The discovery and development of economic methods for combatting insects and diseases which have made relatively certain the production of crops and animals which was previously a gamble;

The improved methods of breeding and feeding all kinds of live stock for increased production in milk, meat and eggs;

The economic use of commercial plant foods and soil amendments;

The invention of the Babcock test and its consequent influence on all dairy practices—not to mention other contributions.

Up to 10 or 12 years ago it was the fashion to descant upon the grave dangers confronting this country and the world at large from our rapidly growing population overtaking our production of food and fabric materials. We hear none of this to-day.

But back of and leading up to these practical results are more permanent contributions to our fundamental knowledge which will bear fruit in the decades to come, for our experiment stations have not been content with knowing "what," but have pressed on to the "how" and the "why."

What of the future?

The financial situation in which many of our experiment stations now find themselves is discouraging. A reduction of state appropriations is very general. What course Federal appropriations will take is uncertain at this writing, but in spite of our tremendous financial depression it is hardly conceivable that the Federal Government will scrap an organization which it has been slowly building up for the last 40 years.

A reasonable support of these institutions would seem to be assured.

QUANTUM MECHANICS AND CHEMISTRY WITH PARTICULAR REFERENCE TO REACTIONS INVOLVING CONJUGATE DOUBLE BONDS[1]

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THE universally accepted conception of atoms as positive nuclei surrounded by electrons make it 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. From this point of view it is convenient to regard the Schrodinger equation as our point of departure. Among the solutions of the Schrodinger equation which satisfy the supplementary quantum conditions only those which in addition obey the Pauli principle, *i.e.*, only those solutions which change sign when two identical particles are interchanged need be considered as having physical reality. Our scheme, though complete, is still much too difficult to proceed with. We must find other simplifying conditions. The first simplification is a familiar one. Because of the much greater mass of atoms than electrons the atoms travel relatively much more slowly so that in calculating the potential energy of any system from the Schrodinger equation we neglect the motion of the atoms without introducing serious error. The result is that we obtain a potential energy for the system under consideration as a function of the distance between the atoms, and this, as we shall soon see, provides just the necessary information for estimating rates of reactions. London was the first to point out that such a scheme probably provided a way for calculating activation energies. We next consider the nature of an activation energy. Consider the reaction $H_2 + I_2 = 2HI$. This is a well-known bimolecular reaction. For the rate of formation of HI, we can write

$$\frac{d(HI)}{dt} = f\,S\,e^{-E/RT}\,(H_2)\,(I_2).$$

The parenthesis around a formula indicates the concentration of that substance. Thus $S\,(H_2)\,(I_2)$ is the number of collisions between molecules of hydrogen and iodine in concentration units and can be calculated from kinetic theory, while the expression $e^{-E/RT}$ is the chance that in a particular collision the two molecules collide with an energy E in a form to permit reaction. The energy E is called the activation energy and has for this reaction a value of 40,000 calories. The precision of activation energy measurements is seldom better than one large calorie; so that activation energies are ordinarily specified in large calories. The proper fraction f in our rate expression approaches one for most simple reactions.

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[1] Based on a paper presented before the Section of Chemistry of the American Association for the Advancement of Science at its Atlantic City meeting for which the anunal prize of the association was awarded.

It is a steric factor which measures the probability of a collision being of a kind to permit reaction even though it is sufficiently energetic. The variations in f for different reactions is of a different order of magnitude than the variation in $e^{-E/RT}$ so that by far the most important quantity in determining rates of reactions is the activation energy. Similar considerations hold for other types of reactions, so that if we can calculate the activation energy for the different mechanisms we are able to answer the very interesting question as to which way the reaction will proceed. For example, the reaction just considered might proceed by the alternative mechanism,

$$\begin{aligned} I_2 &= 2I \\ I + H_2 &= HI + H \\ H + I_2 &= HI + I. \end{aligned}$$

But both theory and experiment agree in preferring the mechanism $H_2 + I_2 = 2HI$, while for the reaction of the other halogens with hydrogen, as well as in the conversion of ortho to para hydrogen, they again agree in indicating reaction by way of the atoms. In the border line case of the reaction of hydrogen with bromine, obtaining the correct results depends somewhat on the assumed ratio of coulombic to interchange binding. The other cases give results so clear cut as to be independent of assumed ratios of interchange to coulombic binding. The fact that the calculations indicate that fluorine should not react with hydrogen at room temperatures seems to have attracted considerable attention, probably because of the early erroneous experiments widely quoted in the literature. Experiments of von Wartenburg, as well as some unpublished experimental results of Kassel and the author, leave no question of the chemical inertness of the mixture in diffuse daylight at ordinary temperatures. As a matter of fact, the contrary result would be startling when one considers the strong homopolar bonds to be broken. There is certainly a correlation between increase in the strength of the bonds to be broken and increase in the activation energy of a reaction. This was noted experimentally and follows as a matter of course from our theoretical calculations.

Before proceeding further with a discussion of our results it is perhaps well to consider in a little more detail the method of calculation. The coulombic portion of the energy of a homopolar bond between a pair of atoms increases from 10 per cent. in the case of non-metals like hydrogen to 28 per cent. in the case of metals like sodium and is independent of the presence of other atoms. That is to say, the attractive potential just adds up for all atom pairs, no matter how many atoms are in the neighborhood of a given atom. The remaining part of the bonds, called the interchange binding, add up quite differently. The laws of addition up to and including eight electrons are now known as a result of investigations in this and other research centers and the indefinite extension to larger numbers of atoms only awaits a real need. The extension offers no more difficulty than that of being very tedious. The evaluation of the coulombic and interchange binding between atom pairs as a function of the distance between the atoms is accomplished by reference to curves constructed from spectroscopic constants. Empirical Morse curves are at present the most convenient for this purpose. Knowing the amounts of interchange and coulombic binding and the laws of addition it is then a simple matter to calculate the energy of any configuration, and so construct a surface which enables us to follow the mechanism of approach of two molecules until they reach a point where new bonds are as strong as old ones and we find a new pairing of the atoms taking place. Such potential surfaces in the simple cases involving three atoms consist of two long valleys corresponding to configurations of the initial and final substances separated by a saddle over which the system must pass. The height of this saddle measured from the initial valley floor is the activation energy for the forward reaction. For the reverse reaction the activation energy is measured from the floor of the other valley. The heat of reaction is of course the difference in the heights of the valley floors. In case of a reaction such as the unimolecular decomposition of N_2O the initial region is a basin instead of a valley separated as before by a saddle from the final valley or valleys. The study of the kinetics of this reaction simply involves the study of a mass point on such a surface. Because of a change in multiplicity in the decomposition of N_2O the reaction surface is a composite of two intersecting surfaces and some attention must be given to transition at the junction. With molecules containing more atoms, more dimensions are required for our surface, but the essential problem of finding the height of a saddle value measured from a valley or basin remains. In my first paper, with Professor Polanyi, these methods applied to the reaction between a hydrogen atom and a hydrogen molecule gave results in good agreement with the experimental activation energy found by A. Farkas.

Pelzer and Wigner, then, carrying the matter further, were able to show that the rates calculated, entirely theoretically, were in very good agreement with experiment; so that apparently in the reaction of a hydrogen atom with a hydrogen molecule we have for the first term a rather satisfactory detailed picture of a reaction.

In cooperation with Mr. A. Sherman these methods were then applied to the reaction in which the conversion of ortho to para hydrogen takes place on a surface. Again, so far as we can now judge, we find agreement with experiment. The process seems to be one in which a hydrogen molecule is split into atoms by two surface carbon atoms which are abnormally far apart, each hydrogen atom becoming attached to a surface atom. These hydrogen atoms are now apt to leave the surface with a different but similarly situated hydrogen atom by the reverse of the absorption process. The conversion is thus completed. The result that for the greatest ease of activated adsorption the carbon atoms should be from four to five times as far apart as the normal distance between the hydrogen atoms is a rather striking part of this picture. This would be achieved in lattices in which some positions are vacant and we should therefore expect the instability to heat treatment customarily found with very active surfaces. Since a particular distance of surface atoms favors adsorption of a particular type of molecule, preferential adsorption is to be expected. These calculations indicate that the conception sometimes held, that an equal distance between surface atoms and the atoms in the gaseous molecule favors activated adsorption, should be abandoned.

With Dr. Kimball an examination was made of the proposed mechanism for the hydrogen chlorine reaction

$$Cl + H_2 + Cl_2 = 2HCl + Cl.$$

The calculations indicated it to be far slower than the reaction

$$Cl + H_2 = HCl + H$$

and so the first reaction could be excluded. This seems to be in keeping with the most recent experimental opinion. Similar although rougher calculations indicated that water should not be helpful in this reaction which apparently contradicted experimental findings at the time but is apparently at present in agreement with experimental findings.

In a paper appearing this month in the *Proceedings* of the National Academy it is pointed out that the difference in zero point energy for compounds of two isotopes makes the lighter isotope more reactive, and so should assist in their separation. Whether or not this is the principal factor in enabling Dr. E. W. Washburn to preferentially electrolyze away the lighter isotope from water remains to be seen.

We thus bring to a new problem a considerable confidence in the essential correctness of our method. It was with this background that we considered the additions of hydrogen and bromine to butadiene. The details of the calculations together with certain extensions will be published elsewhere as a joint paper with Mr. Albert Sherman and Dr. George E. Kimball. The addition of bromine may be expected to occur in either of two ways:

$$\begin{aligned} Br_2 + H_2C = CH - CH = CH_2 &\rightarrow BrH_2C - CH = CH - CH_2Br \\ &\rightarrow BrH_2C - CHBr - CH = CH_2. \end{aligned}$$

Taking explicitly into account in both cases the six electrons which change partners in the first reaction and using simply the methods already outlined we find for the first reaction an activation energy of 36.4 kilo calories, for the second an activation energy of 52 kilo calories. It thus seems sufficiently clear why 1–4 addition is to be expected. The sort of thing which might cause 1–2 addition to be preferred of course is to substitute for a hydrogen on 4 some group that introduces large steric effects. We hope to return to this aspect of the problem in the not too distant future. If the same calculations are made for the substitution of hydrogen to butadiene the activation energy for 1–4 addition is found to be 77 kilo calories and for 1–2, 113. Emphasis is of course not to be placed on the exact value of our figures, but their relative correctness seems reliable. The size of the calculated activation energies indicates, certainly in the case of hydrogen, that any addition can only occur catalytically. In the case of the addition of bromine the indication is less clear cut that the reaction must go by way of surfaces, but it certainly should be examined from that point of view. The factors which favor 1–4 addition in the gas phase will of course be less important for catalyzed reactions.

The significant point again seems to be at least qualitative agreement between theory and experiment. Very much remains to be done in the way of examining more closely the underlying approximations of this method with the idea of obtaining more precise results; but apparently even in its present unfinished form we have a surprisingly powerful tool with which to attack the almost endless variety of problems of chemical mechanism. Something is also gained by having a scheme into which the multitudinous experimental results may be fitted.

OBITUARY

DR. WILLIAM ARNON HENRY

DR. WILLIAM ARNON HENRY, one of the outstanding pioneers in the development of agricultural instruction, research and extension in this country, died at his home in San Diego, California, on November 24, 1932, from an attack of pneumonia.

The life story of Dean Henry, as he was usually called, is one to inspire youth and is typically Ameri-