Recent Reactions between Theory and Experiment.[1]

The Raman Effect: The Constitution of Hydrogen Gas.

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IN watching the advance of science, and particularly of the physical sciences to-day, one cannot fail to be struck by the very close connexion between theory and experiment—a relation which is probably more intimate than at any other period of scientific history. Every new experimental observation is at once seized upon to test whether it can be explained by existing theories, and if not, to find the modifications necessary to include it in the general theoretical scheme of natural processes. The mathematical analysis often suggests the possibility of unexpected relations which can be made the subject of fruitful experimentation. These two, in a sense, complementary branches of physics profoundly react and interact with each other, and their united efforts lead to a greatly accelerated rate of advance in knowledge and understanding of the essential principles involved. The rapidity of advance in physics, which has been so marked a feature in the last decade, is mainly due to this close combination of theory with experiment.

It will be seen that this interaction is clearly manifest in the subjects which I have selected to speak of to-day. I wish to refer briefly to certain recent discoveries which have excited much interest among physicists and chemists, and have thrown much new light on problems which have long been the subject of close investigation.

The scattering of light by small particles and the 'Tyndall blue' of the scattered light, when white light from the carbon arc or the sun falls on a solution filled with a multitude of small particles, are well known. The late Lord Rayleigh in 1871 first gave the mathematical theory of the scattering of light by such particles, and was able to account in a general way not only for the colour of the reflected light but also for its state of polarisation. He suggested that light should be scattered, not only by particles containing many millions of molecules, but also by the individual molecules themselves, and that the blue of the sky was probably due mainly to the scattering of sunlight by the molecules of the atmosphere in its path.

This suggestion of molecular scattering was strikingly confirmed by the experiments of his son, the present Lord Rayleigh, who showed that scattering of light could be observed in gases freed from all dust nuclei, and that the light scattered perpendicularly to the direction of the incident beam was mainly plane polarised.

In recent years there have been a large number of investigations on the scattering of light, not only by gases but also by liquids and solids, with especial attention to the amount of scattered light and the degree of its polarisation. I shall not refer here to these results and the interesting deductions that have been made from them, but concentrate attention on a more recent development. Sir Chandrasakara Raman, of the University of Calcutta, who had for many years experimented on this subject, made an important observation which has thrown much new light on this question. For simplicity, suppose that monochromatic light of a definite frequency passes through an organic liquid, say, benzene or toluene, which has been carefully purified. It was observed that the colour of the scattered light was distinctly different from the incident beam, showing that the light had in some way been altered by scattering by the molecules in the liquid. To examine this change more accurately, the scattered light was passed through a spectroscope. A striking result was observed. The strongest line was equal in frequency to the incident light, as was to be expected on the classical theory, but in addition a number of new lines were observed on the low-frequency side of the main line, and a few fainter ones on the high-frequency side. By the process of scattering, a set of new discrete frequencies had thus made their appearance. An excellent account of these beautiful experiments was given this year by Raman and Krishnan in our *Proceedings*. Similar effects were observed by Landsberg and Mandelstamm by examining the light scattered by certain crystals.

Such experiments are not easy, for the scattered light is very feeble, and long exposures with intense sources of light are necessary to bring out the relatively faint new lines. An examination of the results showed that the changes of frequency depend on characteristic frequencies of the molecule, connected with its vibrational states.

The interpretation of these results is most clearly seen by consideration of the similar effects in gases, and we shall consider these first. For example, if ν be the frequency of the incident light, the frequencies of the new lines are $\nu - \nu_1$, or $\nu + \nu_1$, where ν_1 is always found to be a difference between two fundamental frequencies of the molecule. This is completely in accord with the quantum theory of scattering, which was given formally by Kramers and Heisenberg in 1925. It is to be presumed that the light scattered by liquids is of the same nature, and the frequency shifts are due equally to differences of molecular frequencies; although in molecules, which absorb strongly in the infrared, these differences may themselves appear as actual molecular frequencies.

It is of interest to note that the possibility of a process of this kind, involving the appearance of new frequencies, had been predicted by Smekal as well as by Kramers and Heisenberg. While theory and experiment agree admirably for gases, the theory could not have been legitimately extended to the case of molecules of a liquid, and here the Raman effect provides a new and effective tool for determining frequencies which are naturally present in a liquid or a solid.

It is clear that this new effect may be of great importance in determining the slow characteristic frequencies of molecules in the infra-red, which may be difficult to measure by other methods. This new discovery, of great interest in itself, thus promises to open up a new field of experimental inquiry and to throw valuable light on the modes of vibration and constitution of the chemical molecule.

It is naturally of great interest to consider the processes occurring in the molecule that give rise to these scattered radiations. The action of a train of waves in its passage through the complex electrical system of a molecule, which may be set in vibration in a variety of ways, is naturally very complicated and difficult to explain briefly in simple language. If, however, we content ourselves with a consideration of the energy changes only in the radiation, and disregard the detailed mechanism involved in the radiation processes, a simple explanation can be offered on the ideas of the light quantum.

We start by observing that it is a general consequence of wave mechanics that if a system possesses a number of states of equal energy, there is usually a finite probability of a transition from one of the number to any of the others. Consider a quantum of light, of frequency v and energy hv, falling on a molecule in a given direction. The quantum and the molecule are to be regarded as a single system. This system has a number of other states of the same energy. First, those in which the molecule is unchanged and the original quantum is scattered in a new direction without change of frequency; transitions to these states correspond to Rayleigh scattering. Secondly, other states in which the state of the molecule is changed, its energy being altered by $\pm hv_1$, while a quantum of light of energy $hv \mp hv_1$ is scattered in some new direction. Changes to these states correspond to the Raman effect, where frequencies $v - v_1$ and $v + v_1$ are observed. The actual changes occurring in the molecule to give rise to these new frequencies can only be inferred from a detailed consideration of the possible modes of vibration of the molecule itself.

I shall now consider a very interesting discovery which has been made in the past year. It has been found that, in a sense, hydrogen consists of two different kinds of molecules, which under ordinary conditions of temperature and pressure behave in a distinctive way; for example, the specific heat and conductivity of the two kinds of hydrogen are very different. The hydrogen molecule in the normal state consists of two nuclei and two electrons. On the ordinary views of the gas-kinetic theory, it is to be expected that the molecules, in addition to their ordinary velocity of agitation, may rotate on an axis perpendicular to the line joining the nuclei. On the quantum theory, it has a series of states of rotation which are specified in terms of a quantum number which has the values 0, 1, 2, 3, etc. Experiments on the band spectrum indicate that in ordinary hydrogen gas at atmospheric temperature the molecules

which have rotation numbers 1, 3, 5, are about three times as numerous as those with even rotation numbers, 0, 2, 4, . . . For convenience, the molecules of even rotation number will be termed α-hydrogen, and those with odd rotation numbers β-hydrogen.[2] When in equilibrium, the relative number of hydrogen molecules in the different rotation states at any temperature is governed by the well-known Boltzmann law of distribution and can be calculated approximately. If, however, ordinary hydrogen gas is reduced to a low temperature, say, that of liquid hydrogen, on the ordinary kinetic theory it is to be expected that the rotation of the molecules should practically vanish; that is, the majority of the molecules should have a rotation number 0 and only a small fraction, depending on the temperature, remain in the higher rotational states.

Actually, however, it is found that while α-hydrogen is mainly in the rotation state 0, the β-hydrogen does not change into the state 0, at any rate for a long time, but retains its individuality, although, of course, the ratio of the number of molecules in each odd rotation state is governed by the Boltzmann law. The surprising fact emerges that the β-hydrogen under the influence of ordinary gas-kinetic collisions is only with great difficulty changed into α-hydrogen. The time required for true equilibrium, after lowering the temperature, may be measured in months, or even in years under some conditions. This interval depends, as we should expect, on the pressure and temperature of the gas, since these govern the number and magnitude of the molecular collisions. This means that a molecule with odd rotation number finds a very great difficulty in passing to the even state of rotation.

A general explanation of this can be given on wave mechanics and appears to be intimely connected with the very weak coupling between a rotation state of the molecule with the spin of the minute individual nuclei (protons) which make up the molecule.

While under normal conditions, the passage of β-hydrogen into α-hydrogen and vice versa is excessively slow compared with the duration of an ordinary experiment, yet the transitions can be greatly accelerated by appropriate treatment of the gas. For example, if hydrogen cooled to a low temperature is subjected to an electric discharge, there is a rapid transformation. The passage of the cooled gas through charcoal immersed in liquid air or liquid hydrogen acts in a similar way. When the hydrogen is rapidly cooled to the temperature of liquid air, the odd rotation states are much in excess over the equilibrium value. The passage through the charcoal causes a rapid transformation of the β-hydrogen and the emerging gas at the temperature of liquid air consists mainly of α-hydrogen.

It is of great interest to note that if the gas is warmed to ordinary temperature after passage

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[2] The terms 'para'- and 'ortho'-hydrogen have been sometimes used for what I have called α and β. This seems undesirable, since these names are still required to distinguish the *electronic* states in analogy with those of the helium spectrum.

through the charcoal, it remains mainly α-hydrogen, while hydrogen gas in equilibrium consists only of about one-quarter of α-hydrogen. It has been found that the specific heat of the gas and its heat conductivity at the temperature of liquid air before passage through charcoal are markedly different from the values for the gas at the same temperature issuing from the charcoal. In a sense, we may say that α-hydrogen has been obtained by this process in an approximately pure state. The effect in charcoal cooled to the temperature of liquid helium would be even more complete. It seems probable that the rapid transformation brought about by passage through charcoal is catalytic in nature and may quite likely be due to the dissociation of the molecules into atoms and their subsequent recombination to form new molecules.

This striking and unexpected behaviour of hydrogen—the simplest molecule known to us—is of great theoretical as well as experimental interest. It had been known for some time that no satisfactory theoretical explanation could be given of the change of specific heat of hydrogen with temperature, either on the kinetic theory or with the modifications of the theory based on the older form of the quantum theory.

A new orientation of our ideas was given by the development of the wave mechanics theory. One of the first triumphs of this theory was the explanation by Heisenberg of the complex spectrum of helium. The two types of spectra which appeared were shown to be connected with the different directions of spin of the electrons themselves. In one case, the orbital wave functions were symmetrical and in the other case antisymmetrical. From analogy with the behaviour of the helium atom, Hund showed that it was to be expected that the hydrogen molecules should consist of two kinds; in one, which we have called α-hydrogen, the wave functions were symmetrical in the rotational wave function and in the other, called β-hydrogen, antisymmetrical. It was recognised that, on the wave theory, there must be a very weak coupling between the symmetrical and antisymmetrical states, so that the transition from one state to the other must be fairly slow.

Dennison, in a paper published in our *Proceedings* in 1927, calculated the specific heat of hydrogen at different temperatures on the bold assumption that the time of transition from one state to the other was very slow—of the order of one year—compared with the time required for a determination of the specific heat experimentally. Under these conditions, ordinary hydrogen could be considered to be a mixture of two gases, which have not only different specific heats but a different variation with temperature.

By assuming that the ratio of α- to β-hydrogen was 1 to 3, he found that the calculated and observed specific heats agreed over the whole range of temperature. This ratio between the two states of hydrogen was in accord with the observations of T. Hori on the band spectrum of hydrogen.

Experimental proof of the accuracy of this deduction was soon forthcoming by a variety of experimental methods. Prof. J. C. McLennan examined the Raman effect in liquid hydrogen and found that the changes of frequency observed in the spectrum of the scattered light indicated that hydrogen at this temperature consisted of a mixture of molecules having even and odd rotational states. The relative intensity of the lines was in accord with the relative distribution assumed by Denison.

About the same time experiments were undertaken by Eucken and Hiller and by Bonhöffer and Harteck in Berlin. Eucken and Hiller determined the specific heat of hydrogen under different conditions. Hydrogen at high pressure was kept for some days at the temperature of liquid air, the specific heat was measured at intervals and at different temperatures, and was found to show marked variations with time. The fraction of α-hydrogen was found to vary from 25 per cent at the beginning to 95 per cent after a long interval. It was found that the rate of transition from β- to α-hydrogen at liquid air temperature depended on the pressure of the gas and was approximately proportional to the number of molecular collisions.

Bonhöffer and Harteck used a simpler and more rapid method for following the change of state of the hydrogen under different conditions. By measuring the change of resistance of a heated wire in the presence of the gas, the changes in the heat conductivity of the gas, which varies with the specific heat, were easily followed. We have already referred to their experiments of passing hydrogen through charcoal at low temperature and of the effect of the electric discharge. The results of the beautiful experiments of Bonhöffer and Eucken afford a complete and striking proof that hydrogen under ordinary conditions is composed of two sets of molecules which are transformed into each other so slowly that they may be regarded in a sense as two distinct gases differing in specific heat and conductivity. The specific heat of α-hydrogen at low temperature is greater than that of β-hydrogen. A large quantity of heat is given out in the passage of β- into α-hydrogen. At very low temperatures, the heat evolved in this transformation is greater than the heat of volatilisation of liquid hydrogen.

It may be of interest to note that the peculiar behaviour of hydrogen might have been discovered long ago, for no new experimental knowledge or technique is involved. Attention, however, was only directed to this subject by the failure of existing theories to account for the variation of specific heat of hydrogen with temperature. The development of wave mechanics threw new light on this problem and a happy suggestion, based on this theory, was found to fit in well with the observations on the specific heat. Following this clue, the question was attacked experimentally by several different methods, with results in complete accord with the predictions of theory.