were of unusual value and interest. It is regrettable that some of these discussions cannot be reported in the NUCLEUS as well as the summaries of the addresses which occupy the next few pages of the bulletin. It is hoped that these reports, although necessarily incomplete, represent pretty accurately the principal points of the papers.

1. Photo-chemistry and Catalysis,

Professor W. D. Bancroft of Cornell.

Berzelius was the first to recognize the existence of catalytic phenomena. It was Ostwald who emphasized the relation of the catalyst to the velocity of chemical change. Contact catalysis is of two kinds; (*a*) that which depends upon the formation of an internal compound, and (*b*) that which involves adsorption upon the surface of the catalyzer. Similarly, one school of organic chemists teaches that organic reactions are preceded by the dissociation of the reacting compounds, while the other believes that the reactions require a preliminary combination of the reacting molecules.

Langmuir contributed the conception of oriented adsorption—the idea that molecules are all held to the catalyst by the same definite end group. Should chemistry, then, be held to be unsportsmanlike because the bombarding molecules are beating upon the heads of the others held captive on the surface of the catalyst? An alternative explanation is that the entire electronic structure of a molecule is modified when it becomes attached to

the catalyst, and that this alteration accounts for catalytic activity. Certain organic decompositions which may be effected with the aid of catalysts, may also be brought about by exposure to ultraviolet light, with catalyzers entirely absent. Examples are the splitting of alcohol into ethane and water, of acetone into ethane and carbon monoxide, and of alcohol into acetaldehyde and hydrogen. Such purely photochemical effects seem to offer strong support to the electronic explanation of catalytic action.

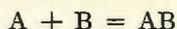
If a narrow enough band of ultraviolet light of sufficient intensity could be brought to bear upon an organic compound, it might be possible by the proper choice of the band to split an organic compound at any particular bond desired, since there is a line or series of lines corresponding to every bond in the compound. Thus organic chemistry may find itself centering attention again upon the radicals of organic compounds.

2. Negative Catalysis, Professor H. S. Taylor of Princeton.

The use of small amounts of acetanilide in hydrogen peroxide and of alcohol in chloroform are familiar examples of the practical application of negative catalysis. Lead tetra-ethyl, which Midgley has found to be an effective anti-knock compound in gas engines, may also function as a negative catalyst, for it can retard the oxidation of benzaldehyde.

A negative catalyst often acts by removing an active positive catalyst, but there are cases not to be explained in this way. Not only is the oxidation of sodium sulfite under the catalytic influence of copper hindered by a substance which removes the copper, but its non-catalytic photochemical decomposition can also be retarded by the same negative catalyst. Very small quantities of the negative catalyst, as little as one part in 10,000, will serve to decrease the velocity of these reactions. There must be present in the mixture of reacting substances one molecule of the negative catalyst for every molecule of reactive substance that undergoes change during a period of a half minute.

One of the reacting substances is present in but decidedly small amount in the usual cases of effective negative catalysis. It is only the dissolved oxygen, for example, which oxidizes benzaldehyde. If, then, to a simple reaction such as



there be added a third substance C, the original change will be checked if either A or B reacts more readily with C than with the other. C, the inhibitor, here acts by forming a molecular compound.

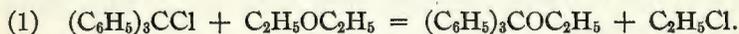
Since most reactions subject to negative catalysis are exothermic, the

molecular compounds at the moment of formation may pass their excess of energy in some way to the uncombined A or B or both, thus greatly increasing the total action. This process may be called a chain reaction. Christiansen suggests that in some way the addition of the negative catalyst C breaks this chain and, by preventing the transfer of energy from AB, reduces the rate of formation. (*Professor Taylor then gave following experimental demonstration.*) Five cc. of benzaldehyde placed in a vacuum-jacketed tube and connected to a manometer shows the absorption of more than two cc. of oxygen in three minutes. Another sample similarly shaken with two drops of lead tetra-ethyl present fails to register *any* fall of pressure in the tube.

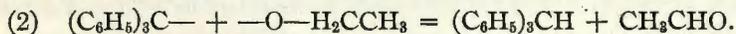
3. New Catalytic Effects of Zinc Chloride and of Aluminium Chloride, Professor J. F. Norris of the Massachusetts Institute of Technology.

The rates at which a single compound reacts with each of the members of a series of compounds of a given type are being carefully determined at the Institute, in order to measure the effects of changes within the molecule upon the reactivity of its atoms. Solvents or catalytic agents outside the molecule also affect the bonds in the activated compound in a similar way. Two molecules when brought together must change the attractions between the atoms within the molecule. Solvents may then be regarded as true catalysts since they alter the strength of the affinities between the atoms of the dissolved molecule.

The molecular compound of benzoyl chloride and aluminium chloride forms condensations with many kinds of substances, such as ethers, esters, ketones, and saturated and unsaturated hydrocarbons. Similarly the compound of triphenylchloromethane and aluminium chloride when treated with ether yields triphenylmethane. The reaction is believed to take place in steps:



The carbon-oxygen bond, the weakest in the compound, is then broken under the influence of the aluminium chloride, after which



The pure ether also breaks down by heating alone, just as it does at room temperature with aluminium chloride present. This work leads to a simple method for preparing triphenylmethane in quantity.

Zinc chloride, when used in the preparation of alkyl chlorides from anhydrous alcohols and hydrogen chloride, has been supposed to act as a de-

hydrating agent. It is possible, however, that it functions here catalytically by activating the hydroxyl group, since it readily forms compounds with alcohols. Primary alcohols have now been found to react well with concentrated hydrochloric acid solution, proving that even in the presence of water some of the molecular compound of the chloride with alcohol is formed. This suggests that other catalytic reactions ordinarily carried out in anhydrous solvents, might be brought about also in the presence of water.

4. Ammonia Catalysis,

Dr. A. T. Larson of the Fixed Nitrogen Research Laboratory.

Probably the greatest single contribution of the Fixed Nitrogen Laboratory has been the development of a very reactive and stable catalyst for the synthesis of ammonia. During the war, a mixture of iron and molybdenum oxides seemed to promise the best results. Using precipitated oxides, the Laboratory has since tested the suitability of about twenty-five metals as catalysts. A number of considerations including the cost of the catalyst showed the iron group of metals to be the most suitable, and pure iron oxide proved to be the most active of the group, but it deteriorated rapidly when the temperature reached 550°.

When precipitated in tap water, the oxide was more active and longer-lived than when distilled water was used. Many substances when incorporated into the catalyst by being stirred with the fused mass, showed a decided promoter action like the impurities in tap water. Combinations of two or more promoters are more active than one alone, if they are not too similar in properties. A mixture of potassium and aluminium, about one per cent. of each, proved the best promoter of all, and gave a 60% conversion to ammonia at 1000 atmospheres pressure. At 300 atmospheres, from 30-35% of ammonia may be obtained when the gases have passed but once. This catalyst is believed to be superior for the purpose to that developed by any other country of the world.

Water, even in amounts less than 0.03%, hinders the promoter action unless the temperature is raised considerably higher. Carbon monoxide and other gases also are poisons. No appreciable amount of the ammonia is held by the catalyst nor is there any apparent relation between the activity of the catalyst and the amount of ammonia adsorbed.

The mechanism of promoter action is still a matter of speculation. Iron oxide containing a promoter does not sinter as the pure oxide soon does, and apparently possesses an increased active surface area. Thus the promoter may stabilize the structure of the catalyst and so preserve its

activity. Its principal function, however, is probably to activate the nitrogen and adjust its time of contact with the catalyst. The activity of the catalyst is probably due to the formation of labile nitrides which are continually decomposing, and the effective promoters serve to render these nitrides less stable.

5. Electro-Catalytic Production of Oxygen, Professor C. J. Fink of Columbia.

There is a great difference between chemical corrosion and electrolytic corrosion. If a number of alloys are set up as anodes in a series of small cells with a solution containing sulfate, nitrate and chloride ions, and a current of 15 to 20 amperes per square foot is passed through for three days, the anodes show marked differences:

(1) Nichrome, ferrochrome and other high chromium alloys are corroded only below the solution line, because they resist atmospheric but not electrolytic corrosion.

(2) Those anodes resisting electrolytic corrosion but not chemical, are eaten away only *above* the surface (by acid spray thrown up by the gases evolved).

(3) Some are corroded both above and below the surface, because they can resist neither type of corrosion.

(4) Alloys like those high in silicon, whose specific resistance is higher than that of the solution, are pitted only just below the surface, at the point where the electric current first comes in contact with the solution.

This paper deals with the alloys of group 2.

At the anode the negative ions may (1) react with the metal of the anode or (2) interact with the water to liberate oxygen. For use with copper solutions, an anode of 100% copper would be ideal. Practically, however, the copper anode must be treated in some way to make the second reaction predominate. Anodes containing more than 80% of copper may be employed if they are plated with alloys high in cobalt which will catalyze the formation of oxygen.

For the electrolytic production of oxygen and hydrogen, iron electrodes plated with nickel are better even than platinum, for not only does the nickel-plated iron resist corrosion, but its use cuts down the voltage required and hence the current consumed, as much as one-third.

Those metals are best for plating which form two or more oxides or which will form insoluble compounds in the solutions used, such as barium, manganese, cobalt, nickel, lead, and silver, the last of which gives remarkable results. Certain oxides may also be used as promoters.

NEWS OF THE SECTIONS

The Northeastern Section

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The meeting on February 8 offers an unusual opportunity to hear of the earlier days of American chemistry and to see the many slides, portraits, rare books, autograph letters, documents, and other memorabilia which Dr. Newell has collected. The address will emphasize especially the work of the early New England chemists. Prof. Newell, well-known as the Head of the Department of Chemistry of Boston University, is the present secretary of the Section of History of Chemistry of the A. C. S.

The Leap Year Party, February 29, is being veiled in a dark mantle of mystery. An able committee, of which Mr. Lythgoe is chairman, has been planning for a long time for the affair but will not talk for publication. They offer a cash rebate to every member who brings with him or her to the Party a guest of the opposite sex.

The Connecticut Valley Section

OFFICERS, 1923-24

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The December meeting of the Section was held at the Nayasset Club in Springfield, Mass., on the evening of December 15. Mr. S. A. Hood spoke on "Some By-products of Chemistry." He dealt particularly with the isolation of essential oils, illustrating his remarks with slides picturing the various stages in the processes from the flowers or fruits to the perfumes or flavoring materials.

A dinner was served before the business meeting which preceded the address. At the meeting the very important matter of classification of members of the Society was discussed at some length and it was voted to take a post-card ballot on the subject.

In the afternoon, at the invitation of Dr. Schadt, the Section visited the New England Laboratories, where a variety of subjects from steel to blood, and paint to milk were under investigation.

The next meeting of the section will be held in Hartford on Saturday, February 9.

An excursion through the South Meadow and Dutch Point power stations of the Hartford Electric Light Company, which will afford an opportunity to inspect the mercury boiler installation, is scheduled for 3 P.M.

Dinner will be held at the University Club at 6 P.M., and at 7:30 Prof. Harry A. Curtis of Yale University will speak on "The Application of The Nitrogen Problem to Agriculture." Mr. Curtis has spent several years in Government nitrate plants and industrial laboratories and is very well fitted to speak on all phases of this subject.

The results of the post-card ballot on classified membership and the matter of co-operating with the Hartford Engineering Club will be considered at the business meeting.

The Rhode Island Section

Samuel T. Arnold, *Chairman*

Robert K. Lyons, *Councilor*

Lucius A. Bigelow, *Secretary*

Tuesday, February 19, 1924, at 8:15 P.M. A joint meeting with the Providence Engineering Society. Speaker—Dr. Marston T. Bogert, of Columbia. Topic—"Science and Art in the Perfume Industry." Place—the Jesse Metcalf Chemical Laboratory, Brown University. There will be an informal dinner before the meeting. This is an open meeting and ladies are invited. All our members are urged to come and bring their friends.

Dr. Bogert intends to make his address non-technical, and to bring home to the layman how chemistry is ministering to the pleasure and happiness of the community. He will tell us about the orange groves of Algeria, the rose plantations of Bulgaria, the sandal trees of India, and much else besides. The talk will be illustrated.

In general, meetings are held on the fourth Friday of each month, at the rooms of the Providence Engineering Society, 44 Washington St., Providence, at 8.15 P.M. An informal dinner usually precedes the meetings. Notify Miss C. R. Crosby, Brown University, if you can attend, and come if possible, to greet and become acquainted with our speakers.

The December meeting was held on the 17th, at the Chemical Laboratory, Brown University. Dr. Charles A. Kraus of Clark University spoke upon the subject "The Properties and Manipulation of Glasses." In the first part of his talk, he outlined the composition of various kinds of glass, and told how the introduction of various ingredients altered the fusibility, solubility, and stability of the product. The best types of glass represent a compromise between these properties, as very often the ingredient which favors one property is unfavorable to another. Methods of sealing together different kinds of glass were described, and interesting samples passed around. Later in the evening, the speaker ably demonstrated with the blast lamp his skill in producing certain types of seals. He also illustrated the manipulation of silica in the gas-oxygen flame. Silica seems to be quite as easy to manipulate as glass, if you only know how!

The audience of nearly a hundred enjoyed the talk and demonstrations.