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CONTENTS.

The American Association for the Advancement of Science:—

The Partition of Energy: PROFESSOR W. F. MAGIE 161

Transportation and Combination: THE HON. MARTIN A. KNAPP 178

Scientific Books:—

Sutton's Volumetric Analysis, Olsen's Quantitative Chemical Analysis: F. L. 184

Scientific Journals and Articles..... 185

Societies and Academies:—

The American Mycological Society: C. L. SHEAR. *The Biological Society of Washington:* DR. M. C. MARSH. *The Wellesley College Science Club:* GRACE E. DAVIS. *The Berkeley Folk-lore Club:* PROFESSOR A. L. KROEBER. *The Chemical Society of St. Louis:* C. J. BORGMAYER..... 186

Discussion and Correspondence:—

Please Excuse the Kelep: O. F. COOK..... 187

Special Articles:—

A New Theory of Sex-production: PROFESSOR E. B. WILSON..... 189

Astronomical Notes:—

The Figure of the Sun; Relation between the Motion in the Line of Sight and the Variation in Brightness of Variable Stars: PROFESSOR S. I. BAILEY..... 191

Current Notes on Meteorology:—

Brief Comment on Recent Articles: PROFESSOR R. DEC. WARD..... 192

Notes on the History of Natural Science:—

Hippocratean Fishes; The Real Unicorn: DR. C. R. EASTMAN..... 194

Robert Bowne Warder..... 195

Scientific Notes and News..... 197

University and Educational News..... 200

THE PARTITION OF ENERGY.¹

As I rise in this place to address you, I recall a dear friend, who stood before you in a similar position three years ago, and whose premature death has dealt so severe a blow to this association and to the science represented in this section. The name of DeWitt Bristol Brace will always be honorably remembered in the history of physics. While a student at Boston University, he began the study of that science, and after his graduation in 1881, he proceeded to Johns Hopkins University to devote himself exclusively to it. After two years of study there, he went to Berlin, where he heard the lectures of Kirchhoff, and worked in the physical laboratory under the direction of Helmholtz. It was in Berlin that he definitely settled the whole course of his subsequent scientific career, by insisting on taking up, as his subject of research, the difficult question of the exact mode of transmission of a polarized ray which is undergoing magnetic rotation. This question was out of the line along which the work of the director and of his students was proceeding at that time, and Brace not only set the problem for himself, but owed entirely to his own inventive genius the brilliant method which he proposed for its solution. I remember how difficult it was for Brace to convince our director of the possibility of transmitting the ordinary and extraordinary beams in a common direction in a crystal of Ice-

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¹ Address of the vice-president and chairman of Section B—Physics, American Association for the Advancement of Science, New Orleans, 1905.

land spar; and the doubts of the director of the realization of the demonstrated conditions, even if they could be proved possible in theory. After Brace had succeeded in experimentally obtaining the conditions which his theory called for, he applied them to the examination of the question of the transmission of a polarized ray in a magnetic field. He was not able at that time to answer the question which he had in mind, but he was able to produce a memoir full of discoveries and ingenious suggestions, which culminated many years afterward in his final resolution of the problem, by the actual separation of the plane polarized ray in a magnetic field into two circularly polarized components.

Brace took his doctor's degree in 1885. After a short service at the University of Michigan, he became, in 1888, professor of physics at the University of Nebraska, where he devoted himself, with the conscientious fidelity which was a part of his nature, to the duties of his position. These duties he did not interpret in any narrow sense. He conceived that it was a large part of the obligation, which lay on him, to promote the progress of physics, not only by his own researches, but by organizing and assisting a corps of fellow workers. By his enthusiastic zeal, and by the wise administration of the facilities afforded him, he was able to draw around him a number of men who caught inspiration from his spirit, and who have, by their published researches, for several years past, been giving to the institution in which they worked an honorable prominence.

In the midst of his official duties Brace gave what time and strength he could spare to his own investigations. His mind was exceedingly fertile in the invention of methods of observation. The subject of optics, in which his first original work had been done, remained the subject of his choice throughout his life. As that science

has developed in connection with certain theories of electricity, fundamental questions have arisen, principally relating to the general subject of the relative motion of matter and the ether, which can only be answered by carrying observation to a degree of refinement which was not attained in the classical experiments of the great French and English investigators. Brace was profoundly interested in this great subject, and his principal task, for several years, was to improve the methods of observation to such a degree that indubitable conclusions might be drawn in regard to the results of experiments left doubtful by earlier investigators. By the union of inventive power with great experimental skill he succeeded in extending the range of observation in his repetitions of the experiment of Lord Rayleigh, to test for possible double refraction in an isotropic medium; the experiment of Mascart, to test for a differential effect on the natural rotation of the plane of polarization; and the experiment of Fizeau, to test for a possible change in the azimuth of the plane of polarization of a ray, polarized by refraction, to so high a degree of accuracy as to be able to confirm with confidence the negative results of Rayleigh and Mascart, and to assert with equal confidence that the positive result, which Fizeau believed he had obtained, must have been due to some experimental error and not to the cause to which it is sometimes ascribed. He had in mind other experiments to test the same general question, and we who knew the rare combination of powers which he possessed did not even despair of his succeeding in making the final test which is necessary, by the determination of the velocity of light when transmitted in one direction only.

This is not the place to enumerate Brace's contributions to science. It is sufficient to notice that part of his work in which his activity culminated, and which

was most closely connected with his hopes for the future. All his other work showed the same distinguished qualities; unusual ability of invention, great experimental skill, and the faculty of choosing central subjects to which to devote his powers.

Brace was for several years a member of this association, and was vice-president and chairman of Section B for the year 1901-2. He was also a member and vice-president of the Physical Society, and considering the distance between his home and the usual place of meeting of that society, a frequent attendant at its meetings. He very greatly enjoyed the opportunities afforded by them to meet with his friends. Under a somewhat retiring manner he concealed a warm heart and a sincere and unselfish admiration of other men's abilities and successes. His encouragement and sympathy were always given to those who came to him to talk about their scientific projects; and it renews my own sense of bereavement when I recall the cordial way in which he discussed with me the subject of the present address. His life of untiring devotion to duty and of genuine goodness will always remain a sweet memory to his friends; as his lofty and unselfish zeal for the promotion of knowledge will be an example and a stimulus to those who know the story of his work.

In the retrospect of the progress of physics during the past year, the attention is first and most forcibly attracted to the work which has been done in the general subject of radioactivity. By the continued labors of J. J. Thomson and of those in his immediate circle of fellow-workers, of Rutherford and Bragg, of Lenard and Kauffmann, and of many others, our knowledge of the details of the radioactive process has been very much extended. Some progress, though not so great, has been made in the development of the theory. But the main result, which, it seems to me,

can be considered as attained during the year, is the final appreciation of what we may call the electrical theory of matter, or at least of the possibility of explaining the properties of matter, even those of the most fundamental character, by the laws of electric action. Of course such an explanation can not yet be given, but it seems to me that, so far as we can judge by the hints and the *obiter dicta* which appear from time to time, the belief in the ultimate possibility of such an explanation has at last become general.

I doubt if the history of science affords another instance of so fundamental a revolution in modes of thinking, occurring in so short a time. For it is only ten years ago that Röntgen discovered the peculiar radiation that is known by his name, and I think we may fairly date the beginning of the study of radioactivity from that important discovery. On the one hand, the facility with which gases can be ionized by the Röntgen rays aided J. J. Thomson materially in his study of ionization, which led to his discovery of the electron and his investigation of its properties. On the other hand, the fluorescent effects of the Röntgen rays incited Becquerel to his examination of uranium, and led to his discovery of its radioactive properties; and from this to the isolation of radium by M. and Mme. Curie, and to the splendid series of researches which have been carried out on that substance and on other allied substances, the way is clear. Röntgen's discovery was made only ten years ago, and it is a marvelous illustration of the large sum of human effort applied to the study of science, and of the active, I might almost say the radical, tendency of the modern mind, that in so short a time we have obtained so great a body of established knowledge, and experienced so complete a revolution in our most fundamental modes of scientific thought.

In the domain of optics, also, there has been considerable progress, of which a very important part is due to our lamented friend, whose work I have already considered. In other parts of our science, the work which has been done is not of so consecutive a character, nor has it been productive of such important results as to call for particular mention.

The subject upon which I wish to speak to you to-day is that of the partition of energy. As is well understood, the energy here referred to is the kinetic energy of the moving particles, which, according to the kinetic theory of matter, constitute a body. The general theorem which I wish to discuss may be stated by saying that the kinetic energy of the body is so distributed among the degrees of freedom, by which the state of the body as a dynamical system is described, that an equal share is, on the average, allotted to each degree of freedom of each type of molecule.

Since the enunciation of this theorem as applied to gases, by Maxwell, in 1859, it has from time to time attracted the attention of the mathematical physicists. Lately it has again been brought forward, and the difficulties which surround it very considerably removed, by the work of Jeans. This author has collected the results of his own researches, in combination with a historical and critical study of previous work on the question, in a recently published book, which covers the ground so completely as to supersede any independent study of the subject which I could have made; but I trust that the exposition of it which I shall give will be of interest as an introduction to the experimental matter which I shall adduce; and that this will at least indicate a way in which we may hope to obtain some confirmation of the theorem of equipartition.

The questions which have always been raised about this important theorem of the

kinetic theory at once come to our minds. First, is the theorem true, or rather, does it state what would be true for an ideal system of particles moving freely within a containing vessel? second, is the proof of the theorem impeccable? third, is there any experimental evidence that it applies to real bodies?

I would remark about the first question that the theorem is so distinguished by its simplicity, and by its aspect as a sort of unifying principle in nature, that few men can set it fairly before their minds without at least desiring to believe it true. Most of those who have recognized that Maxwell's original demonstration was not flawless are still convinced of the truth of his conclusion, or at least believe his conclusion to be so probable as to make it worth while to try for a more accurate demonstration. Their state of mind is like that of Clausius and of Lord Kelvin, when they perceived that Carnot's theorem respecting the efficiency of a reversible engine could not be proved in the way in which Carnot tried to prove it.

With respect to the second question, it was very soon pointed out that Maxwell had made in his proof an assumption that could not be justified by immediate inspection, and which was itself in need of demonstration or of avoidance. The later demonstrations of Maxwell and Boltzmann have been likewise subjected to criticism, and can be shown to involve assumptions that will not be granted on inspection. The difficulties that arise in these proofs come from the necessity of applying in them the calculus of probabilities, and center around the question of the legitimacy of the application of that calculus. It is commonly agreed that Maxwell and Boltzmann have assumed a condition of the system of moving particles, as a requisite for the application of the calculus of probabilities, which is contradicted by many systems of which

we have certain knowledge, and can not without proof be admitted as likely to obtain in other systems, about which less is known. In the method employed by Jeans the application of the calculus of probabilities is made in a different manner, and does not necessitate the introduction of the hypothesis of Maxwell and Boltzmann. It seems to me that, in this last form of the theory, the difficulties which have environed the subject have at last been mastered.

In respect to the third question, that concerning the experimental evidence for the truth of the theorem, it is well known that, in general, Boyle's law follows as a consequence of the general principles of the kinetic theory, that Gay-Lussac's law is an immediate consequence of a relation plausibly assumed between temperature and the kinetic energy of the molecule, that the motion of the radiometer and the laws of transpiration and many other properties of gases can be deduced from the general theory; and, in particular, that Avogadro's law follows from the simplest form of the theorem of equipartition. But further proof of this theorem in its general form is still needed. Such proof as we have will be discussed later in this address.

Let us consider a little more fully the proofs of the theorem of equipartition. It was first enunciated in 1845, in a paper presented by Waterston to the Royal Society, but this paper was not published at that time, and Maxwell's paper of 1859 first brought the theorem to the attention of the scientific world. In that paper Maxwell undertook to prove that when two systems of molecules move in the same vessel the mean *vis-viva* of each particle will become the same in the two systems.

The proof of this proposition by Maxwell is the one still commonly employed in elementary expositions of the kinetic theory of gases. As applied first to a single gas,

he considers the molecules or particles of the gas as elastic spheres, and represents the average number of particles which have a velocity in one direction lying between two very near limits as a function of that velocity. To represent the average number of particles which have a velocity in either of the other two rectangular directions lying between certain near limits, he uses the same function, and he then supposes that the three velocities thus used are independent of each other, so that the average number of particles which possess all three velocities at once will be given by the product of three independent probabilities. Since this number depends only on the relative motions of the particles, and not on the particular directions in which the coordinate axes have been drawn, it may also be represented by a function of the resultant velocity of the particles, or by a function of the sum of the squares of the component velocities. Equating these two expressions, a functional equation is obtained, the solution of which leads to the well-known exponential law of the distribution of velocities among the molecules.

By extending the method just described to the consideration of the relative motion of the particles of two gases, Maxwell proceeded to show that the probable number of particles, whose velocities differ by a certain amount, is expressed by the same exponential function as that already obtained; and he shows further that the probable mean relative velocity is the square root of the sum of the squares of the mean velocities in the two systems.

On the basis of this proposition, Maxwell proves that the average kinetic energy of the molecules of two or more gases, when they are mixed, will be the same for each. To do this he shows simply that the difference of the mean kinetic energies of the molecules of two gases will be diminished by collision, so that it is only neces-

sary that a sufficient number of collisions take place to reduce this difference to zero.

The defect of this demonstration lies in the assumption that the velocities in the three rectangular directions can be considered as independent. As they do not enter independently in the equations of collision between the molecules, we might fairly expect them to be related to each other, until they are proved to be independent.

I have dwelt on this first method of Maxwell's, because of its historic importance, and because it illustrates the difficulty of deciding by inspection on the conditions which may legitimately be assumed for the application of the calculus of probabilities. In the elaborate method subsequently developed by Maxwell and by Boltzmann, the same difficulty is met with in another form. In this method the molecules are considered as spheres, freely moving about within a vessel and colliding with each other. The effort is made to determine the characteristics of the motion of the assemblage of molecules which must obtain if the condition of the assemblage is to be, to outside inspection, uniform. To do this, we consider a number of molecules belonging to a certain class characterized by possessing certain component velocities before collision, and certain other component velocities after collision, and a number of molecules belonging to another class characterized by possessing the same component velocities in the reverse order, and, considering the probable number in each of these classes as a function of the component velocities, we write down the expression for the probable number of molecules of these two classes which occupy the same element of volume and so are in collision. With this expression we can obtain an expression for the average increase in the number of molecules in one of the classes, due to collisions, and this ought to be zero if the condition

of the assemblage is to be uniform. From the discussion of this last expression follow Boltzmann's H-theorem, the formula for distribution and the theorem of equipartition.

When the mode is analyzed in which the expressions giving the probable numbers of molecules in the two classes are combined, it appears that an assumption is involved in it which is not evident on inspection: namely, that the probability of the presence of a molecule of one class in an element of volume is independent of the coordinates of that element, or, what amounts to the same thing, of the probability of the presence, in the same element of volume, of a molecule of the other class. The gas to which this assumption applies is called by Boltzmann unordered with respect to the distribution of the molecules (*molekular-ungeordnet*). Jeans uses for this condition of a gas the very convenient phrase 'molecular chaos.'

Now we evidently can not assert off-hand that this chaotic condition will obtain in all systems of particles which represent real gases. When Boltzmann tries to define it he does so by negative instances, showing what the condition of the system might be which would be 'ordered' with respect to the distribution of the molecules; and then leaves us to infer that the vast majority of distributions do not possess any peculiarities which would put them in the 'ordered' class. But this inference is not readily drawn. It is evident that any condition of the system is ordered, in the sense that the successive conditions follow on mechanical principles from the initial condition. All that we can do by inspection is to cherish the hope that, while all systems are 'ordered' in this sense, yet a vast number of them—an infinite number of them, it may be, in comparison with those 'ordered' in Boltzmann's sense—are still 'unordered' in such a sense that the

application of the calculus of probabilities to them, as made by Maxwell, may not lead to an erroneous result. To assert that this is so requires proof.

An alternative method of dealing with the theory of gases, of which the latest development is due to Jeans, proceeds by treating a gas as a single dynamical system, specified by the positional coordinates and the component velocities of its molecules. We then, to use Jeans's words, consider 'an infinite number of systems, starting from every conceivable configuration, and moving over every path; and investigate, as far as possible, the motion of this series of systems, in the hope of finding features common to all.' Jeans carries out this investigation by representing each particular phase of the system by a point in a generalized space. The successive phases through which one of the systems will pass will be represented by the points along a line in the generalized space. Jeans shows that these lines will be 'stream lines' in the space; and that to investigate the infinite number of systems already supposed comes to the same thing as to suppose the generalized space filled with a fluid, moving along stream lines determined by the dynamical equations of the gas, and to investigate the motion of this fluid. This motion is found to be a 'steady motion.' The advantage of this mode of procedure is that the applications of the calculus of probabilities are made to the elements of the generalized space, and are obviously legitimate.

By an argument based on this fundamental mode of representation Jeans shows that all but a negligibly small fraction of the generalized space represents systems in which the density of the gas is uniform; and that within that part of the generalized space which represents states of the system in which the energy is constant, all but an infinitely small fraction represents systems

in which the velocities are distributed according to Maxwell's exponential law. Such a state of the system Jeans calls the 'normal state,' and his conclusion is that it is infinitely probable that a gas in ordinary circumstances will be in the normal state.

We may consider this result as an *a posteriori* proof of the hypothesis of molecular chaos.

By a treatment that is essentially similar, and without using the hypothesis of molecular chaos, it follows that it is infinitely probable that the energy of the gas is, on the average, distributed equally among the degrees of freedom corresponding to molecules of different types, and also among the degrees of freedom of each type considered independently.

When Maxwell attempted to prove the law of equipartition for the time averages of the energy associated with the different degrees of freedom of a single system, he introduced the hypothesis that the system goes through all possible phases, consistent with the conservation of energy, before returning to its initial phase. It is difficult to see how this can be the case in a system self-contained and entirely subject to the laws of dynamics, such as, for example, a gas within the smooth envelope ordinarily postulated in the theory. But if we think of the envelope as itself an assemblage of moving molecules, it may be that the courses of the gas molecules will be changed so irregularly by impacts at the boundaries that the gas may be thought of as experiencing so many fortuitous disturbances that it will practically fulfil the condition of passing through all possible phases. In this case the law of equipartition can be extended to the time average of any one degree of freedom.

Lord Kelvin has taken exception to this form of the theorem of equipartition, asserting that the proof is invalid, and that

it is not true in fact. To demonstrate the latter statement, in default of any direct experimental method, he has resorted to the calculation of the paths and velocities of a moving body within an envelope of some assumed form, and a comparison of the kinetic energies associated with each degree of freedom. To introduce the element of chance, the courses of the body were mapped out by the help of numbers obtained by drawing numbered cards from a pack. The results obtained differed considerably from the exact equalities deduced from the Maxwell-Boltzmann theorem. I do not pretend to be able to show that these results of Lord Kelvin are of no value as evidence against the truth of the theorem, but I would remark that we can at least justify a doubt about them by noticing how small a deviation in the experiments from perfect impartiality of conditions will suffice to produce a large deviation from the expectation of the theory of probabilities. To test this, and remembering that when I used to play whist we noticed that a black card turned up as trump oftener than a red one, I procured a new pack of cards, which ought to be impartial and unbiased, if anything is, and cut it a number of times, noting the suit of the card exposed by the cut. In 312 cuts the black suits were recorded 196 times, the red suits 116 times. Spades were recorded 111 times, clubs 85 times, diamonds 68 times, hearts 48 times. Practically the same ratio (184-121) between the black and red suits was obtained with an old pack, though the order of suits was different. Such a persistent departure from the expectation of an equal number of each color and of each suit indicates that for some reason the cards are not impartial; and a scrutiny of a new pack shows, I think, the reason for this. When the pack is examined, the bottom card is usually the ace of spades, and then the spade suit follows in order. The

uppermost suit is generally the hearts. I believe that, when the pack is trimmed, the knife is pressed out as it goes down, so that the upper cards are cut a little smaller than the lower ones. The difference in size can be seen if the pack is evened up on a smooth surface. Some cards will then appear a little wider than the others, and if they are picked out, they will generally be found to be black cards. Now I do not know how Lord Kelvin's pack of cards was made, or how the cards were drawn, but I think we may fairly suppose that the discrepancies of 15 per cent. or so, which appeared in his experiments, may have been due, not to a failure of the theorem of equipartition, but to trifling departures from impartiality in his method of experimentation.

We are now ready for the examination of the experimental evidence for the applicability of the theorem of equipartition to real bodies. The most important evidence that bears on the question is found in the observed values of the specific heats of gases, and of the ratios of their specific heats of constant pressure and of constant volume. If we consider the distribution of the energy which enters a gas at constant volume when its temperature rises one degree, designating its specific heat of constant volume by C_v , the increase in the energy of translation of the molecules by C_p , and the ratio of the two specific heats by γ , it is easy to show that

$$\gamma - 1 = \frac{2}{3} \frac{C_p}{C_v}.$$

Now if each degree of freedom acquires an equal share of kinetic energy, say k , the energy of translation increases by $3k$, so that

$$\gamma - 1 = \frac{2k}{C_v}.$$

Furthermore, C_v will equal k times the total number, n , of degrees of freedom of

the molecule, added to an unknown amount, P , of potential energy. We thus get

$$\gamma = \frac{2k}{nk + P} + 1.$$

If we assume that the molecules of the gas do not take up potential energy, so that $P = 0$, and then assume that the molecules are practically points, so that $n = 3$, corresponding to the three translational degrees of freedom, we have $\gamma = 5/3$. This is the number found for this ratio in certain cases, in one of which, at least, that of mercury vapor, we have independent reasons to believe that the molecule is monatomic. If we set $n = 5$, as would be the case if the molecules were solids of revolution, we get $\gamma = 7/5$, which is the value found for several diatomic gases. If $n = 6$, as would be the case if the molecules were irregular solids, we get $\gamma = 4/3$, a number not often found as the value of the ratio, the numbers obtained for gases not belonging to the other two classes being generally less than this. So far we seem to have an imperfect agreement with the theory, but the conditions assumed are evidently not those of real molecules. Staig-müller has shown a way, to which I shall direct particular attention, to modify the formula so that it can be applied to real gases; but before doing so, I wish to consider the general question, which will not be settled by our being able to find that certain assumed values of n will give observed values of γ . Have we a right to believe that the number of degrees of freedom of a molecule, other than the three degrees of translational freedom, are ever, in any case, so few as we must suppose to get the results referred to? Are we not rather bound to believe, from the evidence of internal vibration afforded us by the spectroscopy, that the molecules or the atoms of all gases are vibrating in many modes, or are compound bodies whose parts

are executing vibrations? And should we not therefore set our number n of degrees of freedom very large, and so obtain a value of γ practically equal to unity for all gases, in entire disagreement with the experimental results? The view of the constitution of the atom which prevails at present, that it consists, at least in part, of an assemblage of electrons having the essential properties of mass and moving in orbits with enormous velocities, supports the evidence of the spectroscopy, and makes it all the more necessary for us to admit that the molecule of gas will have a great number of degrees of freedom.

A reconciliation of these views with a modified doctrine of equipartition has been made by Jeans. The proofs of the theorem of equipartition apply to a conservative system, and fail as soon as they are applied to a system in which the energy is not constant. Now we know that, as a matter of fact, every material system is transferring energy to the ether—indeed, as Jeans remarks, our seeing it at all depends upon that operation—and it appears therefore that we ought not to expect the theorem of equipartition to apply to real systems without further examination. To carry on this examination we conceive of a system so constituted that the energy which corresponds to certain of its degrees of freedom can and does pass rapidly into the ether, while that corresponding to the remaining degrees of freedom is dissipated by transfer to the degrees of freedom of the first class. On this supposition Jeans shows that the energy resident in the system may be divided among the degrees of freedom according to a modified mode of equipartition; those coordinates whose energy is not transferred directly to the ether possessing equal amounts of energy, corresponding to the temperature of the body indicated by the thermometer and to the formula $mv^2 = 3RT$, while those coordinates whose

energy is directly dissipated into the ether also possess equal amounts of energy, different from the other amounts, and corresponding to another function t , whose dimensions are those of temperature, and which conforms to a formula similar to the one just given, with the same constant R . The two temperatures thus introduced Jeans calls the principal and subsidiary temperatures, and the degrees of freedom to which they correspond, the principal and vibratory degrees of freedom. He shows that, provided the product of the time occupied by a collision between two molecules and the frequency of the atomic vibration is large, the transfer of energy from the principal to the vibratory degrees of freedom goes on very slowly, and he shows further that we may believe that the postulate here made applies to real bodies; so that, when a gas is heated, we may consider that practically all the energy which it receives is taken up by the principal degrees of freedom. If this be granted, we may ignore, for practical purposes, the multitudinous vibratory degrees of freedom, and are brought back to the simpler view of the constitution of the molecule as a collection of atomic masses bound together into a system. We have thus set before us the task of making plausible estimates of the number of principal degrees of freedom in the various gases, and of calculating the specific heats of these gases and the values of the ratio of their two specific heats. In doing this we shall follow the procedure of Staigtmüller.

In the formula

$$\gamma = \frac{2k}{nk + P} + 1$$

the denominator $nk + P$ represents the energy received by the molecule, when its temperature rises one degree. We assume that the potential energy P is entirely that due to the displacements of the atoms in

the molecule, and that the motions of those atoms are simple harmonic, so that the mean potential energy corresponding to each internal degree of freedom is equal to the mean kinetic energy. Using a to represent the number of degrees of freedom of the molecule as a whole, and i to represent the number of internal degrees of freedom, we have

$$n = a + i, \quad P = ik, \quad \text{and} \quad \gamma = \frac{2}{a + 2i} + 1.$$

When we use θ to represent the sum $a + 2i$, the formula takes the simple form

$$\gamma = \frac{\theta + 2}{\theta}.$$

Our task is to estimate the values of a and i in particular cases, and to calculate therefrom the values of γ .

Before proceeding to do this we will calculate the expression for the specific heat of constant volume in terms of the degrees of freedom. Denoting again by k the energy corresponding to one degree of freedom, which a gram-molecule of the gas receives when its temperature is raised one degree, and by m the molecular weight, we may write $C_v m = k\theta$, and may calculate k as follows:

We know from Joule's calculation, that the velocity of mean square for hydrogen is 1.842×10^5 centimeters per second. From this we get the total mean kinetic energy of translation of a gram-molecule of hydrogen, one third of which is the amount of kinetic energy apportioned to one degree of freedom. We then get the change in the energy apportioned to one degree of freedom, which occurs when the temperature rises one degree, by dividing by the absolute temperature 273, and reducing the result to gram-degrees, obtain for k the value $k = 0.9886$. This value is so nearly equal to 1 that for many of our subsequent calculations k will be taken equal to 1.

We are now in position to calculate not only the values of γ for various gases, but also their molecular heats, that is, the heat capacities of their gram-molecules, from estimates made of the probable number of their principal degrees of freedom.

In the case of a monatomic gas we suppose the molecules to act either as points or as smooth spheres, for which the only effective degrees of freedom are the three translational ones. For these, therefore, we have

$$\vartheta = 3, \quad C_p m = 4.943, \quad \gamma = \frac{5}{3} = 1.66 +.$$

I do not know that the molecular heats of the monatomic gases have been measured, but the values of γ obtained for mercury vapor, krypton, helium and argon range from 1.666 to 1.64.

For the diatomic gases, while we still treat the atoms as points or smooth spheres, we notice that 5 coordinates are necessary, being also sufficient, to determine the position and orientation of the molecule, in view of the fact that its orientation about the line joining the two atoms is indifferent. The only other principal degree of freedom which the molecule can possess is the single one which determines the distance between the atoms. If this distance is fixed, we have $i = 0$, and $\theta = 5$; if it is variable, $i = 1$, and $\theta = 7$. From these assumptions we can calculate the constants for comparison with the results of observation.

$$\vartheta = 5. \quad \kappa(\vartheta + 2) = 6.9202. \quad (\vartheta + 2)/\vartheta = 1.400.$$

		$C_p m$	γ
Hydrogen.....	H ₂	6.809	1.402
Nitrogen.....	N ₂	6.830	1.405
Oxygen.....	O ₂	6.960	1.402
Nitrous oxide.....	NO	6.951	—
Hydrogen bromide.....	HBr	6.642	1.400

$$\vartheta = 7. \quad \kappa(\vartheta + 2) = 8.8974. \quad (\vartheta + 2)/\vartheta = 1.286.$$

		$C_p m$	γ
Chlorine.....	Cl ₂	8.811	1.33
Bromine.....	Br ₂	8.88	1.293
Iodine.....	I ₂	8.50	1.294

When we consider the triatomic molecules, we find several of them of the type of which the molecule of water vapor is an example, in which we may suppose that the bivalent atom stands between the other two similar atoms, at the center of gravity of the molecule. If we can conceive the atoms thus placed and take the coordinates not fixed by this assumption as corresponding to subsidiary degrees of freedom, we may consider the energy of the molecule as determined by the 5 degrees of freedom which fix the position and orientation of the molecule, and by one additional degree of freedom, determining the distance between either of the univalent atoms and the center of gravity. On these assumptions we obtain $\theta = 7$.

$$\vartheta = 7. \quad \kappa(\vartheta + 2) = 8.8974. \quad (\vartheta + 2)/\vartheta = 1.286.$$

		$C_p m$	γ
Water vapor.....	H ₂ O	8.649	1.29
Carbon dioxide.....	CO ₂	8.91	1.285
Hydrogen sulphide.....	H ₂ S	8.33	1.276

For reasons which I will not stop to give, Staigmüller considers the molecule of bisulphide of carbon to be of a different class, in which the above described symmetry does not obtain, so that we have $a = 6$, and each of the sulphur atoms determined as to its distance from the center by one coordinate, so that $i = 2$, and $\theta = 10$.

$$\vartheta = 10. \quad \kappa(\vartheta + 2) = 11.863. \quad (\vartheta + 2)/\vartheta = 1.200.$$

		$C_p m$	γ
Carbon bisulphide.....	CS ₂	12.12	1.197

For the two vapors, phosphorous chloride and arsenious chloride, we may think of the univalent atoms as free to move in planes at right angles to the directions of the valencies of the trivalent atom, each with 2 degrees of freedom, while 6 more are needed to determine the position and orientation of the molecule. We have thus, in these cases, $\theta = 18$.

$$\vartheta = 18. \quad \kappa(\vartheta + 2) = 19.77. \quad (\vartheta + 2)/\vartheta = 1.111.$$

		C_m	γ
Phosphorous chloride...	PCl_3	18.49	—
Arsenious chloride.....	AsCl_3	20.32	—

For the vapors silicon tetrachloride, titanium tetrachloride, and tin tetrachloride, we make the same assumptions as in the last case about the freedom of the chlorine atoms, and get $\theta = 22$.

$$\vartheta = 22. \quad \kappa(\vartheta + 2) = 23.726. \quad (\vartheta + 2)/\vartheta = 1.091.$$

		$C_p m$	γ
Silicon tetrachloride...	SiCl_4	22.47	—
Titanium tetrachloride.	TiCl_4	24.77	—
Tin tetrachloride.....	SnCl_4	24.41	—

There is a difficulty which I can not solve about the methane derivatives. Their specific heats have been determined only in two cases, but we have two sets of values of γ , one obtained by Müller, the other by Capstick. Müller's values conform fairly well to the hypothesis that the hydrogen atoms of the methane (CH_4) molecule are fixed, and that each chlorine atom substituted for a hydrogen atom introduces 2 interior coordinates.

	ϑ	$(\vartheta + 2)/\vartheta$	γ
CH_4	6	1.333	1.32
CH_3Cl	10	1.200	1.20
CH_2Cl_2	14	1.142	1.12
CHCl_3	18	1.111	1.11

The agreement is very good. On the other hand, Capstick's numbers for γ are different, and generally larger than Müller's. They do not fit easily into any similar scheme.

The constant $k = 0.9886$ may be used to calculate the atomic heats of the solid elements. To do this we make the hypothesis that the aggregation in these solids is atomic rather than molecular, and that each atom vibrates in simple harmonic motion about a position of equilibrium. On this assumption each atom will re-

ceive, when heated, twice the energy that is taken up by its three translational degrees of freedom. On the principle of equipartition, the energy taken up by one such degree of freedom is the same as that taken up by one translational degree of freedom of the hydrogen molecule, or is equal to the constant k . The atomic heat should therefore equal $6k$, or 5.93. A comparison of this with the observed values of the atomic heats, which range from 5.5 to 6.3, indicates that the hypothesis upon which the result is obtained is in the main correct. It is useless to speculate on the reasons for the different values of the atomic heats of the different elements. We can account for them without denying the doctrine of equipartition by supposing that the vibrations of the atoms are not strictly simple harmonic.

Hitherto we have followed Staigmüller. It seems to me clear, after studying his results, that it is possible to account for the specific heats of gases by supposing the energy distributed equally over certain degrees of freedom; and it seems to me, further, that the explanations which Staigmüller has given of his choices of the number of degrees of freedom which he selects for each type of molecule are at least plausible. The most striking feature of these choices is the small number of internal degrees of freedom assigned to the atoms. It seems as if the atoms were—at least with respect to certain directions of displacement—rigidly bound together. Lord Rayleigh has remarked that, on the ordinary theory of equipartition, no matter how small the play of an atom may be in the sense of a coordinate, the degree of freedom thus indicated must have its full share of energy; so that nothing short of a truly rigid connection in one direction will allow us to neglect the degree of freedom in that direction. From this difficulty we may escape by the use of the distinction

between principal and vibratory degrees of freedom. We may suppose that the forces between the atoms of a molecule vary with exceeding rapidity for relative motions in certain directions, while they do not vary nearly so rapidly for motions in other directions. If this is so, the period of the vibration due to the rapidly varying force will be very small, and the vibration will be of the type which communicates energy rapidly to the ether, so that motion in that sense will correspond to a vibratory degree of freedom. The other motions, of longer period, will correspond to principal degrees of freedom, and will alone be operative in taking up energy when the gas is heated.

It does not seem possible to extend Staigmüller's method directly to other more complicated molecules, for which it would be impossible to assume the atomic arrangement. But if we accept it as verified by its success in describing the specific heats of gases, we may use it to calculate the degrees of freedom in more complicated molecules from their known specific heats, and can then see if the numbers thus obtained appear to have any relation to the numbers and kinds of atoms in the molecules.

To exemplify this mode of procedure let us take the case of methyl alcohol. Its molecular formula is CH_4O ; its molecular weight is 32; its specific heat between 5° and 10° is given by Regnault as 0.59; its molecular heat is therefore 19. If we may neglect the potential energy of the molecules with respect to each other in comparison with their kinetic energies, this molecular heat is distributed among 6 degrees of freedom of the molecule and the unknown number of internal degrees of freedom which is to be determined. From Staigmüller's formula, $C_v m = k(a + 2i)$, we get for i , $6.5 +$. Of course this is an impossible value for i , which should be

integral, but the specific heat of Regnault's specimen of methyl alcohol is almost certainly too high, on account of the presence of water. We may take 6 as the most probable integral value for i . We might speculate about the possible assignment of these degrees of freedom to the different parts of the molecule of methyl alcohol according to its structural formula, but such a procedure would be too arbitrary to carry conviction. What is immediately noticeable is that the number of degrees of freedom thus obtained is equal to the number of atoms in the molecule; so that if we assign one degree of freedom to each atom we can reproduce the molecular heat of methyl alcohol. This would be nothing more than a coincidence if it were not the case that the same relation holds for the other alcohols, whose specific heats are given in Landolt and Börnstein's tables for about 0° .

		No of Atoms.	i
Methyl alcohol	CH_4O	6	6.5
Ethyl alcohol	$\text{C}_2\text{H}_6\text{O}$	9	9.5
Propyl alcohol	$\text{C}_3\text{H}_8\text{O}$	12	12.5
Isobutyl alcohol	$\text{C}_4\text{H}_{10}\text{O}$	15	15
Isamyl alcohol	$\text{C}_5\text{H}_{12}\text{O}$	18	19

The general tendency of the values of i is to run above the sum of the atoms. This may be taken account of by a special assumption, as, for example, by assigning two degrees of freedom to the hydrogen atom in the hydroxyl group; but it is very likely that the specific heats given in the tables are too high, on account of the diffi-

		No. of Atoms.	i
Ethyl ether	$\text{C}_4\text{H}_{10}\text{O}$	15	15.5
Benzol	C_6H_6	12	10.7
Oil of turpentine	$\text{C}_{10}\text{H}_{16}$	26	25
Hexan	C_6H_{14}	20	18.5
Heptan	C_7H_{16}	23	21.5
Octan	C_8H_{18}	26	26
Decan	$\text{C}_{10}\text{H}_{22}$	32	33
Dodecan	$\text{C}_{12}\text{H}_{26}$	38	40
Tetradecan	$\text{C}_{14}\text{H}_{30}$	44	46.5
Hexadecan	$\text{C}_{16}\text{H}_{34}$	50	53
Toluol	C_7H_8	15	13.5

culty of freeing the alcohols entirely from water. The same general rule holds for many other organic compounds.

In the case of several of the organic liquids, the calculated degrees of freedom can be reproduced by assigning 2, or sometimes 3, degrees of freedom to the hydrogen atoms.

		<i>i</i> Estimated.	<i>i</i> Calculated.
Isoamylene.....	C_5H_{10}	25	24.5
Acetic acid.....	$C_2H_4O_2$	12	12
Naphthalene.....	$C_{10}H_8$	26	24.5
Formic acid.....	CH_2O_2	9	9

And in several compounds containing nitrogen the same rule holds.

		<i>i</i> Estimated.	<i>i</i> Calculated.
Nitrobenzol.....	$C_6H_5O_2N$	19	18.5
Aniline.....	C_6H_7N	21	21
<i>p</i> - and <i>o</i> -toluidine.	C_7H_9N	26	26

Other such compounds can not be treated with success so simply.

We may examine a few of the solid organic bodies by the same method. Let us begin with the three pairs of isomers, dextrose and levulose, mannite and dulcite, resorcin (and hydroquinone) and pyrocatechin. The molecular heats of the two members of each of these pairs differ by 6, and we have suggested to us at once that one characteristic difference of two such isomers may be that the molecule in one of them may retain an individuality that the molecule of the other loses, and may vibrate about its position of equilibrium as a whole, so that the value of θ will contain $a=6$, while that of its isomer will not. If we admit this, we obtain values of the internal degrees of freedom which are satisfied by assigning one degree of freedom to each atom.

		<i>i</i> Estimated.	<i>i</i> Calculated.
Dextrose, levulose.	$C_6H_{12}O_6$	24	25
Mannite, dulcite...	$C_6H_{14}O_6$	26	26
Resorcin, pyrocatechin.....	$C_6H_6O_2$	14	14.3

In the cases of cane sugar and anhydrous milk sugar we can not assume the difference between the molecular heats to be due to the cause previously assigned, but if we examine the structure of these large molecules, we shall find that four of the carbon atoms are differently connected in the molecule from the other eight. If we suppose $a=0$, and assign 2 degrees of freedom to each of the group of eight carbon atoms in the one case, and to each of the group of four carbon atoms in the other case, we obtain a fair agreement with the calculated numbers of degrees of freedom.

		<i>i</i> Estimated.	<i>i</i> Calculated.
Cane sugar.....	$C_4C_8H_{22}O_{11}$	52	53
Anhydrous milk sugar.....	$C_4C_8H_{22}O_{11}$	49	51

In levulose and dextrose one of the carbon atoms is peculiarly connected with the other constituents of the molecule. If we assign to it 2 degrees of freedom, we obtain an exact agreement with the calculated number of degrees of freedom.

When these organic solids are dissolved in water or alcohol, their apparent molecular heats, that is, the molecular heats calculated for them from the specific heats of their solutions, on the hypothesis that the specific heat of the solvent remains unchanged, are constants for all ordinary concentrations, and differ with the different solvents. These apparent molecular heats are generally greater than those of the same substance in the solid state. It may be that the dissolved molecules have so united themselves with the surrounding water as to weaken the bonds of the water molecules and have thus increased their degrees of freedom; but it is also possible that the degrees of freedom of the dissolved molecules themselves have been increased by the process of solution. If we adopt the latter hypothesis, we may construct schemes apportioning the degrees of free-

dom among the atoms of different sorts which will reproduce the calculated degrees of freedom.

		C	H	O	<i>i</i> Esti- mated.	<i>i</i> Cal- culated.
Dextrose.....	$C_6H_{12}O_6$	1	2	1	36	37
Levulose.....	$C_6H_{12}O_6$	1	2	2	42	42
Mannite.....	$C_6H_{14}O_6$	1	2	3	52	51.5
Dulcite.....	$C_6H_{14}O_6$	1	2	2	46	46
Resorcin.....	$C_6H_6O_2$	1	3	2	28	29
Pyrocatechin.....	$C_6H_6O_2$	2	3	2	34	35
Pyrocatechin in alcohol.....		1	3	1	26	26
Phenol.....	C_6H_6O	2	3	2	32	33
" in alcohol		1	3	1	25	23

The supposition made before in the case of the sugar molecules, assigning different degrees of freedom to the two groups of carbon atoms, must be made again in this case.

		C_4	C_8	H	O	<i>i</i> Esti- mated.	<i>i</i> Cal- culated.
Cane sugar.	$C_4C_8H_{22}O_{11}$	1	2	2	1	75	74
Milk sugar.	$C_4C_8H_{22}O_{11}$	2	1	2	1	71	71
Maltose.....	$C_4C_8H_{22}O_{11}$	2	1	2	1	71	69

When we turn to the liquids which contain other atoms than those of carbon, hydrogen and oxygen, we find that for a number of them, containing atoms of the chlorine group, the calculated degrees of freedom can be reproduced by assigning one degree of freedom to each atom of carbon and of hydrogen, and three to the remaining atom or atoms.

		<i>i</i> Estimated.	<i>i</i> Calculated.
Ethyl chloride.....	C_2H_5Cl	10	11
Ethyl bromide.....	C_2H_5Br	10	9.5
Ethyl iodide.....	C_2H_5I	10	8.8
Ethyl sulphide.....	C_2H_5S	17	17
Chloroform.....	$CHCl_3$	11	11
Carbon dichloride.....	C_2Cl_4	14	13.3
Ethylene chloride...	$C_2H_4Cl_2$	12	11.3
Ethylene bromide...	$C_2H_4Br_2$	12	14
Xylol bichloride.....	$C_8H_8Cl_2$	22	21.7
Xylol bromide.....	$C_8H_8Br_2$	22	21
Xylol tetrachloride.	$C_8H_8Cl_4$	28	26.5

In the case of the ordinary solid oxides, the general rule is that the calculated degrees of freedom can be reproduced by

assigning 3 degrees of freedom to each metallic atom and 1 or 2 to the oxygen atom.

The chlorides and sulphides of the metals conform to the choice of 3 degrees of freedom for the metallic atom, and 3 also for the atoms of chlorine or sulphur.

A question of a peculiar kind and of special interest comes up when we examine the heat capacities of dilute aqueous solutions of electrolytes. Julius Thomsen has shown that these solutions exhibit the very remarkable peculiarity that the apparent molecular heat of the solute diminishes as the dilution increases, so that it even becomes negative after a certain dilution is reached. Now it is evident that this can not be accounted for except by supposing that the water is so associated with some part, at least, of the solute as to have its own heat capacity diminished. The heat capacity is evidently an additive property of the solution. When we think of the solute as associated with some of the water, we may conceive of the solution as made up of the following parts: (1) the water lying outside the groups of water molecules affected by the solute; (2) the undissociated molecules of the solute with the water molecules joined with them; (3) the dissociated ions of the solute with the water molecules joined with them. Each of these parts will have its own heat capacity.

This conception of the composition of a solution leads to a simple formula for its heat capacity, of the form

$$H = W + A(1 - p) + Cp,$$

in which W is the heat capacity of the water used to make up the solution, p is the dissociation factor (it being understood that one gram-molecule of the solute is used in making up the solution) and A and C are constants. The A equals the heat capacity of the undissociated molecule added to the difference between the heat

capacity of the water molecules associated with it and that of the same molecules when free. The C is a similar quantity referring to the dissociated ions.

The formula may most easily be tested in the form $H = W + A + Bp$, when $B = C - A$. We may determine the dissociation factor from Kohlrausch's values of the electrical conductivities. Testing the formula for those solutions for which Thomsen and Kohlrausch furnish sufficient data, we find that it reproduces the observed heat capacities exceedingly well. It breaks down sometimes for concentrations so high as to contain one gram-molecule of the solute to 20 of water.

The formula obtains additional credit from the circumstance that a precisely similar formula gives excellent reproductions of the observed volumes of solutions; these volumes being also additive quantities.

In the cases examined, the constant A is positive, the constant B , negative, and the constant $C = A + B$, also negative.

		A	$-C$
Sodium chloride.....	NaCl	39	31
Potassium chloride.....	KCl	97	55
Sodium hydroxide.....	NaOH	32	33
Potassium hydroxide.....	KOH	59	51
Ammonium chloride.....	NH ₄ Cl	39	23
Hydrochloric acid.....	HCl	3.6	36
Sulphuric acid.....	H ₂ SO ₄	37	43
Magnesium sulphate.....	MgSO ₄	24	261

If this conception of a solution is admitted, it leads to the view that the element of the solute is associated with several, at least with more than one, molecules of water. This is not in agreement with the hypothesis made by Traube and by Poynting, by which they have explained the laws of osmotic pressure by means of molecular attractions. They suppose that one, and but one, molecule of water is intimately bound with the molecule or the ion of the solute. We can examine this hypothesis by means of the values obtained for C . This constant represents the sum of the

heat capacities of the ions of a molecule and of the difference between the heat capacity of the water molecules attached to the ions and their heat capacity when free. We may express this by writing $C = a + a(\phi - s)$, in which a is the heat capacity of the ions, a the number of water molecules in the aggregations around the ions, and ϕ and s the two heat capacities of one water molecule. The values of C are all negative and whether we know the value of a or not, it is certainly positive, and not less than that corresponding to the translational degrees of freedom of the ions, or 6 for a solute that splits into 2 ions. Then $a(\phi - s)$ is surely negative and numerically as great as $C + 6$. If we set $a = 2$, as Traube's and Poynting's theories call for in the case of such solutions as those of sodium chloride and hydrochloric acid, we find, from the values of C , that $\phi - s$ is negative, and numerically equal to or greater than 18. But s is equal to 18, the heat capacity of a gram-molecule of water, and we are led to the conclusion that ϕ is zero or negative; that is, that the heat capacity of the water molecules united with the ions disappears entirely or becomes negative. This result is evidently inadmissible, and I am forced to believe that more than one molecule of water, in all probability several molecules, are associated with each ion.

One serious objection may be raised against this conception, namely, that if it were true the molecular conductivities of all binary electrolytes ought to be nearly the same; for the natural supposition is that the molecular aggregates are pushed by the electric force, and whatever the ions at their centers may be, they all contain about the same number of water molecules, so that they will experience about the same frictional resistance to their motion, and will move at about the same rate. We may evade this objection by considering

the aggregates as unstable, and supposing the ions to slip along through continually changing groups of water molecules. This hardly seems compatible with the considerable interaction which must take place between the ions and the water molecules, to reduce their degrees of freedom as much as the figures indicate; but it is the best way out of the difficulty that I have found.

I may remind you that Jones and his fellow workers, in their study of the freezing points and boiling points of concentrated solutions, have found deviations from the laws of van't Hoff and of Arrhenius, which they have accounted for by the assumption of the formation of such molecular aggregates as I have described.

One is tempted to follow out the suggestions of this hypothesis to see if any general relations can be found in the constants A and C . There are really too many unknown quantities in the expressions for these constants to make it possible to proceed at all except by conjecture, and I have already rioted so much in conjecture, that to go further may seem to carry me beyond the bounds of reason. Yet, if you will indulge me, I will describe such indications of general law as I have detected. Each of the terms A and C is a sum of the heat capacity of part of the solute and of the change in heat capacity experienced by the water molecules when they unite with it. A refers to the molecules, C to the ions. We need a knowledge first of the heat capacities of the molecules and of the ions of the solute. In the case of sulphuric acid, its heat capacity in the liquid state is 34, sufficiently near the value of A , which is 37, to make it possible to suppose that its undissociated molecule either does not associate water molecules to itself or, if it does do so, does not affect their heat capacities. To get the heat capacity of the ions, I am reduced to adding together their atomic heats obtained from the tables. In

all but one case where a comparison is possible between this sum and the heat capacity of the solid solute, the two agree well together. The sum for sulphuric acid is 27, agreeing with the heat capacity 26 of the solid acid. Using this number for a in the formula $C = a + a(\phi - s)$, we get $a(\phi - s) = -70$. The symbol a expresses the number of water molecules affected by the presence of each ion, of which there are 3 for each molecule of sulphuric acid. If we venture to suppose that the number of water molecules affected by each ion is 8, the value of a is 24, and $\phi - s = -3$. Now the heat capacity of the water molecules is 18, so that, on these suppositions, the loss of heat capacity of each water molecule due to its association with an ion of the solute is one-sixth its original heat capacity. This would involve a loss either of 3 external degrees of freedom, translational or rotational, or of one external and one internal degree of freedom. I choose the number 8 for the number of molecules of water affected by the ion, because such might be the number of those standing nearest the ion in a regular arrangement which would be compatible with freedom of motion. We may think of the ion as at the center of a cube, with the water molecules at its corners. If the ion reaches out to more distant molecules, the next larger group it will affect will contain 14 molecules.

To a close approximation the values of C and a for hydrochloric acid, ammonium chloride, sodium chloride and sodium hydroxide, lead to the same value -3 for $\phi - s$, on the supposition that $a = 16$, or $8 + 8$. The same result for $\phi - s$ is reached for potassium chloride and potassium hydroxide if we set $a = 22$, or $14 + 8$. In the case of magnesium sulphate the value of C is extraordinarily large, and indicates a much larger group of water molecules around the magnesium ion. That

this element can affect water powerfully is shown from the circumstance that its sulphate crystallizes with seven molecules of water of crystallization.

The values of A are not, except in the cases of hydrochloric acid, magnesium sulphate, and of sulphuric acid, already cited, the same as the heat capacities of the molecules of the solute, but are larger than they are. It is hard to account for this as we did in the corresponding case of the increased heat capacity of the non-electrolytes when they were in solution, by supposing an increase in their own degrees of freedom. We are led rather to suppose that the molecule of solute affects the surrounding water so as to increase its heat capacity. On the assumption that the number of water molecules affected is 8, except in the case of the two compounds containing potassium, and that for them the number is 14, we get in general the value 3 for the change in the heat capacity of each water molecule affected, or an increase of one sixth its heat capacity.

Of course such statements as these are merely suggestions. I hope that in time the specific heats of electrolytic solutions will be so accurately known as to make it possible to feel certain whether or not a law really obtains in the values of the constants of the formula.

Considering the bearing of the relations that have been adduced upon the general question of the equipartition of energy, it seems to me that their general consistency with that principle, especially the way in which the heat capacities of the organic compounds can be portioned out among the atoms by means of simple assumptions about their degrees of freedom, does afford some confirmation of the principle. Mere chance can hardly account for so large a number of successful coincidences.

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TRANSPORTATION AND COMBINATION.¹

WE are so constituted that each of us looks at the problems of life from a somewhat different standpoint. The opinions we form, the principles we uphold, the policies we advocate, are all influenced more or less by the work in which we engage and the kindred range of our reflections. It is natural, therefore, that I should find the origin of many present-day questions in the facts of modern transportation and communication, and that I should entertain views, perhaps indulge in fancies, which those facts suggest.

The primitive man traveled on foot and moved his scanty belongings by carrying them in his arms or on his back. Even the rude vehicles and water-craft which he eventually learned to construct were propelled by his own muscle, and we can only guess how long it was before he obtained any other motive power for the transfer of his person or his property. In every way his life was meager and isolated, for he had not acquired the art of writing, and intercourse with his fellows was confined to ordinary speech. Outside the family to which he belonged, or the tribe with which he gathered, he had no community of interest, felt no friendship and desired no alliance. His associations were as limited as his means of conveyance.

In a later but still very remote period there came a great increase of motive power by the subjugation of animals, and their employment for transportation on land, and by the use of sails and rudders which multiplied many times the efficiency of water carriage. When these two results were secured, man had added to his own bodily powers the superior strength of beasts of burden and the enormous energy

¹Address of the vice-president and chairman of Section I—Social and Economic Science, American Association for the Advancement of Science, New Orleans, 1905.