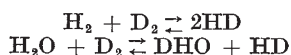


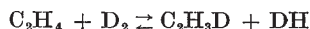
Physical and Chemical Properties of Heavy Water

IN the recent joint discussion of Sections A (Mathematical and Physical Sciences) and B (Chemistry) on September 10, at the British Association meeting at Aberdeen, on heavy hydrogen, two points of some interest were referred to by those taking part. During the last two years, the experimental confirmation of the theoretical anticipations of the differences in behaviour, both physical and chemical, of the two hydrogen isotopes has proceeded at a remarkable speed. In the course of these investigations, in which both light and heavy hydrogen have been employed under similar conditions, it has been found possible to examine by isotopic labelling of the hydrogen atoms in a molecule a certain number of what may be termed exchange reactions.

The two simplest exchange reactions involve reactions between the gaseous isotopes themselves and between deuterium and water



In the catalytic hydrogenation of unsaturated organic compounds, such as ethylene or benzene in the presence of nickel or platinum as catalyst, the experiments on the replacement of the hydrogen by deuterium not only provide a confirmation of the view originally advanced by Sabatier that a metallic surface monohydride is the effective catalyst, but also reveal the interesting fact that exchange reactions occur and that these can proceed independently of the process of hydrogenation, namely:



Whilst the energetics of these reactions have not been investigated in great detail, the qualitative evidence indicates that the energies of activation are small, suggesting that the reactions are brought about not so much by an unexpected fragility in the covalent link between carbon and hydrogen when the hydrocarbon is adsorbed, but rather by a species of atom interchange between adsorbed atoms, one being attached to the hydrocarbon, a mechanism similar in some respects to the *ortho-para* conversion in hydrogen effected by hydrogen atoms. Incidentally, our crude picture of the interactions which occur when a molecule such as ethylene is adsorbed on a nickel surface has to be modified to a very considerable extent, and also the migration of double bonds

in complex organic compounds in the presence of such hydrogenating catalysts may merit thorough investigation.

Deuterium thus provides us with a tool to examine exchange reactions, some of which as we have seen are not only of a somewhat unexpected nature but also could not have been discovered by the ordinary methods of investigation. In addition, deuterium is proving of great value in assisting us to elucidate the mechanism of a number of chemical actions involving hydrogen.

Such reactions may involve participation of hydrogen atoms, hydrogen molecules or unstable intermediary compounds of hydrogen, for example, O_2H in the hydrogen-oxygen reaction or NiH in hydrogenating reactions at a nickel surface. By suitable experiments, it is possible to examine the changes both in the velocity and in energies of activation caused by the replacement of hydrogen by deuterium, and from such data to determine, sometimes uniquely, in other cases by elimination, which is the rate-governing step in the reaction mechanism and which of the three possible participants enumerated above is actually involved in this step. In this way, it has been found possible to confirm that the mercury photosensitised reduction of nitrous oxide takes place through an atomic mechanism, that the rate of the photochemical combination with chlorine is governed by the link involving a hydrogen molecule:



that the mercury photosensitised reduction of ethylene does not proceed through a chain mechanism; and that the chain mechanisms of the thermal combination of hydrogen with nitrous oxide and oxygen differ in that in the former a hydrogen atom is involved in the slowest link reaction and in the latter either a hydrogen molecule or a compound such as O_2H . Further information on the zero point energies of such complexes may permit of a decision between these two possibilities.

It was evident from the discussion that, quite apart from the more sensational and, at present, much more mysterious action of compounds of heavy hydrogen, especially water in biological processes, the new isotope provides an extremely effective weapon with which to extend our knowledge of the mechanism of the reaction kinetics of what are generally regarded as simple systems. E. K. R.

Hydrogenation of Coal in Germany

THE partial conversion of coal into liquid fuels by treatment with hydrogen gas under pressure at high temperatures is a technical process which is finding application in Great Britain, and a description of the method as used in Germany, given by F. Rosendahl (*Die Naturwissenschaften*, 33, 554; 1934), is therefore of interest.

The development of the original process due to Bergius has been brought to a successful stage by the I. G. firm. The conditions for operation require that the reaction should be accelerated by suitable catalysts and that the sulphur, nitrogen and oxygen of the coal should be set free and united with hydrogen. The design of apparatus which could

resist the action of sulphur and hydrogen under high pressure was also a difficult problem. As catalysts, the sulphides of iron, tungsten and molybdenum have been adopted, but the physical state of the contact mass is of great importance. In this way, two-thirds of the coal is converted into light liquid hydrocarbons, and it is possible to produce illuminating oil from coal.

The process occurs in two stages. In the first, the carbon compounds are decomposed and the carbon converted into hydrocarbons. This stage is practically quantitative, 15 per cent of gaseous and 85 per cent of a mixture of low and high boiling oils being formed. This stage is operated with a paste of