# HELMHOLTZ MEMORIAL LECTURE.

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"And Nature, that old nurse, took The child upon her knee, Saying 'Here is a story book Thy father has written for thee.

" 'Come wander with me' she said, 'In the regions yet untrod, And read what is still unread, In the manuscripts of God.'

"And he wandered away and away With Nature, the dear old nurse, Who sang to him night and day The rhymes of the Universe."

LONGFELLOW.

WHEN standing in Chamounix, beneath Mont Blanc, we are no doubt impressed with its majesty, and oppressed with a sense of our insignificance; but we must remove to a greater distance if we would judge properly of the relative importance of the giant peaks around us, if we would see the great mountain towering above its neighbours, the heaven supplied source of those glorious glaciers that in Chamounix seemed to spring from the lesser heights around. We are now only a little more than a year after Helmholtz's death, and hardly sufficiently removed from his times, from the immediate presence of his contemporaries, from the personal acquaintance of so many great minds, for us to judge with perfect confidence of the relative importance of the giant intellects around us. His contemporaries, no doubt, valued "gentle Shakespear, fancy's child," as they valued Ben Johnson or Marlow; but it was reserved for succeeding generations to appreciate how immeasurably this woodland warbler outstripped these in majesty of intellect. That Helmholtz has been one of the great scientific intellects of his time is already abundantly evident. We can, however, hardly judge what his exact position as a founder of the doctrine of conservation of energy, of the theory of vortex motion, of the principles of sight and hearing, is in relation to those other great scientific intellects, Faraday, Maxwell, and Hertz, who have laid on a new foundation our knowledge of the all-pervading ether, or Jenner and Pasteur, who have created a rational foundation for medical and surgical treatment, and originated the conceptions by means of which we hope some day



to learn the structure of matter, or Darwin, who has done more than any other, since Copernicus and Newton, to revolutionise man's conception of the world around him, and of his place in Nature.

It is remarkable how many great men have attributed their peculiar gifts to the peculiarities of their family life. Helmholtz seems to have considered the drudgery of school as little better than a necessary evil. What he liked, that entered into his life; what he disliked, was hardly assimilated at all. He puts it-" What a man does easily he usually does willingly." I would rather say-"What a man does willingly he usually does easily." It is the taste that creates the will to do, and that makes the hard work easy. His love for nature was satisfied by learning geometry from wooden blocks, by walks in the country with his father, by experiments with acids on his mother's linen, by making telescopes with spectacle glasses, by studying books on physics in his father's library. Thus was nursed, that impulse to dominate the actual world by acquiring an understanding of it which became the passion of his existence, and guided his whole life. Thus his real life seems to have been nourished by things quite outside his school experiences, and he seems hardly to have looked upon educational institutions as truly educational till, in the German University, he had scope for expanding in the directions for which his nature was specially fitted. Like an ivy plant in an herbaceous border, clipped here and there to suit its surroundings, it never expands freely, nor does itself justice, nor produces really healthy growth till transplanted to the neighbourhood of the wall over which its nature is specially fitted to make it grow, and where it develops into its perfect ideal. This passion to dominate nature drove young Helmholtz to attack great problems. Young men are favourably circumstanced for doing this. Many try, few succeed. Hope, enthusiasm, energy are theirs. Unencumbered by old habits of thought their minds develop new roads of attack. The development of habits is necessary for the individual, and hence for the race, but it stops development along new lines. Hence the necessity for kindly death, that new minds may grow, that mankind may improve. To young Helmholtz the then being discovered principle of the conservation of energy, seemed almost self-evident. He thought that all the scientific world was as satisfied as himself, except a few medical and biological students, whose studies had kept them out of the flow of physical science. For the sake of these he wrote a paper on the Conservation of Energy, and then it appeared that he was a pioneer. Physical science students had not grasped the generalisations they were engaged on. This young master mind was required to clear the new path, to call the attention of those engaged in removing some immediately present obstacle to the immense prospect

around them, to show them the country they had invaded, and hoist the flag of science in the conquered territory.

To Baconian England it seems strange to be told that physicists had to contend against Hegelianism in Germany. That preconceived notions of what ought to be may obscure mankind's vision of what is, in both scientific and religious circles, is what we all expect; but that what we in England would call metaphysical views of phenomena should obstruct diffusion of truth, shows a seriousness about metaphysics in Germany that it would be hard to parallel in England. Britain has produced one of the most original and brilliant metaphysicians since Plato, the great and good Bishop Berkeley; but this father of Hume, who startled Kant from his scholastic dreaming to create all modern metaphysics, has never been taken seriously by his fellow-countrymen. Metaphysics is to most of them inanity, and we consequently wonder, when we see metaphysical theories taken so seriously elsewhere as to produce effects similar to those produced here by authority or by religion.

Great problems attracted Helmholtz's attention : those of spontaneous generation and of the source of energy in muscular contractions. But after a little work on these, his duties as lecturer in Königsberg on general pathology and physiology, led him to invent the ophthalmoscope, which raised him so much in the estimation of the world and of his colleagues, that he was thenceforth able to devote his time and energies to the subjects he liked best himself, or to such as he could not get others to do for him. To his assistants and students he left the carrying out of investigations whose methods and ends were so far defined that a student or assistant could carry them out with occasional direction from headquarters, while he himself engaged in investigations that might lead to no result, and the methods of attacking which were as yet unknown. How fortunate for mankind that this great intellect had this assistance! that the endowments of German universities should be available for providing such assistance, instead of being frittered away in providing scholarships for wealthy schoolboys to bribe them to devote unwilling energies to the culture of their minds, an end that would be much better attained by the cheaper method of inflicting heavy fines or other such well deserved punishments on those who wilfully and wickedly throw away the great opportunities of improvement presented for their use. Helmholtz thus obtained time for continuous thought, time to wait for discoveries, time to prepare the ground of thought by familiarity with the problem in all its aspects, time for the evolution of all sorts and kinds of hypotheses to be rejected, one by one, till, by a process of natural selection, the teaming brain at last saw the true solution break forth like the sun from behind

the clouds that this sun has all along illuminated, and each bright spot of which had hitherto held out hopes of success. As the natural selection of animals gradually built up mankind from an undifferentiated jelly, so the conscious selection of a genius builds up the great idea from the germs of thought. Continuity and variety are in each case the conditions for rapid progress, and in the brain workshop of a Helmholtz we see the indefatigable workings of a superabundant productiveness bringing forth innumerable varieties for selection: the brain action is natural, too. To Helmholtz the results of his work are the "natural" outcome of what went before. Is there any real difference between the productions of nature and the productions of intellectual activity ?

To oneself, no doubt the selection each time is for the sake of some ulterior end, for the attaining of some object, due to a final cause, but to another observer the brain action must all be explicable as due to efficient causes. These latter do not include the former, rather each makes the other possible. Can it be otherwise in that teaming creation of which we are observers, in which we only see efficient causes, for we are only observers, and not feelers of the thoughts of nature.

And which of all the children of his intellect did Helmholtz value most? Not the ophthalmoscope that took him a week to get to work, nor his investigations on the physiology of sight and hearing that took him years to work out in their innumerable details, nor those theories of chemical and electrical action that occupied his later years. No, it was his victories over mathematico-physical problems of fluid motion, vortex motion, and discontinuous motion that he seems to have looked upon as his greatest triumphs. These seem to be the problems that he speaks of as having given him such months and years of thought to find a solution of; that he attacked this way and that, and at last solved, and having solved, saw then a broad and easy path to lead others by; a path that was obvious enough when seen, but had yet eluded his grasp, till after years of devious wandering he reached the goal, and then discovered the direct route. Their very simplicity now makes it almost impossible for those who follow to see in these works the value Helmholtz attaches to them. Great and magnificently general as they are, laying as they do a possible, nay, probable, foundation for a dynamical explanation of all natural phenomena, they seem now so obvious that, like Gallileo's law of the motion of falling bodies which laid the foundations of all dynamics, they are almost taken for granted as a natural possession of the human mind. We are inclined rather to think our predecessors must have been blind not to see such obvious things than to credit the discoverers with preternatural insight.

To the Chemical Society the question of most importance is how Helmholtz's work bears on chemical theories. Unfortunately, there is very little really known about this in respect of vortex motion. Lord Kelvin has made the brilliant suggestion that atoms are vortex rings, and upon this all subsequent guesses have been founded; for our knowledge in this direction is very little better than guesses. Helmholtz had shown that vortices in a perfect liquid could neither create nor destroy one another. Once created, a vortex ring is permanent, like an atom of matter. It can go fast or slow, it can vibrate, it can enter into partnership with others or rebound from them, according to circumstances, but vortex rings cannot destroy one another. They can change in innumerable ways, can be drawn out into thin threads, or gathered up into spherical knots; but one of their properties, called their vorticity, remains indestructibly the same during all these changes. This was Helmholtz's great discovery, and is the foundation for Lord Kelvin's brilliant suggestion that atoms are vortex rings in a perfect liquid. Advances upon this suggestion have been made, though most of these advances have brought to light serious difficulties in the way of accepting the hypothesis in its primitive simplicity. Something has been done to attack the problem of a medium like a gas of thin vortex rings, and has brought to light two very serious difficulties. The more energy we give to the rings the greater is their inertia, and the slower they move. Now it is generally believed that the inertia of a body is independent of its temperature. We can be sure that the ratio of the inertia to gravitation is independent of temperature to a very high order of approximation. We may be practically certain that the mean temperature of the earth is much higher than that of the moon, and that of Jupiter than of his moons. Now, if the inertia of a body increased with its temperature but its coefficient of gravitation did not, it would lead to very serious discrepancies in the astronomical theory of the motions of the various members of the solar system. An investigation of possible small departures from constancy of coefficient of gravitation would be most interesting in connection with the question as to the effective inertia of electrons. Departures from constancy of refractive power seem to show that the drag of ether on matter is not exactly proportional to mass, and if any sensible amount of the inertia of matter is due to an ether disturbance accompanying its motion there might be a difference between the inertia of the matters constituting what are probably such differently constituted bodies as the planets. We cannot be at all so sure that both inertia and gravitation do not increase simultaneously with temperature. Very few experiments indeed have been made as to the variation of the weight of a body with tempera-

It is difficult to weigh hot bodies accurately, and, in conseture. quence, there does not seem to be any conclusive proof that the weight of a body does not change with its temperature. If it does not do so by a measurable amount the simple vortex ring theory of matter can hardly be true. As regards the velocity with which vortex rings move, the elementary dynamics of how sound is propagated by a medium like gas, in which the molecules are only for a short part of their time in collisions, acting on one another, and are for by far the greater part of their time engaged in flights between collisions, proves that the velocity of sound must be proportional to the velocity of flight. It is known that the velocity of sound increases with temperature, and so we are landed on the horns of a dilemma, either the molecules are not thin vortex rings in an otherwise simple liquid, or else when we give heat to a gas we are in some mysterious way taking more energy from it than we give to it. This latter suggestion, if it can really be worked out, would get over the other difficulty as to the variation of inertia with temperature, for the suggestion is based upon the supposition that we have to deal, not with the motion of the ring as a whole, but only of its rotational core. Some people may have rather a preference for this latter horn of the dilemma, but I certainly think that all we know of matter and the ether points to the conclusion that whatever atoms are, there is certainly a complicated structure in the space between the atoms. This is required to explain electromagnetic actions, and consequently atoms are certainly not simple thin vortex rings in an otherwise unmoving and structureless liquid. It has been shown that an intensely moving liquid could propagate disturbances somewhat like light, if there were no diffusion of the motion, and at the last meeting of the British Association we were told of a structure for that motion which would not diffuse.

In this connection, it may be worth while pointing out that as vortices move of themselves freely and independently of the density of the liquid, there is no necessity for supposing that the density of the liquid is small. In fact, the simple theory would point to the conclusion that its density may be greater than that of platinum. This would require the energy per enbic centimeter of the turbulent motion to which the propagation of light is due to be very large indeed, approaching a million of millions of Kilojoule's, *i.e.*, it would be equivalent to a million horse power for 10 hours a day for nearly a month. It has been suggested that an atom is a hole in a vortex cell ether. The suggestion is ingenious, but is hardly consistent with the separateness of atoms, their ability to combine and separate again regaining all their primitive properties. So far, no better suggestion has been made than that atoms are regions of vortex

motion, and as it seems quite possible that a vortex ring might take up a steady motion of association with a vortex cell, and in moving from place to place may carry energy proportional to the square of its rate of translation, and still more as no one knows with certainty how vortex rings would behave in a structureful medium such as the ether is, I prefer in our ignorance the horn of the dilemma, that holds that atoms are not simple thin vortex rings in an otherwiseunmoving liquid.

The theory does more, however, than land us in dilemmas. There is another result of Helmholtz's work which, though it too is full of difficulties, has a sufficiently curious analogy to chemical facts to make it wonderfully possible that there is some connection between the two. When two parallel vortex threads are near one another, and are both rotating in the same direction, they can take up a steady condition of rotating round one another which is pretty stable. Three vortex threads can do the same, taking up positions at the corners of a triangle. Four, five, and six can behave likewise, but if we try to make seven vortices rotate round one another the condition becomes unstable. That there are unstable states of this kind seems certain, but there is also no doubt that any number of vortices could exist as a stable system, thick vortices being in fact collections of vortex filaments. The chemical analogy is, however, between these systems of vortices that become unstable when more than six are involved, and the chemical fact that no element has ever been required to possess more than six monovalent elements simply connected with it. Now, though the connection is undoubtedly farfetched, and though the suggestion does not seem to explain why three or more hydrogen atoms should not be pretty fond of revolving round one another in a happy family, yet there is undoubtedly something very striking in the numerical coincidence between the number of bonds required for chemical combinations and the number of vortices that can be absorbed into a single system of this kind. Pending any other dynamical suggestion as to why chemical bonds are limited in numbers, there seems sufficient grounds from this coincidence for keeping the matter prominently in view, in hopes that further light may be thrown on these fundamental questions. The other directions in which one might look for numerical coincidences of this kind are in the finite numbers of stable positions of magnets, in the finite numbers of the regular solids, and of the possible crystalline systems. Considering the success that has attended the development of the analogies founded on the geometry of the tetrahedron in the case of carbon, it is certainly well worth while developing corresponding solid geometrical analogies in respect of other elements. Considering that a vortex ring is in many respects

an area over which sources are distributed on one side and sinks on the other, and that sources and sinks behave in some respects like positive and negative electrified points, there seems some possibility that vortices may in some respects behave like polar bodies. From what we know of nature, a kinetic analogy is always to be preferred to a statical one, being more probably like the truth. If it is required to connect the geometry of the tetrahedron as regards the asymmetric carbon bound molecules with the vortex ring theory of matter, we must proceed somewhat as follows. It appears at first sight as if it would not suffice to arrange the four vortex filaments that rotate with the carbon simply at four of the corners of a pentagon to make a system competent to circulate along with the carbon filament at its fifth corner. It is well known that four points in a plane cannot represent the atomic bonds of carbon. One of them must be out of the plane of the other three in order that the rotational properties of many carbon compounds may be represented. In the case of the vortex filaments a corresponding result might be obtained by supposing the attached filaments to be wound corkscrew fashion round the carbon filament. Such corkscrew filaments are, no doubt, possible, but, unless vortex filaments can cross one another, which is certainly not generally possible, no free vortex ring could be wound corkscrew wise round another. The same result might follow by supposing that there are right-handed and left-handed carbon atoms. Though such might undoubtedly exist, this seems a very improbable explanation of the rotational light phenomena in view of the possibility of changing one of these isomeric bodies into the other by a moderate rise of temperature. We must, then, conclude that the difference between the right- and left-hand distributions of filaments must be a difference of their order of distribution round the pentagon taken in conjunction with the circulation of filaments round one another. If we suppose four filaments, a, b, c, d, arranged in this order, when we go in the direction of circulation we can have a complementary system arranged in the order d, c, b, a, taken in the direction of circulation, and these two systems differ in the same sort of way as a right- and left-handed screw. In all these arrangements there would be a greater facility of interchange between a and b, *i.e.*, between neighbouring filaments, than between a, c or b, d, so that in addition to this right- and left-handed isomerism there would be a possible distinction between a, b, c, d and a, c, b, d. This, so far as I know, has not been observed, and would consequently throw doubt on the suggestion that this vortex analogy is founded on any real likeness. There seem also very great difficulties in extending the analogy to complicated cases, such as the benzene ring, where a carbon filament has to be partly satisfied by one bond of a complex

molecule, partly by one bond of another carbon atom, and partly by two bonds of a second carbon atom. Too little, however, is known of the possible combinations of vortex filaments to be at all sure whether six filaments, each with an attendant satellite, could not very well circulate round one another in a stable group. In this case, as in the former one, the direction of circulation would bring us the two isomeric distributions of the satellites round the system that is at present represented by the alternate double and single bonding.

There are several serious difficulties from the chemical point of view to the supposition that these combinations of thin vortex rings are really like what is actually taking place. The possibility of a permanent combination of rings has only been proved possible when the strengths of the components are equal. Now this is quite out of harmony with known chemical phenomena. Compare, for instance, the two similar bodies water and cetyl. Their chemical compositions, H·O·H and C<sub>16</sub>H<sub>33</sub>·O·H, and behaviour show that the complex system  $C_{16}H_{33}$  goes in and out of combination in just the same sort of way as the simple atom H. Now a vortex ring, C<sub>16</sub>H<sub>33</sub>, consisting of thin filaments would according to theory be 65 times as strong as the simple H ring, and consequently would not behave as a whole in at all the same way as this H ring. If it is really necessary that the components of a system must be of the same strength, the consideration of the various alcohols is fatal to the theory that chemical combination is at all like this association of vortex rings. However, the proof that equality of strength is necessary in order to make this association permanent seems to me inconclusive, and so there may vet be something important in the analogy.

Another serious difficulty is as to the explanation of the enormous differences of mass of the atoms. Mercury, for instance, is 200 times as massive as hydrogen. Now, according to the hypothesis that has been proposed, the strength of the mercury ring is the same as that of the hydrogen one, and the only way in which it can have this enormous mass is by its having a radius 14 times as great. If the average volume occupied by an atom be considered as proportional to the sphere upon which the ring would lie as a great circle, it would follow that the volume of a mercury atom would be something like 2,800 times as great as that of a hydrogen atom. This does not seem at all in accordance with what we know of these bodies. This difficulty would be largely surmounted if we could adopt the proposal already mentioned of supposing that when dealing with vortex rings we have to deal with the momentum of the core of the ring, and not with that of the whole motion involved. We might, then, suppose that massive rings had thick cores with a slow rotation, so as to have the same strength but a greater momentum than the thinner rings,

even though the radius of the rings as a whole differed only slightly. The theory of nearly spherical and worm-like vortices would lead to a somewhat similar solution, but then the theory of their association into systems has not been at all fully worked out, and we cannot say whether it does or does not lead to results such as are known to hold in chemical combination.

A further difficulty from the chemical point of view is that carbon should be a diad, and only by becoming doubled upon itself in a way that has never been proved to be possible for a vortex ring can it become a tetrad. Similarly, nitrogen becomes essentially a monad, and there seems to be no explanation of  $N_2O_5$ . The suggested doubling by which carbon becomes a tetrad would produce two allotropic forms of tetrad carbon, one right-handed and the other lefthanded, and there is no evidence for this. In fact the whole system of atomicity as evolved from the theory of the association of thin vortex rings is sadly at variance with that derived from the study of chemical facts.

This should induce study of other forms of vortex motion-study of thick rings and of spherical and worm vortices. There are several ways in which these latter are not subject to the same objections as thin ring vortices. They in some cases increase in velocity when energy is given to them, so that the objections depending on the velocity of sound increasing with temperature would not apply. The change of inertia with temperature would still exist. They could apparently swallow one another up, so that something analogous to chemical combination could exist, but too little is known about this to know whether the theory of their association would be less open to objection than that of thin rings. At the same time 1 expect much more from the investigation of the properties of a complex medium which would be capable of producing electromagnetic actions. Any suggestion as to the nature of atoms that does not explain electrolysis cannot be more than an analogy. There is some hope that a liquid full of energetic motion could explain electromagnetic actions, and a theory of electromagnetic actions depending entirely on the actions of electrons associated with atoms has been worked into The suggestion that electrons have an individual existence is it. undoubtedly tempting, but it is worth while keeping constantly in view the possibility that their constancy of quantity is connected with a constancy of structure of the ether rather than with any individual existence of each electron. This whole subject is so tentative that it is very doubtful indeed whether any real use could be made of these kinetic analogies at all comparable with the use that has been made of the statical analogy of carbon to a tetrahedron. Although kinetic analogies are certainly to be preferred to statical ones, yet our knowledge of the mechanism involved is still so very imperfect that, as in the case of the elasticity of solids, and even of gases, we are perforce driven to think in statical analogies, and though we know that the energy is kinetic, to deal with it as if it were potential. There is therefore no sufficient reason at present for not using corresponding statical analogies to represent chemical equilibrium, even though we may be pretty sure that we are not dealing with the matter in the manner which is absolutely like what is actually taking place.

The possibility of right-handed and left-handed vortex atoms has been mentioned. There are, in addition to the doubling of the atom on itself already mentioned, two ways in which these might exist. There might, in the first place, be a sort of temporary right- or lefthandedness produced by a corkscrew wave motion being propagated round the vortex. Such a vibration could hardly subsist permanently amongst the clash of molecules, but it may be worth keeping in view. There might, in the second place, be a circulation of liquid inside the voltex core either in the right- or left hand direction round the line of motion of the vortex ring. This would be a permanent quality of each atom, one that no interactions of vortices could either produce or destroy. But it is a quality that might be a very serious one for the vortex ring itself if ever it got drawn out beyond a certain length of circumference, for it might then make the circular shape quite unstable, and the result would probably be a vortex tangle instead of a vortex ring. Such a vortex tangle, if it could be kept within bounds, might do very well for an atom and may be better than a vortex ring, but the theory of such a tangle is beyond me, and I am afraid there would be a tendency for it to spread itself throughout space instead of confining itself to one place. May be it is by just such a destruction of vortex ring atoms that the ether has been made, and it may be that from time to time in the immensity of space these tangles undo and reform the atoms, thus rebuilding the universe out of its fragments and utilising the chance, by which the laws of thermodynamics prophesy the end, to prevent this very consummation. Anyway there seems plenty of scope for speculations founded on Helmholtz's discovery of the law of vortex motion. though I fear that until some genius directs our attention aright it can give little or no help to the chemist in his investigations.

One of the most interesting matters of a physicochemical character that Helmholtz worked at was the application of thermodynamics to chemistry. The application is, as yet, very limited. Comparatively few chemical processes can be brought through a complete cycle of operations, and still fewer are completely reversible. Unless these two conditions can be shown clearly to be applicable, we can only

apply the principle of the conservation of energy to the process in making quantitative calculations, and the second law of thermodynamics can give us very little quantitative information. There is, however, one important class of cases of chemical action which is reversible and to which we can consequently apply thermodynamics, namely that of a large number of electrolytic phenomena. Helmholtz has done a good deal in this direction, but a great deal still requires to be done both experimentally and in working out all that can be deduced from the experiments. In his method of treating the subject, he introduced a certain quantity which he named the free energy. This name is rather misleading. One would naturally conclude that it was connected with the proportion of internal energy that can be transformed into work by means of an engine, and it is connected with this, but in such a roundabout way, that anybody might easily make mistakes about it. When the internal energy is described as being divisible into two parts, one of which is bound energy and the other free, one would naturally conclude that no matter what one did, one of them could never be turned into work, while the other could, and that there was some difference in the nature of the energy in the body that made this distinction of quality. Now the internal energy in the body is really homogeneous, and we cannot separate it out into parts having different qualities in this way. As a matter of fact, changes of temperature change free energy into bound energy and vice versa, and free energy is the energy turned into work during isothermal changes, and is not derived wholly in general from the internal energy. In the case of a gas, for instance, there is during isothermal expansion practically no change in the internal energy while free energy is being expended on work. Hence the view that the internal energy can be divided into two parts, one bound and the other free, is a very forced view of what is really taking place. It is worth mentioning this because the name is seductive, and those who are not familiar with a subject are very liable to be misled by the seductive appearance of simplicity conferred by particular names. Of course this does not in the least detract from the value of the function itself which has been used under a variety of names by various investigators, and has proved in Helmholtz's hands a valuable means of deducing all that can be learned from measurements on electrolytic cells and from their alteration with concentration, temperature, &c. The complete determination of the thermodynamic properties of even one substance is not known. We know hardly anything about the changes of the specific heats of bodies with temperature and pressure. A few isolated attempts have been made to determine them, but in general our knowledge of the

thermodynamic functions of bodies is extremely meagre even as regards temperature and pressure, and almost nil as regards chemical changes of composition. This is a direction in which much more remains to be done by the co-operation of the chemist and the mathematical physicist. Many other applications of thermodynamics to chemical actions have been made since Helmholtz's time. By the use of so-called semipermeable diaphragms the process of diffusion of a salt in solution can be made reversible at least ideally. The theory of how semipermeable diaphragms act is not of much importance in these applications of thermodynamics, unless indeed they are nece sarily destroyed by their own action. If this is the case they do not make the processes involved reversible, and all the thermodynamic investigations that have been founded on the supposition that they are themselves permanent and unaltered are invalid. All that is necessary for the thermodynamical theory is that a semipermeable diaphragm is possible, and the fact that actual diaphragms are by no means absolutely semipermeable is an objection no doubt to the observations founded on what they do and is a serious difficulty in comparing observation with calculation, but it is no more an objection to the calculation of what would take place if a semipermeable. diaphragm is possible than the fact that even ice and air offer resistance is an objection to the prediction of what would occur if a stone were sliding over a perfectly smooth surface by calculation from the known principles of dynamics.

Very little is known about the theory of semipermeable mem-It is generally assumed that there are no heat effects. branes. depending upon their presence, but the corresponding mistake in neglecting the heat effects that occur when currents of electricityenter and leave a liquid lead to serious errors in the theory of galvanic cells, and until the theory and practice of semipermeable membranes agree more closely than they do at present, it is worth while looking for something of this kind. They are often spoken of as if they were merely some kind of molecular sieve. They seem really much more analogous to Graham's second class of membrane which only permit the passage of gases which dissolve in the membrane, so that their behaviour is quite different from that of simple sieves like earthenware, &c., for which the laws of diffusion are so very simple. When we come to deal with really molecular magnitudes, it is impossible, however, to draw a hard and fast line between physical and chemical permeability. One molecule may be able to penetrate amongst others, not so much because it is of the right size to get between them as because it has the right shape to do so. One cannot fit a square bar properly into a round hole. This question of shape is here mentioned merely as an example of one of various VOL. LXIX. 3 p

peculiarities of a molecule which may enable it to associate itself intimately with others in a way peculiar to itself. Such a peculiarity can in our ignorance only be called by the general term one of its chemical peculiarities. From the peculiarities of organic diaphragms there seems some reason to hope that we may be able to produce a set of judiciously constructed diaphragms each suited to let through molecular groups peculiar to itself and thus enlarge our means of what may be called chemical filtration. So far we seem to have attained very little farther than to be able to filter water from salts in solution.

At the same time many organic processes seem to require an actual carrying of material by currents such as we see in the living cells of plants. By such currents materials can be taken out of dilute solutions and then transported to places where they can, under new circumstances, be given up to strong solutions. Actions of this kind, of course, like the carrying of heat from low to high temperatures. require expenditure of energy. In living organisms we have many sources for this energy, and currents of the kind can easily be produced by superficial actions like the motion of camphor on water, which might continue till all the camphor was used up if clean water were constantly supplied.

In applying thermodynamics to chemical investigations there are some serious pitfalls into which investigators have fallen. In the application of the law of the conservation of energy there is great risk of assuming that the heat supplied is equivalent to the work done without bringing the system through a cycle. A very serious mistake of this kind has been recently published as a proof that osmotic pressure is proportional to the absolute temperature. This is very possibly true, although the experimental evidence is by no means for it, but rather the contrary, yet the proof given, which assumes that the heat supplied is all used in doing osmotic work, is entirely inconclusive. A complementary mistake is to neglect the external work entirely when it is small in the cases in the mind of the calculator, and to assume that the heat supplied is all spent in changing the internal energy. This may lead to very simple laws, and to ones that are approximately true in a great many cases, but a proof founded on any such neglect and which does not clearly point out the degree of approximation attained is utterly unsound. Yet a mistake of this very kind occurs within the first seven pages of a very valuable treatise on theoretical chemistry, so that it can hardly be considered unnecessary to warn others of such Another pitfall is to neglect the necessity for operations mistakes. being reversible. Theories as to explosions in guns and gas engines have been propounded and published in which this is neglected. The

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# FITZGERALD: HELMHOLTZ MEMORIAL LECTURE.

operations in both these cases are not reversed in the engines considered, and so the generally applicable second law of thermodynamics cannot be applied to them accurately. A similar mistake has been made in calculating the efficiency of engines when the feed supply, *i.e.*, the return process, is worked by a separate engine. If this method were used in an air engine, it could easily be arranged to give an efficiency much greater than what is generally called the theoretically possible efficiency. In a recently published work, it is stated, in connection with a thermodynamic investigation, that one of the processes involved is the mixture of water and salt solution, an irreversible operation unless by means of a semipermeable diaphragm, which is not mentioned. There are several proofs in vogue depending on the supposed incapacity of a system to cool itself below These sometimes neglect the fact that for this to its surroundings. be impossible the operations must constitute a cycle. By evaporation, bodies cool themselves below their surroundings, and in some cases where vapour pressures of different materials are considered in two limbs of a closed vessel, this possibility is overlooked, and at the same time the possibility is overlooked of both the limbs getting coated with the same material by distillation of a small quantity from one to the other. The failure of these proofs does not of course involve the falsehood of the thing proved, but it shows how careful those who apply physical principles should be, to be quite familiar with the subject considered. It is as risky for a chemist to apply mathematics as for a mathematician to lecture to chemists : we should work in co-operation.

In the case of calculating the connection between osmotic pressure and the lowering of boiling point by supposing that the level of the solution is raised above that of the pure water by means of a semipermeable membrane, an extension of the theorem may be obtained by supposing the membrane sunk to different depths in the water when an interesting theorem connecting the osmotic pressure with the total pressure in a liquid can be deduced.

Notwithstanding all these pitfalls and mistakes, great advances have been due to the applications of thermodynamics to chemistry, at which Helmholtz worked so fruitfully.

Along lines closely allied to those of thermodynamics, there are an immense number of chemico-physical investigations waiting to be attacked. A good deal is known about the way in which variation of composition affects capillarity for instance, and from this it is possible to calculate how capillarity ought to affect chemical composition, but there is very little indeed known as to whether it behaves as it ought. There are an enormous number of similarly reciprocally related phenomena which are connected with one another in a

manner analogous to the way in which, for instance, freezing point and pressure are reciprocally related, and which demand attention. In all such work, the co-operation of chemists and mathematical physicists are eminently desirable. We cannot often expect the two to be united in one person with the energy and time at his disposal to do double work.

Helmholtz laid the foundation for considerable advances in our knowledge of electrolysis. By a very carefully conducted series of experiments he distinguished between the diffusion currents and electrolytic currents. The former seem to be the only representative of metallic conduction in an electrolyte. For the latter he verified with very great accuracy Faraday's law of electrolysis and showed that the chemical forces are balanced by electrical forces. and that so far there was no reason for doubting that the chemical forces are electrical. This was Faraday's position, and is largely justified by subsequent investigation. At the same time there seems no doubt but that chemical phenomena are much more complex than simple electrolysis as we know it. There are too many irreversible chemical actions for us to be able with certainty to co-ordinate them with simple reversible electrolysis such as Helmholtz specially studied. There are too many good reasons for being sure that other forces exist than merely electrical ones for us to be at all certain that it is only these latter which are of importance in chemical changes. We can balance gravitation by the elastic force of a spring, or by the centrifugal force of a pair of governor balls, but that can hardly prove conclusively that all these are of the same kind. We can balance electrical forces against chemical forces, but this does not prove conclusively that they are of the same kind. We know that gravitational forces and magnetic forces must exist between atoms, and though they may produce only a very small part of the effects observed, we hardly know enough about them to be perfectly certain that their effects must be very small. One of Helmholtz's own theories seems to prove conclusively that there are forces acting which are not electrical. Helmholtz worked fruitfully at a theory of electrical diffusion through fine tubes which assumes that there is a double electrical layer on the surface of contact of the liquid and solid caused by a differential attraction of the two materials for positive and negative electricites. Now this attraction cannot be a force varying inversely as the square of the distance, for if so, it would merely neutralise the action of the electricity it attracted. A layer of positive electricity attracting one of negative electricity would just attract enough to neutralise all force on the layer and Helmholtz in assuming that nevertheless the electric force along the tube due to the current flowing in it does act on the layer practically

assumes that the attraction of the liquid for electricity is not an electrical attraction but is a specific attraction of a different kind. If we assume that an attraction of this kind can exist between atoms and electricity, we can hardly be justified in denying that atoms can act on atoms in a similar way. If the law of action of these forces be a much higher power than the inverse square, almost all the work done in separating atoms might be done against electrical forces, although at the very small distances involved in atomic dimensions these other forces might be very much greater than the electrical forces at the same distances, and might control chemical combination.

A good deal of labour has been expended on investigating a theory of solids and liquids upon the hypothesis that atoms attract one another with a force varying inversely as the fourth power of their distance apart. Very interesting results have been obtained, many of them independent of the law of action. This particular law of action seems absolutely inadmissible, however, because it is one of the most interesting conclusions from the hypothesis that at one centimetre apart two atoms would have an attraction for one another due to this cause approximately equal to their gravitational Anything at all approaching this is conclusively attraction. negatived by the substantial agreement of the various experiments, some on a large scale and some on a small scale, by which the coefficient of gravitation has been determined. If this suggested attraction existed there would be no sort of agreement between the results obtained on a large and on a small scale. There seems every reason to think that in the case of atoms we are dealing with phenomena of a much more complicated nature than that of laws of force of this kind. We know almost certainly that in the first place we are dealing with forces which are anyway like electrical and magnetic ones, neither all attractive nor all repulsive, but some one and some the other. From the arrangements of the molecules in crystals, and the tetrahedron analogy of carbon, we may be practically certain that as far as we can deal with the question as a statical problem at all, we must deal with atoms as much more complicated structures than merely centres from which forces radiate uniformly in every direction. There seems every reason to think that atoms have special centres of attraction, and there is even good ground for thinking that the force emanating from each of these centres is directed, *i.e.*, is very much greater in some directions than in others. No theory of solids certainly can be satisfactory which overlooks this, and any theory of liquids which overlooks electrolysis must be rather lame.

It must always be recollected that no statical theory of a solid or

liquid medium is possible with electrical forces alone acting. Such a medium would be essentially unstable. Hence, so far as we can deal with solids and liquids as statical systems, we may be quite certain that other than electrical forces must be postulated. From our knowledge of solids, crystals especially, and from the success that has attended the tetrahedron theory of the carbon atom, it seems almost certain that provisionally, at least, we may safely assume that a very large number of the properties of molecules can be deduced from purely statical theories of their structure. Hence we may be quite sure that so far at least as we are working on these provisional lines, we must assume other forces than electrical ones, or any others varying inversely as the square of the distance. Take, for instance, the suggestion that when an electrolyte is subject to electrostatic induction the superficial induced charges are due to a layer of electrified ions upon its surfaces. If there were no forces other than electrical ones, these ions would fly off the surface like dust. The pressure of the surrounding gas would certainly not prevent this, for a gas never prevents the diffusion of atoms. Hence we must suppose that there are other than electrical forces keeping these ions attached to the liquid. Helmholtz, himself, states as a conclusion of his investigation of the action of reversible electrochemical actions. "A remarkable feature in these processes appears to me to consist in the fact that the attraction of the water to the salt to be dissolved can constitute so great a part of the chemical force acting between the oppositely propelled elements." There seems to be considerable danger that these forces may be neglected. So much advance has been made by assuming that bodies in solution behave in some important respects like the same body in the gaseous state, that there has been a serious danger of assuming that the physical conditions are at all like. The dynamical condition of molecules in solution is essentially and utterly different from that of a molecule in a gas. The essential condition for applying any known dynamical theory of gases to calculate their behaviour is that the time during which two molecules are within the sphere of one anothers' action is small compared with the time during which they are apart, and that consequently the chances of three or more molecules being in simultaneous collision is very small. It further follows that the character of one kind of collision has no influence upon the character of the immediately succeeding collision, a condition which is not, however, fulfilled in the succeeding chatters of the chattering collision of elastic solids. Now this essential condition for the application of the dynamics of a gas to molecules in solution is very far indeed from being fulfilled. A molecule is never outside the sphere of action of its neighbours. All we know of the

magnitudes of the interspaces between molecules in a liquid shows that each molecule is within the sphere of action of hundreds, probably of thousands, may be of millions, of its neighbours. It is probably jostling about with a path for its centre between its jostles about one hundredth part as great as its own diameter. If its centre moves at a rate comparable with that of a gaseous molecule, which seems probable from the fact that liquid molecules can escape through the surface into the surrounding gas, the molecule would bang about in its confined space, making nearly 1014 bangs per second, and these vibrations would be quite comparable with those of heat radiations, and the concomitant vibration of the atom may be a large part of the source of ordinary heat radiation of solids and liquids. In the case of a gas the external virial is large and the internal is small and negligible, in the case of a liquid it is exactly the reverse, the external virial is small and negligible, and the internal large and important. The dynamical theory of a medium composed of molecules which can only jostle about through distances about a hundredth part of their diameter, is evidently essentially different from that of one in which the molecules describe free paths thousands of times the molecular diameter.

The theory of semi-permeable diaphragms is in a very doubtful They are often spoken of as if they were sieves, and as if the state. forces between them and the substance in solution were unimportant. A consideration of the relative behaviour of the only really effective semi-permeable diaphragm known with that of the solid diaphragms shows that there are some important differences. The surface of a liquid with a non-volatile salt in solution is a perfect semi-permeable diaphragm. Water molecules can and do get through quite freely, but molecules of the solvee cannot. Now the presence of these nonvolatile molecules in the surface certainly prevents the egress, but either does not prevent the ingress, or possibly facilitates the ingress of the volatile molecules. We know this, because the presence of the solvee reduces the vapour pressure. On the other hand, the whole theory of osmotic pressure assumes that the presence of the body in solution produces no effect, or the same effect on the ingress and egress of the molecules of the solvent. It is, no doubt, a most remarkable thing that osmotic pressure should be even roughly the same as what would be produced by the molecules of the body in solution if in the gaseous state, but to imply that the dynamical theory of the two is at all the same, or that the dynamical theory of a gas is in any sense an explanation of the law of osmotic pressures is not at all in accordance with what is generally meant by the word "explanation." These osmotic pressures are much more closely connected with Laplace's internal pressure in a liquid which is essentially

dependent on the forces between the molecules than with the pressure of a gas which is essentially almost independent of the forces between the molecules. The existing dynamical theory of a liquid shows that the molecules are kept apart by the mutual jostling of the molecules, and that the dynamical pressure of this jostling must be equivalent to the Laplacian pressure pulling them together. When we make a rough calculation we find that molecules going with velocities approaching those of gaseous molecules, and jostling about in the narrow interstices between molecules that have been already mentioned, would produce pressures comparable with those that have been calculated for the Laplacian pressure. Hence we conclude that although the dynamical conditions in the liquid are so very different from those in a gas, nevertheless, the two methods of calculating these internal pressures from the mutual jostlings that keep the molecules apart and from the attractive forces that keep them together lead to very much the same result, and that the velocity of motion of the centres of the jostling molecules may be of somewhat the same magnitude as that of the same material if it were in the state of a gas. It must be seen from this how the coincidence of these two ways of considering the same question is no matter of accident, but depends on the theory that it is the mutual kinetic jostling of the molecules against one another that keeps them apart. Hence we need not be surprised if the theory of osmotic pressure has a dynamical aspect from the point of view of attractions between the membrane and the water, the water and the body in solution, and the body in solution, and the membrane. There must be some dynamical reason why the solvent gets through the membrane while the body in solution does not. It must be due to what may be described as capillary forces between the solid and the molecules of the solvent. There is no sufficient reason for supposing that the membrane acts merely as a sieve. Calculations have been made, founded on the assumption that the membrane acts like a number of fine tubes of molecular dimensions, and that the capillarity of the solution differed from that of the solvent in contact with the walls of these tubes. Upon the supposition that the tubes are of molecular sizes, the observed osmotic pressures can thus be explained by possible capillary differences. That there is a direct relation between the osmotic pressure and capillarity can be shown by causing capillarity to raise a solvent so high in a fine tube that the vapour pressure at its concave upper surface is the same as that of the salt solution, when it is readily seen that this height is that producing osmotic pressure. By means of a fine mesh, that the solution does not wet, the converse experiment, is possible, namely, to have the surface of the solution so convex that the vapour pressure near it is the

same as near a flat surface of the solvent. These diaphragms, made of an ordinary porous material, with the only known perfect semipermeable surface, namely, the surface of the liquid itself, kept by capillarity in its pores, prove the theoretical possibility of semipermeable diaphragms in all cases where the body in solution is non-volatile, and enable us to discuss the theory of their working more satisfactorily than when dealing with semi-permeable diaphragms whose modus operandi is uncertain, or, at least, matter of dispute. These perfect semi-permeable diaphragms enable us to apply thermodynamics with confidence to calculate osmotic pressure. They enable us to calculate what is taking place at each point and to be sure that osmotic pressures thus calculated are not dependent on some unknown function of the diaphragm itself. We may, then, be pretty sure that, at least approximately, osmotic pressure is nearly equal to the vapour pressure of the solvee, because that is approximately the result deduced from observations on the vapour pressure of solutions. At the same time our attention is attracted by the dependence of the whole phenomenon on capillary phenomena. We naturally ask such questions as whether the vapour pressure near a newly made surface is the same as near an old surface. It is known that the capillarity of a newly formed surface differs in some cases from that of an old It is known that there are cases in which the solvee is concenone. trated into the superficial layer, and there are means for approximately calculating how far this is the case. One would naturally expect that the vapour pressure near this concentrated surface layer might be quite different from that near a newly formed surface layer which had not had time to concentrate the solvee into it. Which of these vapour pressures is the one from which we ought to calculate osmotic pressure ?

That osmotic pressure is proportional to the numbers of active molecules is not particularly remarkable. When small changes are made, the effect is generally proportional to the amount of change. It is, however, very remarkable that the amount of osmotic pressure can be even approximately calculated from the gaseous pressure that would be produced by these same molecules if they alone occupied the *whole space* filled by the solution. The molecules have not got all this space to move about in. They can only move about in the interstices between the other molecules which we have every reason to think constitute only a very small part of the whole volume. From the rate of diffusion of a salt in solution we know that its molecules do not go about as if they passed freely through the water molecules. It is evident that the simplest theory of what would be the effect of substituting for a certain number of water molecules a certain number of other molecules must include a consideration of

their relative attractions and sizes, and the resultant change in the space available for jostling, to say nothing of such additional complications as direct chemical combination between the two. This latter seems to be the complicating cause in electrolytic solutions in which each of the molecular components of the salt molecule produces its separate effect. If that effect be due to pressures exerted by each component banging about independently of the other, a very moderate amount of independence of the two components on one another would enable them to bang about independently in the extremely narrow interstices within which they are confined. That they can thus independently produce pressure only lends a very moderate amount of confirmation to the theory that these ions are quite independent as pairs. Possibly the mere substitution of an inverse square law of action between the ions for some other law of action between particular points on each, would be quite sufficient to account for the independence observed. This suggestion is founded on the supposition that the action of an ionising solvent is to substitute electrical attractions for the more complex chemical attractions which act between molecules. The difficulty of gaseous thermodynamic theory is to explain how two atoms can be sufficiently firmly fixed together not to have independent motion, rather than to account for this independence. According to this suggestion, the special forces on ions would be electrical ones, and from the known instability of bodies subject to forces varying inversely as the square of the distance, we might naturally expect a continual interchange of partners to be taking place. This, of course, does not assume that there are no other forces in the liquid than electrical ones. I have already called attention to this necessary consequence of any theory that deals with molecules as even approximately statical systems. What it does assume is that in dilute solutions these other forces are so symmetrically distributed that they do not produce stable equilibrium within the liquid. The principal difficulty in explaining how sufficient interchange of partners can take place is in explaining the apparently very great independence required by such results as that the velocities of the ions are functions of themselves alone and independent of those to which they are attached. This difficulty would be largely got over by assuming that in solution the ions are quite as much attached to the elements of the solvent as to one another. because then the interchanges that take place will be almost always interchanges amongst molecules of the solvent, and only very seldom amongst the very sare molecules of the solvee. It is almost impossible to explain dynamically the supposition that free ions with their electrical charges are meandering about in the liquid in a condition that can be at all rightly called dissociated. The term "dissociated"

should be confined to a condition in which the components of a molecule are not connected by any chemical bonds at all. In that case they can diffuse freely and independently through porous diaphragms. Hence the possibility of this independent diffusion is the simple and necessary test of the independence of the components which can rightly be called dissociation. In an electrolyte there is The component ions cannot diffuse indenot this independence. pendently through porous diaphragms. There is the acknowledged electrical force between the various oppositely charged ions, instead of their being free from one another. In even very dilute solutions this force is very considerable. If we assume that a negatively charged ion is exactly half way between two positively charged ones of course the forces on it are balanced, but if we suppose it as little as 1 per cent. nearer one than the other it becomes subject to a force of 400,000 volts per cm., drawing it to the nearer electron. This at once illustrates the instability of such a condition as that described by saying merely that these charged ious are moving about independently in the liquid. Without some other important actions existing at the same time such a condition is dynamically impossible, and although to consider the matter from this point of view may help us very much, because it gives us a rough and ready analogy to work on, yet there is great danger that it may stop important advances by an illusive appearance of explanation. In just this way the emissive and elastic solid theories of light and the caloric theory of heat gave apparent explanations of optical and heat phenomena which helped for a long time in advancing these sciences. But these same theories, by being upheld, after they had been conclusively shown to be inadequate, were great stumbling blocks in the way of further advances.

A good deal of importance has been attached, and rightly attached, to the fact, that the heat produced by the neutralisation of dilute alkalis by dilute acids is the same as that due to the combination of H and OH. This is certainly a most remarkable fact, but to concentrate attention on it, as if the statement that ions in solution are dissociated, took away all the difficulty surrounding the matter, obscures a very important question, namely, why is there then so little heat absorbed when the ions are dissociated by going into solution? It has been proposed to explain this by various suggestions which do little more than re-state the facts in some other form, and call for new properties of ions specially invented to suit the circumstances, which remind one very much of the ingeniously invented properties of light corpuscles that were, one by one, superadded in order to explain optical phenomena.

One way, that depends on a known cause, by which solvents may produce ionisation, is by diminishing electrical actions by their high

specific inductive capacity. There scems a good deal of reason for this supposition. High specific inductive capacity in a material can hardly mean anything else than that its molecules can have electrical charges easily produced on them at a considerable distance apart. Α considerable distance apart, of course, means considerable, compared with the distance apart of charges on molecules generally, which seems to be often a very small part (about one hundredth) of the molecular diameter. This follows from considering that the work done in the combination of H and Cl may be mostly due to the attraction of electrons. It is comparatively easy to calculate at most how far apart these electrons can be in order that the known amount of work done in combination may be produced by their approach. When we do so, we find that the electrons must be jammed up quite close together. This is quite accordant with what we know of their independence from spectral observations on molecules; but it at the same time shows how very much work must be done in order to separate them to even the thickness of a molecule apart. In separating them to a hundred times their former distance one does 99 per cent. of the work that would be done in separating them altogether. Why is there not an enormous absorption of heat due to solution? The suggestion mentioned is that the presence of a body of high specific inductive capacity, like water, very much diminishes the force of attraction between the electrons by providing, what come to the same thing, as induced electrons in the water molecules to help in drawing those in the salt apart. This is an excellent suggestion; but is it not really the very same thing, under another guise, as stating that it is by chemical combination with the water that the salt has conferred upon it the property of exchanging partners? What are these electric charges supposed to be induced on the water molecules, but electrons thereon? and what is the attraction of electrons among molecules but another name for one form of chemical combination? All this hangs together, but it lends no support at all to the dynamically impossible theory that the ions are free. What it suggests is that this so-called freedom is due to their being in complete bondage with the solvent. That atoms or molecular groups within a molecule often can and do exchange places is quite in accordance with chemical phenomena. That they should do so of their own accord when the molecules are arranged in a particular way is also quite in accord with such phenomena as crystallisation where the molecules, of their own accord, arrange themselves into the crystalline form, if they are first polarised by near approach to the surfaces of a crystal, but not otherwise, as is cyident from the well-known phenomena of supersaturation. These crystalline forces are able not only to arrange the mclecules in the solution, but to move massive crystals, and it is

an important matter for investigation whether they are simply electrical or of the more complex type of chemical action. This is perhaps the simplest example of so-called catalytic actions where change is induced by the presence of a material which itself is unchanged, and shows the extensive applicability of the general principle that chemical changes depend upon particular arrangements existing, and go on of their own accord so long as the arranging power exists. It is conceded that electrolysis and its consequences can be explained by this hypothesis, and the only outstanding phenomenon that does not obviously come under this explanation is that of why osmotic pressure is the same, or approximately the same, as the gaseous pressure of the same number of molecules and which is supposed to be "explained" by saying that the molecules in the solution are free. This so-called explanation is, however, as I have already pointed out, not a dynamical explanation at all, it is only a very far-fetched dynamical analogy. Thus this supposed advantage of the free ion theory is not only illusory but misleading.

Helmholtz has called special attention to the superficial electrical layers produced at the contact interface of different materials. He worked at it in connection with electrical endosmose. The whole subject is replete with interest. We want to know more about this attraction of matter for electricity. To suppose that this is electrical itself is illusory. It would require another force to keep on this permanent electrical charge; and, besides, in our present condition of semistatical explanation of nature, we must postulate forces that vary according to other laws than the inverse square of the distance in order to produce stability. That there are these superficial actions, which are partly electrical, is beyond doubt. That these electrical layers must produce effects on capillarity is unquestionable. That the forces between bodies in contact are affected by them must be the That energy is involved in producing and destroying these case. electrical layers must be. But, how much? Is the great question in all these cases. Is the electrical force the most important one acting? Is it the one that pulls hardest? Is it the one upon which most work is done? Is it the one that controls, for instance, the heat produced when insoluble powders are mixed with water? Are the already mentioned superficial crystalline forces that polarise a solution and cause molecules to arrange themselves upon its surface; are these mainly electrical? Conversely, are the forces that cause solution mainly electrical? The cause of solubility is very imperfectly understood. May we not hope that by following up Helmholtz's investigations of these superficial layers we may discover the causes of solution. The way seems also open for investigating the causes of other catalytic actions, and thus, possibly, of chemical action in

general, which may depend essentially on suitable arrangements of molecules. The capture of a comet by the solar system depends on a suitable arrangement of the planets. By suitably arranged approaches a set of stars may either stop the relative motion of one of their number so as to cause a resulting binary system, or may confer upon one of their number a velocity such as that of 1831, Groombridge, which, unless it meet with suitable circumstances, will peg away to infinity, as it cannot be stopped by the general attraction of those it is leaving. Two stars coming from a distance will in general recede to the same distance, but two systems of stars need not all do so. After collision there may be re-arrangements of components. Similarly, the approach of two simple systems would in general lead to these receding again into the condition from which they came, while the presence of a third system to absorb or re-arrange the energy and moment of momentum of the approaching systems might enable the last state of the systems to differ essentially from that from which they came.

The whole question of the nature and existence of these forces and their connection with electrical forces, is of the very greatest interest. We may hope that ultimately all forces may be explicable by a kinetic theory of nature, but, so long as no satisfactory theory of the ether exists that explains the very simple electro-magnetic laws, we can hardly expect anything more than rough analogies in explanation, or rather illustration, of other causes for these more complex chemic actions. The actions of a medium, like a perfect liquid in intense vortical motion, are capable of illustrating these actions. In the first place, there are possible actions such as those of one vortex on another which are not propagated from place to place, but are due to every vortex, in a sense, occupying all space, and each acting on the other simultaneously everywhere. Each changes the other by a simultaneous action everywhere; there is in such actions no question of propagation. Such actions in a liquid seem to best illustrate gravitation. It is not pretended, of course, that any theory of the nature of the turbulent motion or of matter has yet been invented which would lead to the known laws of gravitation. All that is suggested is that in some action of this kind we may look for an explanation of gravitation, and that in the meanwhile these actions in a liquid are a rough illustration of how actions may exist for which we have no evidence of any propagation. A second class of action of a turbulent liquid is that due to different kinds of polarisation of its motion. Such, for instance, as that vortex filaments are concentrated in various places, or move through the liquid in various directions. There is every reason for believing that such actions would be propagated from place to place with a velocity

depending on the energy per unit volume of the turbulency of the liquid. Such actions, due to polarisation of the motion in bulk, can be made to illustrate electro-magnetic actions in a wonderfully satisfactory way. Besides these two, there are the possible movements of such things as vortex rings, vortex spheres, and, in general, closed vortices, through the medium. These illustrate for us matter with its molecular structure. But besides these two, there are effects that may be due to the crinkling and waving of individual vortex filaments, to their being distorted from their circular shape of section. It is such action as this that may be expected to illustrate the chemic forces, and to which one would naturally look for an explanation of these actions, more complicated than simple electro-magnetic action. The question naturally arises, "Can these actions be propagated ?" To judge from the analogy, there seems every reason to expect that they could. When we look round for any evidence of propagation of actions other than the already known sound and light vibrations, we find mysterious velocities of propagation of earthquake waves and some chemical actions on sensitive silver salts that have not yet been explained by known material or electro-magnetic laws. These may, of course, be explicable by a combination of known material and electro-magnetic action. Ether waves, of lengths comparable with a millimeter, may act on molecular groups that are much smaller than the length of the wave in a somewhat similar way to that in which light waves act on the atoms whose diameter is very much less than the lengths of the waves. Vibrations of sound frequencies seem capable of helping molecules of iron to set under magnetic force. Long ether waves alter the structure of a metallic powder; may we not expect some of the enormous range between sound and light to disturb chemical equilibrium. Besides the direct propagation of light through matter, there may be electro-magnetic actions propagated by the joint action of matter and ether. There is evidence of this in the propagation of cathode rays through solid partitions, and an investigation of this and similar cases will, it is hoped, decide whether these actions are due to the interaction of matter and ether under known electro-magnetic laws, or whether we are in presence of a propagation of energy by means of those underlying properties of the ether that seem required to explain fully what we know of chemical actions, and which might be called the chemical properties of the ether.

As we then follow out the directions pointed out by Helmholtz's work, we cannot help being impressed with how far ultimate explanations of nature lead us closer and closer to the conclusion that these phenomena of our consciousness are all explicable as differences of motion. It is the motion which is imposed upon us. Is there not,

then, reason in the suggestion that colour and sound, nay, space. time, and substance are functions of our consciousness, produced by it under the action of what may be called an external stimulus, and that the only part of the phenomenon which essentially corresponds to that stimulus is the always pervading motion. And what is the inner aspect of motion? In the only place where we can hope to answer this question, in our brains, thought is the internal aspect of motion. Is it not reasonable to hold, with the great and good Bishop Berkeley, that thought underlies all motion. A purely rational machine might get on very well through the world without believing that other brains than his own had underlying thoughts. It is the position of the consistent positivist. To him nature is what others Such a position posits nothing that would call a consistent dream. is not positively felt. It is consistent, but inhuman. For human life we require sympathy and affection. For the highest life we require the highest ideal of the Universe to work in. Can any higher exist than that, as language is a motion expressing to others our thoughts, so Nature is a language expressing thoughts, if we learn but to read them. May we not hope that studies of physiological actions, of chemical constitution and change, of vortex motion, of the laws of matter and ether, may some day enable us to discover the motions in our brains underlying sound and light, and smell and touch, and pain and pleasure, hate and love. And may we not hope, then, to be able to form some dim analogies by which we may divine what underlies the much more complex motions of organic nature as a whole, and have a scientific basis for investigating what underlies the whole sequence of organic evolution.

And Helmholtz, by his physiological researches, by his chemical researches, by his physical researches, by his mathematical researches in fluid motion, has advanced mankind by a measurable amount in the road to this splendid goal. By his physiological researches we are measurably nearer a knowledge of the mechanism by which brain motions are affected. By his physical researches we are measurably nearer a knowledge of how to apply the doctrine of the conservation of energy and thermodynamics to discover a dynamical explanation of physical processes. By his chemical researches we are measurably nearer a knowledge of how to apply these same doctrines and electromagnetism to investigate the complex problems of chemical change. By his mathematical researches on fluid motion we are measurably nearer a knowledge of that simplest form of motion in which the postulated properties are so few that it seems almost the only direction in which we can hope for a really ultimate dynamical explanation of Nature.

And Helmholtz has gone from us. Let us venerate his name.