DISCUSSION.

Dr. T. M. Lowry opened the discussion. He said that Prof. Kahlenberg's paper was not an easy one to criticise briefly. The theory that Prof. Kahlenberg attacked was not the theory of electrolytic dissociation as he interpreted it, and his standpoint differed from that of the author in reference to nearly all the questions discussed in the paper.

The real founder of the theory of electrolytic dissociation was Clausius, who in 1857 first called attention to the necessity of assuming that a conducting solution contained free ions as well as molecules. Clausius supposed that the period of freedom was very brief, that the ions had only a transitory existence, and that the proportion of ionised molecules in the solution was very minute. All that Arrhenius had done was to suggest (1) that the proportion of ionised molecules was greater than Clausius had supposed, and (2) that in certain instances it was possible to calculate the magnitude of that proportion —the "coefficient of ionisation" of the solution. There was therefore little essential difference between the theory of Clausius, which Prof. Kahlenberg appeared to accept, and the theory of Arrhenius, which he appeared to reject *in toto*.

In the case of dilute solutions, Arrhenius had indicated two methods of determining the coefficient of ionisation, the electrical method and the osmotic method.

(1) *The electrical method.* The author considered the idea of molecular conductivity to be meaningless. The molecular conductivity of a solution of salt in water was, however, quite as significant a quantity as the specific rotatory power of a solution of camphor in alcohol. In neither case was there any reason why the influence of the solvent should be overlooked, even though the power of carrying a current or rotating the plane of polarisation was expressed in terms of the concentration of the solute only. In the case of a mixture of acetic acid and water, neither of which is a conductor *per se*, the molecular conductivity might be expressed in terms of the concentration of either constituent.

The molecular conductivity of a solution was given by the equation

$$\Lambda = a(u + v),$$

whilst at infinite dilution $\quad \Lambda_\infty = u_\infty + v_\infty.$

The relationship $a = \dfrac{\Lambda}{\Lambda_\infty}$ was therefore only valid so long as

$$u + v = u_\infty + v_\infty.$$

The error due to the changing viscosity of the solution was alone sufficient to vitiate all attempts to measure the coefficient of ionisation in solutions of decinormal strength, and it was scarcely safe to extend the method to solutions stronger than N/100. The theory of electrolytic dissociation was, how

ever, equally applicable to the case of concentrated solutions, and even of fused salts, and this in spite of the fact that *the coefficients of ionisation of these liquids are at present entirely unknown.*

The remaining questions discussed by Prof. Kahlenberg were in no sense vital to the theory of electrolytic dissociation, though they had sometimes been used as illustrations by ardent advocates of the theory.   Prof. Kahlenberg had called attention to the difficulties that were sometimes encountered in attempting to determine the coefficient of ionisation of an electrolyte.   Because these difficulties had in certain instances been only partially overcome he denied the validity of the methods adopted, and put $a = 0$ in all cases.   This assumption obliterated the useful working hypothesis afforded by the dissociation theory, but gave no alternative explanation, either of the facts covered by the theory or of the discrepancies to which the author had called attention.

Prof. Kahlenberg had referred to the case of the caustic alkalies in which the molecular conductivity first increased and then decreased as the dilution was increased.   Why had he suppressed the well-known explanation of this fact ?   The decrease was simply due to the neutralisation of the alkali by the dirt in the water, which, even when highly purified, behaved like a dilute solution of (*e.g.*) ammonium carbonate.   The maximum conductivity was shown in an exaggerated form when ammonium carbonate was added to the water, but appeared at greater and greater dilutions as the water was purified. The opposite case, in which the molecular conductivity showed a minimum value and then increased with the concentration, was generally an indication that the solute was a conductor *per se*, and that whilst the conductivity in dilute solutions was mainly heterolytic (due to the action of the solvent on the solute) and increased with the concentration of the solvent, the conductivity in concentrated solutions was mainly autolytic (as in the case of fused salts) and increased with the concentration of the solute.†

(2) *The osmotic method*, like the electrical method, was only applicable to dilute solutions.   But the fact that the molecular lowering of the freezing-point of water was exactly twice as great for potassium chloride as for sugar, could not be passed over as merely due to the greater affinity of the salt for water ; a quantitative explanation must be given of this exact relationship, and this had hitherto only been supplied by the theory of Arrhenius.   The deviations from the simple gas laws observed by Jones and others in moderately concentrated solutions had been admirably explained as due to the presence of hydrates in the solution, but Prof. Kahlenberg, whilst quoting the experiments, made no reference to the explanation of the apparent discrepancy, preferring rather to use it as an argument against the theory of electrolytic dissociation.

Mr. W. C. Dampier Whetham (*communicated*) :   I have read with much interest Prof. Kahlenberg's paper on " The Theory of Electrolytic Dissociation."   Prof. Kahlenberg refers therein to the view of the nature of electrolysis which I have ventured to suggest as most in accordance with the facts known at present.   In the hope of making that view more clear than I seem to have done in my former communication to the Faraday Society, I send the present remarks.

Firstly, may I once more emphasize the distinction between the problem of the nature of solution and the problem of the essential difference between an electrolyte and a non-electrolyte ?   I agree with Prof. Kahlenberg that a study of the phenomena of solution, whether in the laboratory or at the

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* For an attempt to approximate to the coefficient of ionisation of concentrated solutions see Bousfield and Lowry, *Roy. Soc. Proc.*, Nov. 17, 1904.

† Bousfield and Lowry, *loc. cit.*

writing desk, tends more and more to the idea that solution is intimately related to chemical action—represents, perhaps, the general process of which what is known as chemical action is but one case. But, in my view, such a result leaves untouched the question as to the nature of an electrolyte. Though chemical union may take place between the solute and the solvent, the electrically charged parts of the molecules of the solute may still possess the migratory freedom assumed by the theory of dissociation. Freedom from each other is all that is needed by the ions, not necessarily freedom from all chemical combination.

Whatever view we take of the nature of a solution, the phenomena of electrolytes, as distinguished from non-electrolytes, call for explanation. The conformity of electrolytes to Faraday's laws and to Ohm's law when polarisation is eliminated, the phenomena of ionic migration and the concordance of the calculated and observed values for the ionic velocities, show that the fundamental ideas of the ionic hypothesis are well founded. Conduction, that is to say, is best explained by the supposition of the passage of oppositely charged particles through the conducting material.

The ions must be free to move ; but this migratory freedom might be secured either by ionic interchanges between the molecules at the instants of collision, as Clausius imagined, or by a prolonged separation in accordance with the dissociation hypothesis of Arrhenius and Planck. The essential point in the general ionic theory is the migratory freedom, and this freedom may be secured in different ways in different cases. It may well be, I still think, that in the subsidiary point as to how the freedom is produced, the process in fused salts may possibly differ from the process in aqueous solutions of those salts. I do not say such a difference is established ; further evidence seems to me to be needed before any conclusion, one way or the other, can be reached. But I wish to point out again that if the validity of the dissociation hypothesis were disposed in certain other cases, the evidence in its favour in the case of aqueous solutions would still remain and could, I think, be explained satisfactorily in no other way.

The evidence of the phenomena of aqueous solutions was considered in some detail in my paper of last year. I can only summarise in briefest fashion what I said therein :—

(1) The conductivity of a dilute aqueous solution is roughly proportional to the concentration, whereas, on Clausius's view, or any similar theory of ionic interchanges, it should be approximately proportional to the cube of the concentration.

(2) The only really satisfactory measurements we possess on very dilute solutions show that the freezing-points of solutions of sugar are very accurately those deduced from the gaseous value of the osmotic pressure, while those of solutions of potassium chloride give exactly double values. On the thermodynamic theory of osmotic pressure, which is independent of all assumptions as to the nature of that pressure, this result requires some kind of binary dissociation.

(3) No agreement is to be expected at any but the highest dilutions, and there is no reason on the theory to expect concordance or parallelism between the electrical and osmotic curves drawn with concentration.

(4) Although it is quite likely that colloidal solutions are coagulated by different processes, clear connections have been traced between the coagulative powers of salt solutions and their electrical properties. Granting this connection, the extraordinary relation between coagulative power and the valency of the potent ion has been explained satisfactorily on the assumption that the ions move about independently of each other, carrying their charges with

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them.   Chance conjunctions of ions, it has been shown, on the principles of the kinetic theory would lead to the observed results.

We shall await with interest the publication of Prof. Kahlenberg's osmotic experiments.   It would be unfair to criticise the conclusions based on a preliminary account of them, though some of the considerations advanced seem to need further explanation.

I hold no brief for the dissociation theory.   I shall be ready to give it up as soon as any more satisfactory explanation of the phenomena is forthcoming. But at present I do not see how the facts of electrolysis can be explained without the assumption of the assistance, in certain cases at any rate, of a prolonged separation between the ions.

Professor Richard Abegg (*communicated*): I cannot but consider Prof. Kahlenberg's reasons for doubting the dissociation theory as merely based on facts, the explanation of which requires something more than the Arrhenius theory alone.

The fundamental Raoult-law of solutions was not found during the many investigations on freezing-points of aqueous solutions, because of facts complicating the simple relation between depression and concentration.   As soon as Raoult worked with other solutions not showing such complications the law was discovered.

The same seems to me to be the case with the theory of ionisation ; it was detected because of the relative simplicity of the behaviour of aqueous solutions, but it is not sufficient to explain the much more complicated behaviour of non-aqueous solutions.   Therefore it is far too much to say that the theory must on that account be discarded.

It must be considered as a piece of good luck, that just the aqueous solutions were the first object of a detailed study with respect to conductivity and molecular constitution, for here things are apparently as simple as possible ; the non-ionised molecules are for the most part and for most substances *not associated*.

But when association occurs—and association has nothing to do with ionisation—the simple formulæ of Arrhenius's theory cannot possibly hold for calculating, *e.g.*, degree of ionisation from depression of freezing-point, etc.   Now we know that even non-electrolytes, while not associated in water, form associated molecules in other solvents ; why not allow the same explanation for the non-ionised part of electrolytes ?

Another objection to Kahlenberg's views is this : he speaks of the conductivity as being a *measure* of the ionisation, whereas according to Arrhenius's theory the presence of ions causes electrolytical conductivity, but nothing can be said about the magnitude as far as *comparison between different solvents* is concerned.   We may have, for instance, a very small amount of ions causing a great conductivity in a solvent which offers very little resistance to their motion ; on the other hand we can have in another solvent a great amount of ions giving a very poor conductivity because of the friction between the ions and this solvent.   In other words the conductivity must not be used for determining degrees of ionisation without any knowledge concerning the mobility of these particular ions in the solvent under consideration.   Such knowledge has hitherto been very meagre ; we only know that many solvents form very good conducting solutions, though it is impossible to reach a nearly complete ionisation judged from the variation of molecular conductivity with concentration.   Such observations speak in favour of the assumption given above, that the solvent-friction has a great effect on conductivity.   Therefore even Kahlenberg's observations *could* be explained in the same way—observations which show that solutions reacting

like electrolytes with one another form " excellent insulators," or better, conductors of about the same—although small—conductivity as pure water, for Walden * has found that most pure solvents show a conductivity of the order of magnitude 10^{-7}.

Apart from that it may be emphasised, that the assumption of instantaneous action being conditioned by the presence of ions is by no means an integral part of Arrhenius's theory. †

Concerning the assumption of chemical action between solvent and solute I am glad to state that I am almost in complete accord with Prof. Kahlenberg, as he can convince himself by reading any of my later papers. ‡ But I cannot see how these old and generally adopted views interfere with the Arrhenius theory. At least I have myself never found any difficulty in combining both ideas. §

Further objections of Prof. Kahlenberg seem to me founded on faulty logic. In the same way that one has to concede that the additive properties of electrolytic solutions are no proof in favour of the Arrhenius theory (although lack of additivity would be a proof against it), so may a solution of a copper salt in benzene show the colour exhibited by copper ions in aqueous solution even if no copper ions were present. All copper ions must be blue, but all blue things are evidently not copper ions !

The law of mass action not being in harmony with the constitution of electrolytes is another objection of Kahlenberg to the theory in question, but it is not, I believe, "a well-known fact." I think we have every reason to believe the contrary ; Rothmund and Drucker ‖ have shown that the law of mass action holds good for strong acids such as picric acid and others by measuring only the un-ionised part by a method of sufficient accuracy. Jahn, on the other hand, has made it probable that conductivity is not, as hitherto assumed, a perfectly exact measure of the degree of ionisation, and that this inexact assumption answers for the apparent differences of the strong electrolytes from the law of mass action.

I cannot possibly answer all Prof. Kahlenberg's objections without writing a new paper instead of remarks in a discussion. But I have selected the most important points to show how they *can* be brought into accordance with the Arrhenius theory and give a *possible* explanation of the experimental facts, even of the many important and interesting facts which Prof. Kahlenberg has collected himself with such admirable experimental skill.

I do not wish to enumerate the almost interminable series of facts of which the Arrhenius theory has given the most successful quantitative explanations, but what I should like to say is this : if one wishes to overthrow any successful theory it is not sufficient for the progress of science to point out its difficulties —in that case not one theory in science would be valid !—but it is necessary to find another theory likely to explain not merely the difficulties of the old one but also the many phenomena and observations already embraced by it, a procedure a classical example of which you see in the history of the theories of light.

Dr. G. Rudorf (*communicated*) : I would like to amplify Prof. Abegg's remarks in one or two instances. First with regard to colour. I do not

* Ostw., *Zeitschr.* **43**, 409 (1903).
† See Haber, *Zeitschr. f. Electrochem.* **10**, 775 (1904).
‡ See *Christiania Vidensk-Selsk. Skrifter*, 1902, No. 12 ; or *Ztsch. anorg. Chem.* **39**, 330 (1904).
§ See Abegg, *Theorie d. electrolyt. Dissociation*, Ahrenssche, Sammlg., Bd. VIII. Stuttgart, 1903.
‖ Ostw., *Ztschr.* **46** (1903), 827 ; **49** (1904), 563.

for a moment think that any believer in the dissociation theory would assert that because, *e.g.*, copper sulphate is blue, therefore it must contain only copper ions. Ostwald,* in 1892, pointed out that the apparent disagreement of Magnanini's results with the dissociation theory could be explained if one assumed that the molecule of copper sulphate had nearly the same light-absorbing properties as the ion. There is absolutely no difficulty in the assumption. I have gone into this question of colour of solutions fairly thoroughly in my monograph † on the subject published in the well-known Ahrens collection, and have come to the conclusion that all known facts admit of an explanation using the dissociation theory and allowing for complex formation. I might, however, mention that Prof. Kayser, of Bonn, wrote to inform me that while preparing Vol. III. of his magnificent treatise on Spectroscopy he had come to a rather different conclusion.

I quite agree with Prof. Abegg that hydrates or solvates, as Noyes has suggested to call them for liquids other than water, do exist in solution. Why should they not do so? Ions are there too.

The reactions mentioned in benzene solution are also easily explained. We have only to assume that there are a very few ions present. The reason the solution will not conduct is then either that the friction is too great or that there are so few ions that to measure the conductivity requires a more delicate instrument than Prof. Kahlenberg used. Granted, then, that it has not been proved that absolutely no ions exist. The next stage is simple. If the velocity of ionisation of the molecule in the solvent is not less than the velocity of formation of the precipitate, then the precipitate will continually form as fast as the precipitant is added. We need, therefore, only assume that very few ions are present, and the whole set of reactions admits of easy explanation. In conclusion, I would like to be allowed to record my very high appreciation of Prof. Kahlenberg's experimental work. It is truly beautiful, but it has not yet overthrown Arrhenius's theory.

Dr. H. J. S. Sand (*communicated*) : I think the Faraday Society is to be congratulated on obtaining from Prof. Kahlenberg a summary of the facts which have led him to discard the ionic theory. The objections raised will, I think, serve as a salutary corrective to the tendency which to my mind pervades contemporary chemical thought to exaggerate the scope of the, ionic theory and to use facts which neither contradict nor support it as arguments in its favour.

Nevertheless I think most chemists and physicists will agree in believing that Prof. Kahlenberg, in altogether rejecting the ionic theory, is going a great deal further than the facts quoted by him warrant. It is difficult to see what view should be taken if the ionic theory were discarded. Prof. Kahlenberg refers at the beginning of his paper to Clausius's theory. Now Clausius's theory differs from that of Arrhenius only in stating more in one respect and less in another ; but there is no contradiction whatever between the two.

Clausius, as is known, assumes that the constituents of which the molecules of electrolytes are built up are continually changing partners, and that it is the pieces which are passing from one molecule to another that conduct the current. These pieces are essentially ions, and at every instant a definite fraction of the total number of molecules is therefore necessarily in the ionic state. No doubt Clausius himself thought it probable that the degree of ionisation was very slight and the essential difference between his theory and

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* *Z. phys. Chem.* **9,** 759.
† G. Rudorf, *Die Lichtabsorption in Lösungen vom Standpunkt der Dissociations-theorie.*

that of Arrhenius therefore lies only in the very much greater degree of ionisation which Arrhenius assumed to exist in certain cases.

Now it must be admitted that the methods put forward by Arrhenius for the determination of the degree of ionisation do not always lead to correct results, and in certain cases give altogether misleading ones. These methods are based on one of two assumptions, neither of which is absolutely essential for the maintenance of the ionic theory. The first is that the degree of ionisation is proportional to the molecular conductivity, the second that the ions obey the gas laws. I do not think that the many cases in which these different assumptions lead to results which agree with each other can be passed over so lightly as is done by Prof. Kahlenberg, yet these assumptions undoubtedly do not always hold. The strongest evidence in favour of complete dissociation in certain electrolytes is, I think, to be found in the strictly additive nature which all those properties of these solutions which are capable of exact measurement have shown. I refer specially to conductivity, optical rotation in the case of salts of optically active acids, and, most important of all, internal energy as revealed by thermochemical measurements. It may be argued, as has been done by Prof. Kahlenberg, that approximately additive properties occur also where there is no electrolytic dissociation ; but in all these cases the properties are subject very strongly to constitutive influences, and they are by no means strictly additive, like the properties of those dilute solutions of electrolytes which we believe to be completely ionised.

In conclusion, I think it is no very serious argument against the ionic theory that certain substances which are not ionised show properties that are also exhibited by ions. Thus it has, of course, been apparent as long as the ionic theory has been in existence, that copper sulphate crystals are blue, although they probably contain no copper ions. This fact has never been considered a very serious argument against the ionic theory, yet it appears that many of the cases brought forward by Prof. Kahlenberg as arguments against the ionic theory, such as the colour of benzene solutions of certain oleates, the instantaneous precipitation of cupric chloride in non-ionised solutions, and the action of non-ionised trichloracetic acid on metals and carbonates, can only be classed with the colour of copper sulphate crystals, and I think their importance must be considered to have been somewhat exaggerated.

Dr. C. H. Desch (*communicated*) : With reference to Prof. Kahlenberg's interesting experiments with copper oleate in benzene solution, I should like to call attention to an experiment which I made in the early part of 1901, and which is described in a paper by Prof. Hantzsch and myself in Liebig's *Annalen* for 1902. The ferric compound of acetylacetone dissolves in water or benzene to form coloured solutions. Even a large excess of hydrochloric acid has little effect in destroying the colour of the aqueous solution. The reaction—

$$Fe(C_5H_7O_2)_3 + 3HCl \rightleftarrows FeCl_3 + 3C_5H_8O_2$$

only proceeds very incompletely in the sense of the upper arrow. In dilute solution, the salt may even be boiled with twelve times the quantity of hydrochloric acid theoretically necessary to decompose it without destroying the colour.

But in dry toluene solution, on adding a dry solution of hydrogen chloride in toluene—which has no electrical conductivity—decolorisation takes place instantaneously when the exact theoretical quantity is added.

It has been sometimes said that Prof. Kahlenberg's solutions must have been imperfectly dried. That this would not explain his results is shown by

the fact that here is a case where the reaction proceeds incomparably *better* in toluene than in water.

The ionic theory holds the field as a working hypothesis, but non-aqueous solutions undoubtedly present great difficulties, and Prof. Kahlenberg's objections require very serious consideration.

Dr. H. Borns remarked that they were indebted to Dr. Kahlenberg ; this contribution by so eminent an opponent and experimenter would help to clear the ground. The author seemed to attack the dissociation theory as if everything that had been written in favour of it formed a chapter of an orthodox Bible. The previous speakers had already shown that Dr. Kahlenberg criticised many views that were not really held by the majority of modern electrochemists, and as regards the physiological action of electrolytes, Nernst differed from Arrhenius. Dr. Kahlenberg, moreover, dealt with his subjects as in the days when one simple formula was supposed to cover the whole range of the problems of a reaction. He did not refer to complex ions, association, hydrolysis, and friction between ion and solvent, though the consideration of these points had successfully overcome many of the apparent inconsistencies to which the author objected.

Dr. Kahlenberg's own suggestions hardly touched the real difficulty, the explanation of the fact that ions migrate at different rates, and it was not at all clear why we should begin with the most concentrated solutions. There were always two limiting cases, and not only one, as Dr. Kahlenberg said, and the reasoning of differential calculus would lead us to begin with the minimum, the most dilute solutions. Any method proceeding from the maximum would, however, be welcome.

Mr. F. S. Spiers drew attention to a theory of solution recently put forward by Traube,[*] which was similar in many respects to the theory apparently held by Prof. Kahlenberg, but which was of particular interest in this connection because it gave numerical expression to the Arrhenius dissociation factor i in terms of a certain kind of affinity between solvent and solute. As it had not been referred to by any of the speakers, he thought it of sufficient interest to put before the meeting. Traube is of opinion that the calculation of the so-called coefficient of dissociation is the indisputable merit of Arrhenius, but recent work compels us to reject his interpretation of that quantity.

Let n molecules of a non-volatile solute be dissolved in N molecules of the solvent, and suppose each of these n molecules are associated (in the case of water to form a kind of unstable hydrate) with a molecules of the solvent.

Then this association prevents an molecules of the solvent from evaporating.

Then since the vapour-pressure must be proportional to the number of molecules of solvent available for evaporation, we have

$$\frac{f}{f_0} = \frac{\text{vapour-pressure of solution}}{\text{vapour-pressure of solvent}} = \frac{N - an}{N}$$

$$\text{or } \frac{f_0 - f}{f_0} = \text{proportional diminution of vapour-pressure} = \frac{an}{N}$$

If for non-electrolytes we put $a = 1$, for binary electrolytes $a = 2$, and so on, this equation becomes the law of Raoult.

Traube gives a physical meaning to a by supposing that one molecule of a non-electrolyte, such as urea or sugar, wanders about through the solution (after the fashion of Clausius's theory) at all times loosely combined with *one*

[*] See *Phil. Mag.*, August, 1904.

molecule of solvent. But an ion—which may be conceived as only being actually free at the instant of dissolution—has the power of dissociating complex molecules of the solvent, and then attaching a single one of these molecules to itself. Thus a binary electrolyte like NaCl would then become associated with *two* molecules of water, so that a in the above equation is equal to 2 : and so on.

Therefore Arrhenius's coefficient of dissociation is given by the relation of the number of particles of the electrolyte joined with 2, 3, etc., single molecules of solvent, and the number of its particles joined with one molecule of the solvent, or none. Traube further shows how the Rudolphi-van't Hoff formula, which the author said was merely empirical, may be deduced from these considerations, and thus have a theoretical basis.

He thought that Prof. Kahlenberg was not acting quite fairly towards the dissociation theory—was, he believed, not historically accurate—when he complained that the ideas of the theory had been applied to other cases of conduction such as that of electricity through gases. As a matter of fact the very reverse was the case. The conception of ionic conduction in gases arose quite independently of the theory of solutions, and indeed it actually afforded corroborative evidence of a very high order in favour of the possibility of the existence of free ions.

Mr. H. D. Law (*communicated*) : With reference to the subject of Dr. Kahlenberg's paper, there are a few points to which I should like to draw attention. As is well known, there are many just objections to the present theory of electrolytic dissociation. To those already mentioned by other speakers might be added the conduction of certain earths. Many of these in a pure state offer a very high resistance to a current of electricity, but when contaminated with foreign matter conduct fairly well. At first sight this example appears to be analogous to solutions of electrolytes in water. However in these oxides no separation of elements is observed at the poles, as is the case with water solutions. So it has to be assumed that the current is handed along from ion to ion. No such assumption is made in the case of water solutions.

In many cases there seems to be a close connection between viscosity and molecular conductivity. This fact has been used to explain many anomalous results. Gelatine solutions, however, conduct in much the same way as solutions in water. Here the viscosity is exceedingly high. Other examples of similar results might be quoted, and on the whole it must be concluded that any such connection is extremely small.

It seems to me that electrochemical investigators lose sight of the fact that electricity is one form of wave motion, resembling in many respects light and heat. To light and heat many substances are opaque, many transparent, and others take intermediate positions representing every grade of transparency. A similar state of affairs occurs in the case of solutions and electricity. It is assumed that to conduct light from place to place some very attenuated substance is necessary—namely, ether. It is probable that a similar substance—or the same—is necessary for the conduction of electricity in solutions. As the conduction of currents in solutions is very closely connected with the solute, it may be assumed that this medium is formed by a further dissociation of the ions already present. The work of Prof. Thomson makes this view very probable. However until electrolysis and other electrolytic phenomena are more fully explained, it is impossible to discard our present theory.

The Chairman said they all felt very grateful to Prof. Kahlenberg for the opportunity he had afforded the Society for having such a good discussion

on the theory of dissociation. Certainly the discussion served to show that the theory was far from being obsolete, and that it would still give rise to much very useful work ; but they none the less welcomed and valued Prof. Kahlenberg's trenchant criticisms, which in themselves, he ventured to think, gave evidence of the vitality of the theory. He hoped the meeting would accord Prof. Kahlenberg a very hearty vote of thanks for his most interesting and stimulating paper.

Prof. L. Kahlenberg (*communicated*) : A detailed consideration of each point raised in the discussion would lead very largely to an elaboration or reiteration, in somewhat different form, of what has already been stated in the paper. I shall therefore only touch briefly the most important points brought out by the various speakers.

The theory of electrolytic dissociation considered by me is that which is expounded in all standard texts on physical chemistry and in Arrhenius's own treatise on electrochemistry. With regard to the Clausius hypothesis I would only claim that it really contains about all that is of consequence in the Arrhenius theory. The distinguishing and vital point in the latter hypothesis lies in the claim of the relationship between the conductivity of solutions and their vapour tensions, which fact some of the speakers have apparently overlooked.

The objection to calculations of molecular conductivity lies in comparing these values for solutions at different concentrations as is usually done. In this process resistances of different cross sections are directly compared, which is clearly not allowable. This has been fully set forth by Mr. Reed in the article cited above, and need therefore not be dwelt upon further here. In determining the specific rotatory power of a solution, no notice whatever need be taken of the area of the cross section of the liquid column examined.

That the influence of viscosity on electrolytic conductivity is not so important a factor, as claimed by Dr. Lowry and also by Prof. Abegg, is well brought out by the remarks of Mr. Law. The increase and then decrease of the molecular conductivity, with increasing dilution in the case of caustic alkalies, has always been found, even when water quite free from ammonia and carbon dioxide was employed.

Efforts to apply the law of mass action to the behaviour of solutions of sodium and potassium salts and strong mineral acids have all signally failed. And, since it is now generally admitted, even by the most ardent supporters of the Arrhenius hypothesis, that there is no unobjectionable way of calculating the so-called degree of electrolytic dissociation, what becomes of the array of *quantitative* explanations of the interminable series of facts which Prof. Abegg says the theory has furnished ?

With regard to the colour of solutions the reasoning is not at all as Prof. Abegg and Dr. Rudorf take it. It is simply that since both conducting and non-conducting solutions of copper salts are blue, the colour of the conducting solutions can evidently not be used as an argument for the existence of free copper ions, in other words, as an argument in favour of the dissociation theory.

In view of one of Prof. Abegg's remarks, it becomes necessary to say that the electrical conductivity of benzene, and of the solutions in that solvent under consideration, is far less than 10^{-7}.

Dr. Rudorf says, if we "assume" the presence of a few ions in the benzene solutions, then the reactions can be explained. Here he clearly assumes the very thing which it is incumbent upon him to prove. Again, he merely asserts, concerning the content of solutions, "ions are there too"—the very matter of contention.

Prof. Abegg would lead us to think that non-aqueous solutions present the acme of simplicity as long as they are non-electrolytes, and again aqueous solutions are quite simple in their behaviour as long as they are conductors ; but when non-aqueous solutions are conductors, then their case is quite complicated as compared with aqueous conducting solutions.   We have here an excellent illustration of how a preconceived theory may lead one to see complications where none exist.   Viewing the facts independent of all theory, there is no reason for considering the case of aqueous and non-aqueous conducting solutions, and of fused electrolytes as well, as being at all different. The existence of association in non-aqueous solutions and its absence in aqueous solutions is generally founded upon the assumption of the van't Hoff theory of solutions.

The existence of hydrates, complex ions, associated undissociated molecules, have each, and often all, been assumed to uphold the dissociation theory, and very frequently without any reason whatever except to maintain that theory at all hazards.   It is for this reason that the matter was not deemed of sufficient import to be further exploited in the paper above.

I am grateful to Mr. Spiers for mentioning the recent paper of Traube. I cannot agree with the latter, however, that the calculation of the degree of electrolytic dissociation by Arrhenius is a matter of special merit ; and, though Traube has formed a better basis for the Rudolphi-van't Hoff formula, it must be borne in mind that the latter has at best but limited application. I would further thank Mr. Spiers for pointing out that I have not given sufficient weight to the experimental work done on the conductivity in rarefied gases.   While this work has an important bearing on the problem of the nature of electrical conduction, it has no bearing on the vital point of the Arrhenius theory, namely, the relation between vapour tension and electrolytic conduction.

I fully agree with Mr. Whetham that the problem of the nature of solutions and that of electrolytic conduction are to be considered separately. The dissociation theory really confuses the two propositions by asserting a relationship between electrolytic conduction of solutions and their vapour tensions, which facts show does not exist.

In a solution of sodium chloride in water, for instance, *all* the salt is to be considered as combined with *all* the water.   Only thus can the lower vapour tension of the solution as compared with that of the pure solvent be explained. Were only a part of the water of the solution combined with the salt, the free water would cause the solution to have the same vapour tension as the pure solvent, and this condition of affairs would remain until all the free water had evaporated from the solution, and then only would the vapour tension of the solution fall below that of pure water.   Similarly in every solution *all* of the solvent is to be regarded as combined with *all* of the solute.   Now, at any given temperature, the vapour tension of solutions is a function of the concentration, and a similar function in the case of similar solutes in the same solvent. Upon this basal consideration our views of solutions must, to my mind, be built.   Further details can of course not be given here, but whether a solution will conduct electrolytically or not cannot be foretold from its vapour tension.

Perhaps some time we shall be able to predict from some property of a solution as to whether it will conduct electricity.   We are, however, not able to do this now ; nor can it be done in the case of conductors of the first class. We have no adequate conception of the nature of electrical conduction in metals (to be sure attempts have recently been made to give such an explanation on the basis of the electron theory), nor has the necessity for such a

mechanical explanation of how electricity passes through a wire been generally felt in the development of electrical science.

In the case of electrolytes, the migrations, upon which Mr. Whetham lays so much stress, may be considered as simply secondary diffusion phenomena caused by the fact that certain products are eliminated or introduced at the electrodes. This would apply to all electrolytes without exception, and there are no experimental facts with which this conception would collide.

It has been argued that it is not enough to show that a theory is inadequate, but that a new theory to replace it must be forged. I confess that I am not hankering for more theories. The pathway of the progress of science is strewn with defunct theories, and not always has a new theory replaced an old one. I would not depreciate the value of a working hypothesis, but I would also not minimise the power it has to lead the biased investigator astray. I consider the attitude which Faraday always maintained toward theories the ideal one.

At present I incline to the opinion that electrical conduction in rarefied gases, metals and electrolytes is essentially the same in character. Further careful experimentation will no doubt give us more correct views of the electrolytic process, though it has been the subject of study for a century.