

DR. HENRY EYRING

CHEMISTRY

Dr. Eyring Explains Winning Accomplishment

This is the abstract of the paper on "Quantum Mechanics and Chemistry with Particular Reference to Reactions Involving Conjugate Double Bonds" which won the \$1000 prize of the A.A.A.S. Atlantic City meeting.

By DR. HENRY EYRING, Princeton University.

THE UNIVERSALLY accepted conception of atoms as positive nuclei surrounded by electrons make it seem obvious that some sort of mechanics of such particles will properly describe their chemical behavior. The success of quantum mechanics in atomic physics where it gives quantitative agreement with experiment, shows us clearly enough the general means to be employed. Because of the complexity of the mathematics, we must use a perturbation theory. A careful application of a perturbation theory, however, may be expected to be as fruitful as such methods have been found to be in astronomy, for example. Among the many results already obtained only a few bearing most directly on the problem in hand can be

Heitler and London's calculations for the homopolar bond (Turn to page 15) CHEMISTRY

Chemist Who Works in Library Wins Coveted Award

Textbooks Proved Wrong by Achievement of Young Scientist Which Brings Him A.A.A.S. \$1000 Prize

YOUNG CHEMIST who works with mathematical equations in a library instead of with chemicals in a laboratory has won the \$1000 American Association for the Advancement of Science prize for the Atlantic City meeting because his applications of the new quantum mechanics of physics to binding energies between the atoms (valence) have resulted in predictions later verified by experiments. These show that in some cases even elementary text books in chemistry are wrong.

Dr. Henry Eyring, research associate and assistant professor in Dr. Hugh S. Taylor's Frick Chemical Laboratory at Princeton University, is the prize winner. He is 32 years of age.

He has applied quantum mechanics to several branches of chemistry. Through his calculations he utilized the binding energies between atoms in solving problems of how rapidly chemical reactions occur.

The first notable success of his work came two years ago when he showed the conditions governing the conversion of parahydrogen to orthohydrogen. These are two molecular arrangements or varieties of ordinary light-weight hydrogen (atomic weight one) which Prof. Karl Bonhoeffer, then of the Kaiser Wilhelm Institute at Berlin and now at Frankfurt, demonstrated experimentally. There was question as to just how the para sort of hydrogen changed over to the ortho arrangement of the hydrogen atoms. Dr. Eyring's calculations showed that the conversion proceeds more easily by interaction of an atom with a molecule, and not through mere molecular rearrangement.

Mistaken About Flourine

Next Dr. Eyring studied the interaction of hydrogen with fluorine, bromine, iodine, and chlorine, those chemicals known as the halogens. His applications of the new physics showed that contrary to all chemical expectation fluorine is really the least reactive of these chemicals with hydrogen. All the

texts and technical chemical literature declared the opposite, that fluorine reacts much more easily than the other elements, chlorine, bromine and iodine.

Here was a clean-cut test of Dr. Eyring's methods. From Germany through experiments performed by Dr. H. Von Wartenburg of Danzig came the verification. He prepared pure fluorine and pure hydrogen and found that they would not react at room temperature. This is what Dr. Eyring predicted and now textbooks that state the contrary are out of date.

Mathematics of Heavy Hydrogen

To the problem of separating ordinary hydrogen from the heavy weight hydrogen discovered a year ago, Dr. Eyring's latest developments of quantum mechanics are applied. This work is not yet announced and will be published in a forthcoming issue of the Proceedings of the National Academy of Sciences. At the Bureau of Standards in Washington Dr. E. W. Washburn found recently that when electric current breaks down water into hydrogen and oxygen gas, the first hydrogen given off is almost all lighter hydrogen or the wellknown isotope of mass one. The double weight hydrogen isotope of mass two is given off practically not at all in the early stages of electrolysis. Dr. Eyring has shown that this is a necessary consequence of his method of calculating the speed of chemical reactions when applied to surfaces such as those of the electrodes through which the electricity is applied to the water.

In his prize paper delivered to the American Association, Dr. Eyring extended his methods to organic chemistry. Bromine might be added to an organic molecule, butadiene, by two alternative methods. Dr. Eyring calculated which of these methods occurred more easily. His result indicates that the addition occurs in that manner which experiments by organic chemists had showed to be that actually occuring. But he also showed by calcu- (Turn Page)

From Page 5

in the hydrogen molecule was followed by London's suggestion the same method applied to two approaching molecules would lead to an activation energy which might well explain at least some of the observed activation energies. It is, perhaps, well to consider what is meant by an activation energy. A reaction between two molecules can only occur during the rare cataclysmically violent encounters in which a particular atom being so near a new one is as apt to depart with the new partner as to return to the old one. This unusual situation is called the activated state and the energy with which they must collide is the activation energy. To calculate the activation energy involves a knowledge of the energy with which pairs of atoms are held together. The suggestion that the spectra of diatomic molecules would suffice for the evaluation of these quantities was embodied in a paper by Eyring and Polanyi. In this paper the activation energy calculated for the conversion of para-hydrogen to the equilibrium mixture was found to approximate closely the experimental findings. Calculations of a later paper indicated correctly the particular mechanism by which the various halogens react with hydrogen. The reaction of hydrogen and fluorine is particularly interesting because of the frequent statements in the literature that the reaction proceeds even at very low temperatures. The calculations indicate it is really the least reactive of the halogens and is only able to react at ordinary temperatures after a chain has been started by a catalyst or some dissociating agent. The large amount of heat released by the reaction of even a few atoms, however, makes an explosion extremely probable. The method also enables us to eliminate as extremely improbable certain proposed mechanisms in the hydrogen, chlorine photochemical reaction. A satisfactory picture of the catalytic conversion of ortho- to parahydrogen at a surface has been obtained. The concentration of the heavy hydrogen isotope in water by electrolysis is a necessary corollary from this point of view arising from the lower zero point energy of the adsorbed heavy isotope. We thus bring to a new problem a reasonable certainty of the essential correctness of a method which in view of the approximations might otherwise be open to rather serious doubts. It is to be emphasized that all of these results

and those to follow involve no assumptions not introduced in the original paper of the series, and that qualitatively the conclusions are even largely independent of these assumptions.

The question as to why bromine adds to the first and fourth carbon atoms of butadiene (with the consequent disappearance of the two end double bonds and the appearance of a double bond between carbon atoms two and three) has long been a question for speculation. Our calculations show that 1,4 addition should proceed with an activation energy roughly 10 kilo calories less than 1,2 addition and that the former compound even when formed is more stable than the latter by almost as many calories. Thus 1,2 dibrombutadiene even if formed would rearrange at moderate temperatures to the 1,4 compound. The same calculations for hydrogen instead of bromine indicate that homogeneous hydrogenation can only proceed at a very much higher temperature than bromination so that the results will probably be impossible of experimental verification because of alternative polymerization reactions. Similar calculations indicate that so far as we may judge by energy considerations a satisfactory picture of the benzene ring is obtained by regarding six of the twenty-four valence electrons on the carbon atoms as paired with the six electrons of the hydrogen atoms. Twelve more form six single bonds between carbon atoms and the additional six electrons by rapidly oscillating between all the possible ways of forming bonds between them provide approximately the additional binding energy observed. The activation energy for the hydrogenation of such a benzene molecule is then calculated in the manner previously outlined.

There is thus accumulating an empirical foundation for the method more compelling than that which may at present be adduced from strictly theoretical considerations. The qualitative correctness in all cases of the calculations indicate that it is a surprisingly powerful tool with which to attack the almost endless variety of problems of chemical mechanism.

Science News Letter, January 7, 1933

Manufacturers of incandescent lamps turn out approximately 3,000 kinds, including many unusual designs made only on special order.

PHYSICS

Economic Revolution Seen As Atom Releases Energy

THE BEGINNING of an economic revolution is seen by Prof. Bergen Davis, Columbia University physicist, in the successful extraction of energy from the heart of the atom that has been accomplished within the past year.

When Dr. J. D. Cockcoft and E. T. S. Walton at Britain's Cavendish Laboratory this spring smashed the lithium atom and obtained 16,000,000 electronvolts energy for an input of only a few hundred thousand electron-volts, this was a landmark in the conquests of physical science, in Prof. Davis' opinion.

In delivering the vice-presidential address in physics before the American Association for the Advancement of Science, Prof. Davis predicted that the younger physicists listening to him may see and take part in a remarkable revolution in physical science and in industry.

"Enormous stores of energy will be

made available and mankind will be largely relieved from physical toil," he declared.

"The methods of using this nuclear energy are not yet developed, but new discoveries will be made," Prof. Davis said. "The difficulties will be rapidly overcome. One might imagine the following hypothetical process. The bombardment of aluminium by alpha-particles gives high energy protons. The bombardment of lithium by protons gives high energy alpha-particles. By bombarding a mixture of aluminium and lithium with protons the future physicist may start a process similar to but much more intense than the more familiar thermite reaction. The mixture in a certain sense is an explosive mixture. It contains within itself the possibility of maintaining the action if it is once started."

Science News Letter, January 7, 1933