REPORT ON FURLOUGH STUDIES.

AS-004396

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A comparison of methods in vogue at Oxford and Allahabad as regards the higher teaching of Chemistry, with suggestions for raising Indian standards and for encouragement of research work.

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Report on Furlough Studies, by E. G. Hill, B. A., D.Sc., Professor of Natural Science, Muir Central College, Allahabad.

1. Personal research and study .-- Of all branches of Natural Science, that of Physical Chemistry is undoubtedly the one which has been most developed during the last 10 or 15 years. This branch, however, is the one which in India has least attention given to it, because it is the one with which teachers themselves have least acquaintance and with which they have the least opportunity of becoming familiar. It was to Physical Chemistry and especially the practical side of Physical Chemistry that I devoted the greater part of my time, and to get the greatest advantage from my surroundings I entered as a research student in the University of Oxford. This was a somewhat unusual proceeding for one of my university standing, but it brought me into touch with both students and the tutorial staff, among which latter were several of my personal friends. Of the system prescribed for research students, I shall have to speak later. It is not necessary for me to refer to my own research beyond saying that I was eventually awarded the research degree of the University. An account of my work appeared in the Journal of the Chemical Society, August 1906 (appendix A.). In addition to the research just mentioned I went through an advanced course of physical chemistry, one which is somewhat in excess of the requirements of the University for its honours school, and I have prepared an advanced course which may be useful in India, chiefly from the course in use at Balliol College, where the laboratory is specially devoted to the study of physical chemistry.

2. Scope of Report.—My work was not, of course, confined to actual study of chemistry and chemical methods, but was extended to the methods of study and the courses of study in vogue at Oxford. It is with these latter and with their comparison and contrast with Indian methods that this report will largely deal. It will be as well to trace the career of a student from his matriculation to his final school, before attempting to describe the conditions under which he is allowed to begin original work.

3. Preparatory work in Oxford and India compared.-Most, if not all. of the Oxford undergraduates, who intend to make a serious study of Chemistry, have already had a thorough grounding in the subject at school, and are prepared to take the Preliminary scientific examination without further tuition. This examination is held during the first year of residence and is of a considerably higher standard than the Intermediate examination of Indian Universities. A student taking up Chemistry is examined in Chemistry and Physics by both written papers and practical tests. The Chemistry consists of elementary organic and inorganic, and simple inorganic analysis, and preparations, and is but little, if any, lower in standard than that of the Chemistry for the B.Sc. of Allahabad. The Physics is similarly higher than that for the Indian Intermediate examinations and the examination also carries a practical test. There is no examination in Mathematics for the Preliminary Science, but many candidates with a mathematical bent offer themselves for Mathematical Moderations at the end of a year and then continue their chemical studies.

After passing the Preliminary Science, which is strictly a pass as opposed to an honours examination, the student has practically nothing to study except his special subject, i.e. Physics or Chemistry. This report deals only with the latter subject. The usual time for the examination is at the end of the 4th year from matriculation, but it may be taken at the end of the 3rd year. The average man has thus three full years after his Preliminary in which he can devote himself to Chemistry in its usual branches, and his course of studies would be more or less as follows. He would attend from three to six lectures a week given by University (as distinct from College) lecturers or by what may be called "privat docents," i.e. lecturers who are

allowed to lecture in the university lecture halls. These lectures are arranged so as to break into the day's practical work as little as possible, and are often given from 9-10 A.M. or 10-11 A.M., or sometimes in the evening. The rest of the morning is given to practical work at either the university or a college laboratory. The afternoon is occupied with some form of recreation, and the evening from 5-7 again with practical work. Dinner is at 7, and the time after dinner is spent in private reading. A diligent student would probably get through his practical course in two years' time after the Preliminary Science if he worked on this plan, and would possibly help in a research for part of his 4th year or spend much of his time in reading original papers, specializing in some particular branch of chemistry. The course given above is the public course open to all members of the university, but Oxford and Cambridge differ from all other universities, in that they consist of system of corporate institutions each of which assumes the responsibility for the tuition of its own undergraduate members. Not all colleges make provision for the study of the Natural Sciences, but those which do so, have a special tutor whose business it is to look after the interests of the science students of his own college. This he does in many ways. He guides the student in his choice of the public lectures, arranges for his practical work, and as a general rule, supplements the university instruction by private tuition in the college. This latter method of instruction is in my opinion the most important feature of the Oxford system, since an enthusiastic tutor certainly stimulates enthusiasm in his pupils, and the system of private tuition gives opportunities for discussion and arousing interest which can never be afforded in public lectures.

The extent of the course for the honour school is of course much greater than that for the B.A., or B.Sc., degree of Indian universities, and it is generally understood that the M.A., or 2nd D.Sc., examination of Allakabad more or less corresponds to the Oxford B.A. As a matter of fact such a correspondence did exist some six or seven years ago; but whereas Oxford has marched with the times, Allahabad has remained precisely where she was when the new courses were instituted. The reasons for this will appear below.

4. Low Indian Standard.—It must now be conceded that whereas an Oxford honours degree does fairly well fit a student for research work, the same cannot be said so confidently of an Indian Master of Arts. The latter has a good working knowledge of text book chemistry and practical methods up to a certain point, but that point is now decidedly below the level attained by an Oxford graduate. For instance, as was indicated at the beginning of this report, practical physical chemistry is only known in Indian Universities in its most elementary form, but in Oxford one laboratory (Balliol) gives up all other subjects in order to specialize in that branch alone. In organic chemistry much highly important modern work (such as that of Hantzsch on the *Pseudo-acids* to give only one example), has been ignored in India, simply because it has not yet filtered into the text books. Thus it will be seen without further enlargement that both in practical and theoretical work Indian universities have again fallen behind. It is as well to consider whether this is a necessity, and if not so, where the remedy lies.

It has already been stated that after the Preliminary Science the Oxford student has three years of specialized work in Chemistry, and to this may now be added that he works under highly favourable conditions and with the best instruction. But the Indian student on the other hand works at Chemistry as a special subject for only two years after passing an examination of a corresponding standard in Chemistry and Physics (he has or had till recently, it is true, the great advantage of extra mathematics), so that the Oxford man has a clear advantage of a whole year's work. In the present writer's opinion this year must be made up in one way or another, not necessarily for the M.A. examination, but certainly for the doctor's degree which is awarded for original work. This can be done in two ways. The course for the doctorate may be extended by one year, that is to say, a candidate for the degree should be a Master of two years' standing, or the B.Sc. standard may be raised. Either of these courses is perfectly practical.

At present the Intermediate Chemistry course is almost ridiculously easy and it contains no practical work at all. A good teacher can get through the Allahabad Course in one year working three hours a week. The course might thus be extended considerably. Similarly the course for the B.Sc. until last year contained no organic Chemistry. The introduction of this subject will undoubtedly allow a wider and deeper reading of students for the Master's degree, but perhaps the point which is weakest in the whole Chemistry course in Allahabad is the practical work for the B.Sc. (there is none for the Intermediate !).

This includes a very easy set of preparations and ordinary simple qualitative analysis, but no quantitative work of any kind.

It would not be impossible in a properly equipped and properly staffed laboratory to take almost the whole of the B.Sc. practical work and put it in the Intermediate course, certainly all the 'preparations' should be there. Then there would be room (almost a vacuum!) for some quantitative work in the B.Sc. course. It is most essential that a change should be made in the B.Sc. course, for the practical work there is already too light, and the change should be in the introduction of quantitative as distinct from qualitative work. A change on such lines should not be sudden, but on the other hand it should not be too gradual, and in the meantime the research student will find that a year (the minimum time allowed by the Allahabad University) of post-graduate research work is not sufficient for a research degree. These remarks find striking confirmation in Professor Kuchler's Report on Physical Laboratories in Germany (page 10).

The Teaching Staff .- The above is only one reason for the lower standard 5. of the degrees in Indian Universities. A second and equally, if not more, important one lies in the teaching staff. The average Indian student is not stupid or slow to learn the physical sciences, even when he begins them for the first time in College and not in School, but it is lamentably the fact that he is as often as not, badly taught from the beginning, and insufficiently taught as his work becomes more advanced. Now there are very few, if any, colleges which confine their advanced classes to only those students who have received their elementary instruction in their own lower classes, and the consequence is that, in the majority of colleges, a large percentage of the students in B.Sc. (3rd and 4th year) classes are derived from colleges of a lower grade altogether. They have often only just managed to scrape through the Intermediate examination. This fact obviously tends to keep down unduly the standard of the B.Sc. course. Thus the remark that one of the reasons for the low standard of Indian degrees lies in the teaching staff, does not necessarily imply defect in those who are instructors for the degree classes, but it implies a defect in the general average of the teaching staff in all classes from the very beginning. There is no doubt that things are slowly improving, but that so long as chemistry or physics are taught from the book apart from practical work, in whatever class at all, so long will the teacher tend to deteriorate; the converse holds equally true. The extension of practical work to all classes is a necessity.

If we consider the M.A. classes, the highest classes for Chemistry or Physics, we find that the number of affiliated institutions is small indeed. It is so small that for obvious reasons a criticism of the staff is impossible. But a very serious question here arises. If we consider Northern India we find that there are not more than half a dozen institutions which profess to be able to give M.A. instruction, that is to teach up to a standard which is admittedly lower than that of English University degree. In these institutions there is never more than one teacher for the course and he in every case has to assume the responsibility and share in the teaching for all the lower examinations. This defect will be



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referred to more fully subsequently. Another even more serious drawback to research is the fact that teachers do not keep up with the times. In fact they cannot. They lack libraries, periodicals, in many cases materials, and not least they lack absolutely that intercourse with those engaged in similar scientific pursuits, which is the very spirit of progress. The above applies, in its degree to colleges of a lower standard. Those who are teaching up to the B.Sc. standard only, have no stimulus from keep abreast of the times. Our courses vary but little from year to year, and the majority of teachers are quite content to extend their knowledge as the courses are extended. Some suggestions will be made later in this report, for the amelioration of this state of affairs.

6. Laboratories and Accommodation.—Since the introduction of Lord Curzon's Education Bill, with the consequent inspection of all affiliated laboratories, these latter in the United Provinces have undoubtedly enormously improved. The majority of them are quite satisfactory for the work they undertake. There are moreover in India several laboratories of quite as high a standard as a firstclass English one, and they differ from English ones only in their equipment. With the equipment of a research laboratory I shall have some remarks to make subsequently, but as regards a description of the laboratory building itself, there is no need to take up time or space.

7. The Research Course.—Hitherto my remarks have been limited to what I have called preparatory work, that is the period of study which is necessary to fit a student for independent or even assisted research. I now come to the Research work proper.

8. The post graduate course at Oxford .--- In appendix B. will be found the regulations which concern the research degree at Oxford. To make the course quite clear this needs a little amplification. After taking his final examination and subsequently his B.A. degree a student wishing to take a research degree must decide on a subject in which he is prepared to carry on some original investigation. As a general rule he is dependent on his college tutor, one of the university professors or readers, or some other official for his subject, and when he has made his choice he sends in an application to the Board to get his subject officially sanctioned. This step is a very useful one, because it prevents waste of time over an unsuitable subject, and at the same board meeting one or two tutors of some standing in the university are appointed as supervisors of the students. Supervisors are selected who have special knowledge in the subject which the student intends to investigate. The supervisors are intended to criticise the student's work from time to time, to offer suggestions and to give advice if any peculiar difficulties crop up in the research, also to see that the whole of the practical work is actually done by the candidate himself. On the completion of his work a thesis embodying all the details of his research is submitted to the board by the student, when examiners are appointed who report on its merits. If it is up to the mark the degree is duly awarded. It should be added that the candidate may work in the university laboratory or in any college laboratory as he wishes, or as he may find convenient.

9. Amount of research at Oxford and its manifold Nature.—The research done by students is of course the least important of that which is going on at Oxford. Every professor or demonstrator, and tutor has his piece of research which he carries on in the time which he can spare from his duties as a teacher, and naturally the field covered by these researches is very wide indeed. Even that of the research students is selected from many different branches of chemistry. While I was in Oxford there were about a dozen students working or preparing for the research degree in chemistry, and the widely divergent natures of the work going on at Oxford may be shown by the list of researches in progress last year (see appendix C.).

10. Specialization at Oxford.—In this respect Oxford is perhaps rather different from German Universities, which tend to concentration more on the

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particular subject in which the Professor and his chief assistant are specially interested. It must be remembered, however, that owing to the system of college tutors above described, the total number of teaching experts is much larger proportionately than in German universities, and a wholesome spirit of co-operation and interchange exists between the colleges, which enables them to specialize in particular branches of the science without any detriment to any of their own students whose inclinations may turn to some other branch. The University lecture list for the present year shows the large variety of lecture courses open to students, each of which is in the hands of a specialist, and it will be seen to include some seven different subjects given by fifteen different lecturers (see appendix D.). This does not include the college tuition mentioned above. Most of these courses are in a varying degree in advance of the requirements of the degree examination. To illustrate in some degree the manner in which colleges interchange, and the benefit of the system to specialization, it is enough to say that Balliol takes physical chemistry, Christ Church inorganic, Magdalen quantitative analytical, while most of the organic work is done at the university laboratory.

The feeling for the maintenance of the existing college laboratories as opposed to all work being carried on at the university laboratory is very strong and a new laboratory is in course of construction at Jesus College which will be opened next year, with a Fellow of the college in charge. The great benefit of the system is that it enables a college tutor to specialize in a degree which would be quite impossible if his duties were more general, with the consequent advantages to the students. Thus the specialized inorganic chemist would have little or nothing to do with organic work and the students from his college would get their organic work done at some other laboratory and so forth. Now this specialization is of supreme importance in research and the guidance of research students. While dealing with this point, I should like to call attention to Professor Kuchler's remarks on the guidance of research in German Universities (Occasional Reports, 1905, page 11). It is essential that a supervisor should be "conversant with the literature of all the work that has been done up to date in the special line of research," and it is obviously, as a rule, quite out of the question for a professor or tutor to direct studies in many different lines of research at the same time. Professor Kuchler's remarks on this point deal with Physics, but they apply with equal truth to Chemistry, a science which has developed in the last twenty years into a group of sciences which no single intelligence can master.

11. India and difficulties .- When we turn to Indian Universities we find a different set of conditions. Here each college is independent and instead of being a supplement to other similar institutions it is too often a rival, and specialization in different branches of Chemistry by a college is out of the question. In small colleges, as has been shown, teachers have no opportunities for becoming acquainted with recent work, much less of doing research work on their own account. The large colleges, those in which research work is being carried on for university degrees, are prevented from co-operation by distance, and we are confronted with one real difficulty to research in India which is the limited nature of the laboratory staff, and consequent impossibility of any college keeping abreast of the time in every branch of chemistry. If in Oxford it is recognised advisable for one man not to attempt to even teach all branches of Chemistry it is hardly possible in India for one instructor to stimulate research in all branches. Now, I do not wish these remarks to be understood as a protest that the staff of the laboratories is inadequate for the work which they at present undertake. On the contrary, for my own part, I have always found the Government of United Provinces and Government of India ready and anxious to meet reasonable demands for extra help. But it might be beneficial if colleges which profess to guide research in Chemistry, would agree among themselves to take special interest in different branches of the Science. It might even be advantageous if the different universities did the same, a course of action which to some extent

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at any rate holds in German universities. Under some such system it would be possible for a student in, say, Lahore to come to Allahabad for his research course, or for some from Allahabad to go to Bombay or Calcutta, if his professor was of opinion that he would there get better assistance in his special subject than at his own college.

12. Indian Professors and Research.—It is also of the greatest importance that the teachers in colleges which guide research should themselves do research work. Nothing stimulates research like research. A professor's work need not necessarily be of a deeper kind that than of his pupils, but he should always have something going on in which his students can take an interest and share. Every opportunity should be afforded to a science teacher to take either courses in European universities or to go for the purposes of study or actual research. It is astonishing how one research leads to another often of quite a different nature, and a term of work in Europe and the consequent association with others engaged in research is bound to result in a sheaf of new ideas which can be utilized for self and students on return to India. I mention this because I consider it very important that furlough studies should not be limited to pedagogics, but extended so as to include the subject actually taught by the Professor.

13. Libraries .- If there is one thing more than another which is absolutely essential in a college where research is carried on, it is a good library. In this respect Oxford is particularly well off. The scientific library known as the Radcliffe library adjoins the chemical laboratory, and it contains practically all the modern books on chemistry together with a valuable collection of older works of historical value, and all journals of value bearing on chemistry. This library is a reference library only. No books may be taken away, but tables are provided which may be reserved for a term by students, and the library is largely used by them and professors alike for referring to articles in current literature and for abstracting. This library is largely supplemented by the various college libraries some of which are really excellent. Here again the tendency is for specialization, and the physical literature would be found in the laboratory devoted to physical chemistry, and so on. It must be understood that the literature in any research centre must be as comprehensive as possible ; it is otherwise quite impossible to know whether one is repeating work which has already been accomplished or is working in the right direction. In consequence of this German, French, and American as well as English journals and books must be included. I have drawn up a list of books and periodicals which are absolutely necessary in a research laboratory, but it would be a great advantage if a larger central library could be instituted at some central institution, which could be used as a lending library for the whole of India, to supplement the university libraries which would be smaller. For instance, it is not necessary for each research institution to possess complete sets of all the periodicals, but there should be one complete set available in India. Similarly all the American and even English and German journals are not needful, but these again ought to be within a few days' reach. Allahabad would be a suitable spot for such a central library, where there is already a large library under Government control, but of course there are other equally suitable places, and the Tata Institute, or Asiatic Society of Bengal in this scheme (see appendix E.).

14. Scientific Societies.—Undoubtedly one of the most important of all stimuli to research in Europe is the Scientific Society with its Journal. Such societies in Great Britain include the Royal Societies of London and Edinburgh, the Chemical Society of London, the Institute of Chemistry, the Society of Chemical Industry, and similar societies at the new provincial universities. It is in such institutions that chemists meet to read papers on and discuss their work, and in the journals that they publish their researches. In addition to these learned societies we have the more local and less pretentious society or club in Oxford which corresponds exactly to the colloquium or seminarium of the German universities

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(see Kuchler, page 12). Such institutions at Oxford are the Junior Scientific Club and the Alembic Club, the latter of which confines itself to the study of Chemistry, while the former is more comprehensive and includes other sciences. Each of these societies has its Journal in which papers of real value may be published, and in addition to the ordinary meetings there is a grand annual meeting at which some European savant gives a special lecture. The Junior Scientific Club also gives a conversazione with a special display of recent advances in the various branches of science. These two institutions have a very great educational value. The reading of original papers by the students, of the reproduction by a student of some important piece of recent research, together with the free discussions which follow such papers are invaluable, and I cannot express too warmly my entire agreement with Mr. Kuchler's remarks on the advantages of these meetings. (Occasional Reports, page 13). Here again, the distances between centres of learning renders it difficult to found and carry on societies of the kind I have mentioned, but the time has come when some such steps should be taken in each of our research centres. Such a society would be the colloquium of Germany and the larger co-ordinating society must for the present be left as a goal for which to aim. With the introduction of research chemists in Forestry, Agriculture and Mining, its attainment is by no means impossible. Possibly an intermediate step would be the formation of a chemical section to the Asistic Society of Bengal, whose journal would, even now, form a suitable medium for the publication of chemical notes on indigenous products.

Since my return to India, I have been given to understand that the research chemists from the colleges of Agriculture and Forestry are to meet for discussion and formulation of plans yearly in Calcutta. It would be a great boon to Teachers in the provinces if they might be allowed to join these meetings and share in the discussions.

15. Possibilities for Research in India and its Scope.—I hope that in the above I have made clear that it is practically impossible for Indian Universities to compete with those of Europe in research, and specially that it is impossible for any individual institution to be all embracing in its field of research; also that the average Master of Arts is not thoroughly fitted to embark on original work.

I am very far from meaning by these statements that research should have no place in our Indian Universities. It would seem that for the present at any rate the manner in which such research as that for the Oxford research degree (B.Sc.) or the German Ph.D. can be best helped on, is by the encouragement of somewhat specialized research by the Professors of government institutions, and of research on indigeneous products. The Professors' research is sure to have offshoots which can be handed over to students, while the latter is as a rule work of a comparatively simpler nature, and would be work such as a student might well embark on within a year after his Master's degree. The Agricultural Institute at Pusa and the Forest Department College at Dehra Dun might both give valuable assistance in suggesting indigenous products in which research might advantageously be carried on, and I should suggest that such institutions might also be affiliated to the universities for post-graduate research work.

16. Equipment and grants for research.—That our laboratory buildings are on the whole adequate, I have already mentioned. I am afraid that most institutions are somewhat badly off in the matter of apparatus. Since my return to India I have been informed that any attempt of mine to introduce quantitative work into the B.Sc. course will be opposed by affiliated colleges because of the *expense* which would be incurred in the puchase of balances. This is typical of the attitude of many of our affiliated institutions towards progress.

On the other hand in Government institutions where the grant for apparatus is liberal, there is too frequently the difficulty which arises from the fact that all large indents *must* go to England and so be delayed for a year at least, and secondly the difficulty arising from the impossibility of getting inexpensive but necessary bits of apparatus and chemicals in India. I am sorry to say that not



only the Professor's but the student's research suffers in this way, and I cannot urge too strongly that either a more direct control of all the funds for Science should be given to the Professor, or that he should at any rate be given a special grant for the research department to be spent how, when and where he finds it *necessary*. The recurring expenses need not be large, but in order to avoid delays through having to order through the Secretary of State, I would suggest that an initial sum of say Rs. 1,500 should be put at his disposal with a recurring grant of Rs. 500 per annum. This should be strictly limited to research and at the end of a year any unspent balance above Rs. 1,500 should lapse.

The actual apparatus required for research work varies so much with the nature and conditions of the work that it cannot be discussed here. Any well fitted laboratory is suitable for research work and advanced students gain a great deal from seeing research work carried on, so that the research room should not be isolated from the main laboratory.

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APPENDIX A.

CXXX.-The Hydrolysis of Ammonium Salts by Water.

BY EBNEST GEORGE HILL.

VELEY has recently described (Trans., 1905, 87, 26) a method by which he attempted to measure the amount of hydrolytic dissociation of aqueous solutions of ammonium salts. The method consisted in boiling the solutions in Jena flasks under an inverted condenser and estimating the loss of ammonia at the end of a given time. The results were not very satisfactory, but the conclusion was drawn that three cases are presented: (1) that hydrolysis may be inappreciable, (2) that it may be dependent on dilution, (3) that it may be independent of the dilution beyond a limiting value. Veley also showed that the extent to which various acids retain ammonia is more or less analogous to their avidity, but that the absolute order of magnitude is not the same in the two cases.

Veley's most striking results were these obtained from the nitrate and chlorate, which allowed the escape of comparatively large quantities of ammonia, whereas both nitric and chloric acid, being of the same order as hydrochloric, should hydrolyse to a very slight extent. Thus, taking hydrochloric acid as 100, Veley found the avidity of chloric acid to be 6.9, and he omitted nitric acid, from the discussion on the assumption that at the temperature of the experiment the nitric acid decomposed and caused secondary reactions. Formic acid also gave anomalous results.

It was suggested by Dr. Veley that measurements of the electric conductivity of the solutions of ammonium salts before and after treatment as in his experiments would give a more accurate means of determining the amount of hydrolysis. A few preliminary experiments showed that this was not so, and that in the case, for example, of ammonium sulphate there was very little change, before or after boiling.

The amount of ammonia escaping is so small, and the ionisation in the solution is so great, that the variation in the conductivity of a normal or fifth-normal solution was almost inappreciable, and the method was abandoned. It seemed, however, possible that if the escaping ammonia could be led into pure water, the conductivity of the water might be used to measure the amount of ammonia evolved. This method proved much more satisfactory.

Estimation of very dilute Ammonia by the Conductivity of its solution.— From the conductivity or resistance curve, it is possible to estimate the amount of ammonia which corresponds to any particular conductivity. Accordingly, if precautions are taken to avoid contamination of the water, it should be possible, by aspirating a current of purified air through a solution containing free ammonia, and passing the ammoniacal air into conductivity water, to obtain a solution of ammonia in water, the conductivity of which is a measure of the ammonia dissolved. The method would be specially applicable when the ammonia to be measured is very small. After a number of experiments with various forms of aspirators, flasks, and absorption vessels, it was found necessary to purify the aspirated air from all carbon dioxide, to secure a uniform rate of flow, to avoid transfer of the ammonia solution from one vessel to another, to avoid condensation of water vapour on the limb of the flask containing the ammonium salt solution, and to measure accurately the ammonia solution before taking its conductivity, also the air passing through the whole apparatus.

These conditions were obtained as follows :

The air was supplied from an ordinary gas holder and was purified by passing it through a series of wash bottles containing potassium hydroxide solution, and then through a tube containing glass wool moistened with water. The rate of flow was regulated once for all by placing a constricted capillary tube between the purifiers and the laboratory vessel to be described.



The volume of air passed was measured by collecting it, after it had passed through the absorption vessel over water at 15°, in a graduated 800 c.c. flask with a narrow neck. To avoid condensation of water vapour on any part of the apparatus before the absorption vessel, a special form of vessel was designed for containing the salt solutions, every part of which was kept at the temperature of steam, so that no condensation could take place until the air passing through the apparatus had reached the absorption vessel. And lastly, to avoid transfer of solutions and to obviate the difficulty of measuring the volume of the solution before taking its conductivity, the cell itself was graduated and was designed of such a pattern that it served as the absorption vessel.

The Conductivity Cell and Absorption Vessel.—A tube of about 4 mm, cross section, bent twice at right angles, was constricted at the end D and sealed into the cell E. The constriction was less than 1 mm, the diameter of the cell being about 10 mm. The cell was about 6 cm. long, and at its upper end a tube of 6 mm, diameter was sealed with a slight constriction at the joint. At a distance of 16 cm. from the cell, a small pipette-like bulb was blown as a safety trap for any water forced up the tube, but this was never needed during the experiments. The electrodes were as large as possible and about 5 mm, apart. They were drawn up against the sides of the cell, so as to be quite rigid, and the connecting wire passed into mercury cups ben t upwards and extending well above the cell.

The cell was graduated on the two limbs to hold exactly 20 c.c. (see diagram, p. 1277).

The Laboratory Vessel.—This vessel, used for containing the solution of a salt of ammonium during the passage of 800 c.c. of air, was made as follows:

One of the tubes of a 50 c.c. pipette was lengthened considerably and the other was replaced by a narrow tube with a constriction at the entrance to the bulb. This tube was bent twice at right angles, and the end of it (O) shaped conveniently as in the figure. The wider tube was bent so as to incline at about 115° to the bulb, and on this was placed a small condenser, the end subsequently being bent downwards parallel to the bulb. The construction is best shown by the figure. The end A was drawn out into a strong, narrow point, which could enter the narrow limb of the conductivity cell. The condenser was kept hot by a supply of steam from a boiler, and the bend of the tube was covered by lengthening the condenser with wide bore rubber tubing cut to shape.

Round the narrow limb of the cell a second steam jacket was placed, so that the latter met the rubber prolongation of the condenser described above. Thus the whole of the limb B B B was kept at the temperature of steam. It was therefore no longer possible for any condensation to take place in this limb (see diagram).

The bulb of the pipette was immersed in a very deep water-bath, and the latter was covered with the usual rings and a small cap, which fitted over the ends of the condenser and the side tube C. In this way the whole of the laboratory vessel was kept at a high and constant temperature. Owing to the shape of the limb BB there could be no spurting of the solution into the cell.

The end of the tube BB was connected with the cell by a small piece of rubber tube, which was wired on to the outside of the narrow limb of the cell, the latter being widened for 10 mm, at its end to allow the tube BB to enter. This joint was so made that the glass of the two tubes just touched and the rubber came into contact with only the outside of the tubes. The point A entered into the limb of the cell for about 8 mm. The cell was immersed in cold water during the experiment.

Method of Experiment.—At the beginning of an experiment, conductivity water, prepared as subsequently described, was placed in the cell and its conductivity

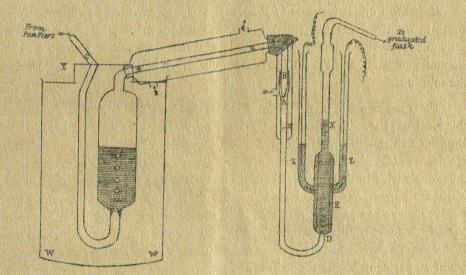


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measured. This was found to be slightly diminished by passing the air, purified as above, through the cell for fifteen minutes. No water was considered suitable which had a greater conductivity than 1.5×10^{-6} units.

A solution of the salt was made in conductivity water in a 200 c.c. flask kept for the purpose. Of this solution, 50 c.c. were withdrawn by a pipette, also kept for this purpose but not specially standardised, placed in a small beaker, and immediately drawn into the laboratory vessel by connecting a rubber tube to BAand aspirating the solution through C. The rubber tube was then removed and the end of the glass tube A rinsed with conductivity water. The laboratory vessel was then placed in the water-bath and joined up with the cell, which contained about 16 c.c. of water at the beginning of an experiment A bent hood fitted over the top of the cell by means of a rubber collar led by a long delivery tube to the 800 c. c. flask inverted over water, in which the air passing through the apparatus was collected and measured. The water was always kept at 15° , and towards the end of the experiment the flask was sponged with water at that temperature.

When the connections were made, the boilers and water-bath were heated, and after a few minutes air regulated as previously described was passed until exactly 800 c.c. had been collected in the measuring flask. This took a little less than an hour. The air was then stopped and the cell disconnected. The cell was filled up to the graduation mark with water directly from the conductivity still and placed in the thermostat, which held several gallons of distilled water. It was



W, water-bath; XX, graduation mark on the cell; Y, copper cap fitting over the water-bath rings, with openings for the limbs of the vessel; ZZ, mercury cups.

heated to little above 18° by a current of steam and allowed to cool slowly. When the temperature reached exactly 18°, the conductivity was measured.

With the apparatus above described, sixteen experiments were made with five different concentrations of ammonium sulphate solution. The results were quite satisfactory, the resistances measured differing by less than three per cent. from the mean for a particular concentration. Thus for normal ammonium sulphate the values were 1019, 1027, 1069, 1087, 1083. These were the most discordant results obtained, and a resistance of about 1000 ohms is the least favourable resistance for estimating ammonia by the conductivity method. The reason is that when the resistance is less than 1000 ohms, the nature of the resistance curve is such that only a small difference in resistance is shown by a comparatively large difference in the ammonia present. In these cases, therefore, the ammonia was estimated by titration. For such determinations the laboratory vessel was used in conjunction with a long test-tube containing a measured quantity of standard acid. The tube was fitted with a doubly-bored rubber stopper, which carried a straight tube passing to the bottom, and a short bent tube, which just passed through the stopper. The long tube



(12)

was connected with the end A of the laboratory vessel, whilst the short end was connected with the delivery tube leading to the collecting flask. The test-tube was rather more than three parts filled with acid. The acid was titrated before and after the passage of 800 c.c. of air, with a very dilute ammonia solution. The latter was standardised for every experiment with standard hydrochloric acid, which also was standardised from time to time with both silver nitrate and sodium carbonate. Experiments were made to ascertain wherther a second absorption tube was required, but it was found that one tube of acid, containing 50 c.c. of acid (1 c.c. = 0.000475 gram HCI), absorbed all the ammonia.

With ammonium acetate, the following values were obtained on different days with different solutions :

Grams of ammonia absorbed in the acid :----

	N.	№ /5.	N/25.
А,	0.0323	0.00861	0.00169
B.	0.0322	0.00816	0.00163

To compare the absorption method with the conductivity method in the least favourable cases of the latter, measurments of N/5 salicylate may be quoted.

Two experiments gave 1042 and 1030 for resistances, the mean of these corresponding to 0.00111 gram of ammonia. By the absorption and titration method, the estimated ammonia was 0.001145 gram.

Reduction of Resistances to Percentage of Ammonia.—In order to reduce the numbers obtained for the resistance of the ammonia, solution to percentages of ammonia, it was necessary to plot a curve for the specific resistance of dilute ammonia solution, and read off the values corresponding to the specific resistance of the solution.

These are two sets of figures at 25° for the conductivity of ammonia, and a third set at 18°. The first mentioned are by Ostwald (Allg. Chem., 1893) and Bredig (Kohlrausch and Holborn, Leitvermogen der Elektrolyte), and the latter by Kohlrausch (Landolt and Bornstein, Phys. Chem. Tabellen). For dilutions such as those dealt with in this paper, these figures do not agree among themselves, and when the curves are plotted side by side it is seen that Kohlrausch's curve and Bredig's curve run parallel, and that when the latter is corrected by the temperaturecoefficient for the dilute ammonia, the two curves differ by about 10 per cent. Kohlrausch's figures for the resistance due to a given percentage of ammonia being about 10 per cent. higher than those of Bredig.

Ostwald's curve almost touches Kohlrausch's at 0.25 per cent. ammonia, but then diverges and cuts Bredig's at the point corresponding to 0.0125 per cent. of ammonia.

The difference between these curves was sufficient to make it necessary for the author to determine a curve of resistance for dilute ammonia, and it was obviously most satisfactory to do this part of the work under conditions as similar as possible to those under which the resistances to be converted were obtained.

The method adopted was to pass air through a solution of ammonia in the laboratory vessel, absorb the issuing ammonia in conductivity water in the cell, and determine the resistance. It was found, as will be shown, that the ratio of the escaping ammonia to the total ammonia in the laboratory vessel was constant, and for the conditions of the experiments was 87.5 per cent.

The ammonia solution was prepared by mixing pure ammonium nitrate and a solution of frashly prepared potassium hydroxide in conductivity water in a Jena distilling flask. The arm of the flask passed into an ordinary Jena flask fitted with a doubly-bored rubber stopper, the second hole of which carried a potash tube. A current of washed hydrogen was then passed through the two flasks for several

(13)

minutes and the distilling flask gently warmed. The ammonia dissolved in the conductivity water, and the distilling flask was removed. The latter was replaced by a burette fitted with a potash tube, and the ammonia solution was drawn up into the burette. It was then titrated against N/100 hydrochloric acid. To perform an experiment, a few c.c. of the titrated ammonia solution were run into a small graduated flask containing conductivity water, and the volume was made up to 100 c.c. Fifty c.c. were then introduced into the laboratory vessel, and the other experimental conditions were precisely similar to those already described. During these experiments care was taken to keep the air of the laboratory as free as possible from carbon dioxide.

Two series of experiments with different ammonia solutions were performed. The agreement was satisfactory.

SERIES	L Barris A.	SERIES II.				
Ammonia în laboratory		Ammonia in laboratory	Multiple With Street			
The second second second second	Resistance in cell.		Resistance in cell.			
vessel. 0.000391	2056	vessel, 0.000759	1321			
0.000860	1216	0.001518	939			
0.0001955	2990	0.000555	1880			
0.0000977	4200	0.001897	840			
0.0008338	2311		and the second s			
0.000489	6601	One c.c. of the ammonia				
0.0001075	1077	0.0000759 gram of ammo	11.124.			

One c.c. of the ammonia solution in the burette contained 0.0000782 gram of ammonia.

From these values a curve of resistances of the ammonia in the cell was plotted and used for converting the other resistances into percentages of ammonia. The porportion of free ammonia passing from the laboratory vessel into the cell was stated above to be 87.5 per cent. This was shown as follows :---

A solution of ammonia free from carbon dioxide, prepared in the manner previously described, was titrated against standard acid. Of this solution, a measured quantity was run from the burette into a graduated flask and the volumo made up to 200 c.c. Fifty c.c. were now drawn into the laboratory vessel and 800 c.c. of air aspirated through it in the usual manner. The issuing air passed through standard acid which was titrated before and after the experiment.

The following experiments were peformed :---

The original ammonia solution contained 0.001643 gram per c.c.

The standard acid used for absorption was titrated against the orginal ammonia solution before and after the experiment. Thus the difference between the two values gave the amount of ammonia absorbed by the acid.

A HARDER Days		
Ammonia introduced into the vessel in c.c.	Ammonia passing into the acid in c.c.	Mean.
15-0	13:25 13:15 13:15	13-18
10'0	8·70 8·70	8.70
5.0	4·85 4·40	4+375
2.50	2·20 2·15 2·20	2.183
1.25	1.10	1.10

The ratio of ammonia in the vessel to the escaping ammonia absorbed by the acid is consequently-

1:0.879, 1:0.870, 1:0.875, 1:0.873, 1:0.880.

The ratio may thus be considered constant, and it may be assumed that 87.5 per cent. of the ammonia passes from the laboratory vessel into the cell under the conditions of the experiments.



Effect of Dissolved Salts on the Escape of Ammonia .- In the hydrolysis of ammonium salts with water, the amount of free ammonia in the salt solution is small compared with that of the total salt dissolved. It was necessary to ascertain what influence the dissolved salt had on the rate of escape of ammonia under the conditions of these experiments. Raoult (Ann. Chim. Phys., 1874, [v], 1, 262), who used strong solutions, states that ammonium chloride decreases the solubility proportionally to the amount present, but that ammonium nitrate has no effect. The latter statement was confirmed by Gaus (Zeit. anorg. Chem., 1900, 25, 236).

Perman (Trans., 1902, 81, 482) gives details of two series of experiments, from which he concludes that ammonium chloride may form a complex molecule with ammonia and that the effect of this is to decrease the vapour pressure of the ammonia. He, however, was working with very strong solutions of ammonia (12-15 per cent. NH3), and his conclusions were derived from a comparison with an ammonia solution containing the same percentage of ammonia and water. If the comparison is made with a solution containing the same mass of ammonia in unit volume, it is seen that the effect of the ammonium chloride is to increase the vapour pressure, or to decrease the solubility to the ammonia. Perman's figures also seem to show that the alteration in vapour pressure increases with the amount of salt in solution.

It was necessary, therefore, to de termine what happened with such concentration of salt as the author was using.

To ascertain the effect of ammonium salts on the rate of escape of ammonia from its solutions under the conditions of the author's work the following experiments were made :----

A dilute solution of pure ammonia was prepared, 50 c.c. of this introduced into the laboratory vessel, which as in all cases was heated in the water-bath and 800 c.c. of air passed through it, the issuing air and ammonia passing through a tube of standardised acid. The conditions of this experiment were in all respects similar to those previously described. The acid was subsequently titrated with dilute ammonia. In another experiment, a gram-molecular solution of ammonium nitrate was made up in some of the ammonia solution and 50 c.c. of this used in the laboratory vessel, and in a third case ammonium chloride was used.

Two series of experiments with different ammonia solutions, which, accidentally, were of the same strength, gave-

Fifty c.c. of each solution used,	Standard ammonia required for neutralis- ing the acid after passing the air.			
Ammonium chloride (10.7 grams in 20 of ammonia solution)	0 c.o. 	44:75 c.c.		
Ammonium nitrate (18.0 grams)		,, 44*70 "		
Ammonia solution alone	***	, 44.70 "		
The amount of animonia required h passing air was	efore 	, 52·70 "		
Series B		·		
Ammonium chloride as above		44·70 c.c,		
Ammonium nitrate ,, ,,		44.75 "		
Ammonia solution alone		44:70 n		

SERIES A.

It may thus be concluded that the dissolved salts do not exert any influence on the escape of ammonia when the amount of the latter is small compared with that of the dissolved salt.

There seems no doubt, therefore, that the ammonia evolved under the conditions of the author's experiments is a measure of the relative hydrolysis of the salts used.

The Conductivity Water.—The water used in these experiments, both for preparing the solutions of the salts and for the absorption of the ammonia, was made by distilling tap-water (which had been well boiled for ten minutes) through a dilute solution of permanganate acidified with dilute sulphuric acid and then through a solution of permanganate made alkaline with potassium hydroxide. The two permanganate solutions were contained in Jena flasks of 1000 c.c. capacity and were kept about one-third full.

The issuing steam passed through a trap and was finally condensed in a specially kept Jena flask. With this apparatus it was easy to get a sufficient supply of water with a conductivity not greater than 1.5×10^{-3} at 18° .

The cells were standardised by comparison with solutions of potassium and sodium chloride at 18.0°, and the following values were obtained :---

	Solution.					Cell 1.	Cell 2
(1)	N/50 Sodium chloride	0.010	005			0-09041	0.06609
(2)	N/50 Sodium chloride	••••	444	\$48			0.06609
(3)	N/500 Sodium shloride			444		0.09025	0.06549
(4)	N/500 Sodium chloride				898	0.09029	except
(5)	N/500 Sodium chloride	40.4		0-5-0		0.09020	
(6)	N/100 Potassium chlori	dø				0.09031	0.06597
						and the second s	aranapana (
	Mean		***	010	***	0.09024	0.06591

Hence the ratio of the cells to one another was 0.09024 to 0.06591, or 1.369 to 1.000. The first three values were determined before the commencement of the work, but the values in experiments (4), (5), and (6) were obtained during the research (6) being taken on the completion of the experimental portion. The value of the cells had, consequently, not changed during the work.

The Salts.—The salts used were the chloride, chlorate, nitrate, sulphate, oxalate, salicylate, succinate, citrate, benzoate, acetate, and formate. Of these the organic salts were kindly supplied by Dr. Veley, whilst the others were recrystallised from good specimens in the laboratory. An exception must be made in the case of the chlorate, which was prepared from barium chlorate in the usual manner. It gave no trace of chloride after two crystallisations. The organic salts were all recrystallised with the exception of the citrate, and had all been supplied originally by Kahlbaum.

The ammonium acetate was dried over solid potassium hydroxide in an atmosphere containing ammonia gas after the crystals had been dried as far as possible on blotting-paper.

In addition to the above, fine crystalline specimens of the ammonium salts of monochloroacetic and trichloroacetic acids were prepared. Unfortunately both decomposed under the conditions of the experiment, the former yielding a considerable amount of hydrechloric acid and the latter chloroform.

The Solutions.—The solutions were made by weighing out exact quantities of the salts in a weighed beaker and making up to 200 c.c. with conductivity water. The strengths used were normal, fifth-normal, and twenty-fifth normal. The



solutions were always used immediately after being prepared, and the following table gives the measurements obtained :---

°		Nor	mal.	0.2 normal.		0.4 normal.	
Salt.		Cell 1.	Cell 2.	Cell 1.	Cell 2.	Cell 1.	Cell 2.
Chloride	an air	3550	(2595) _		3470	(5549
Childring			2420		3577	7814	(5345)
Nitrate		8423	(2495)	5198	(3796)	7611	(5559)
Millaro	600		2638	-	8602		5448
Chlorate			2495	R annia	3569	7156	(5227)
	100 (900 (10),	100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100	atom		1030	8172	(2317)
Salicylate				1427	(1042)		2223
m in the li					830	2399	(1752)
Succinate	402						1639
A Stranger				n an	- Anna		1345
Formate	No and a	- N. (**) - N.	1048	2298	(1678)	ata an	2681
Sulphate	400			Carefo	1662	and a second	2780
		A PARTY OF A	AND A DECK OF A DECK	法行动的国大规模学 化最高的原	and other		

The numbers in brackets are the values for cell 1 divided by 1.369, and hence would be the resistances of the solution in cell 2.

As previously stated, the conductivity method was not accurate when the resistance in the cell was less than 1,000 ohms, but in such cases the titration method already described could easily be applied. As an example of two experiments, we have-

Ammonium acetate, N/1 solution, 50 c.c. acid used for absorption.

Ammonia solution used for titration, 1 c.c. = 0.00087 gram ammonium hydroxide.

Before absorption, 50 c.c. acid = 114.00 c.c. ammonia, after absorption = (a) 77.30, (b) 76.50, mean = 76.90; hence ammonia absorbed = 37.1 × 0.00087 == 0.0323 grams.

By using the above method as a supplement to the conductivity method, the following table was obtained. In it the resistances are converted into ammonia, which is given as the actual amount passing over from the laboratory vessel.

In all cases except that of the chlorate, the values are the mean of at least two concordant results. In the case of the chlorate, the values are for single experiments :---

NAME OF A			N/1.	N/5.	N/25.
Salt.		1 Strate	0.000255	0 000118	0.0000523
Chloride			0.000243	0.000111	0.0000520
Nitrate			0.000256	0.000119	0.0000559
Chlorate			0.001015	0.000443	0.000218
Sulphate		00.0	CONTRACTOR OF STREET, S	0.00113	0.000301 *
Salicylate	sufficient.	100	0.00552	0.00378	0.000798
Benzoate	144		0.01998		0.00166
Acetate			0.03230	0.00838	0~000640 *
Formate			0-01121	0.00225	
Succinate	1000 A		0.00990	. 0.00200	0.000420
Ozalate			0.0088	0.00185	
Citrate			0.01217	0.00574	0.00272
Monochloroaceta			0.0024		
THE OTHOOTHOUT CORPORE	and the second second			a de la servición de la servición de	All a state of the

* Values high; obtained by conductivity method; probably slight decomposition and evolution of carbon dioxide, hence lowering the resistance in the cell.

In the case of dibasic acids, half molecular weights were dissolved in a litre of normal solution.

In the preceding table we have several sets of cases. There are monobasic, dibasic, and tribasic acids, and the two former contain both weak and strong acids.

Monobasic Acids .--- These form only one simple salt, and consequently only one type of hydrolysis is possible. According as the acid is strong or weak, the equation for the hydrolysis constant will be

 $\frac{C_{\text{AH}} \times C_{\text{BOH}}}{C_{\text{salt}}} = K, \text{ or } \frac{C_{\text{AH}} \times C_{\text{BOH}}}{C_{\text{salt}}^2} = K.$

(17)

Dibasic Acids.—In the case of the salts of dibasic acids, hydrolysis may take place in two ways :--

(1)
$$A''B'_2 + H_2O = A''BH + BOH.$$

(2) $A''B'_2 + 2H_2O = A''H_2 + 2BOH.$

Where the amount of hydrolysis is small, as in the above experiments, it may be assumed that the first of these equations holds, and the equation for the hydrolysis constant becomes $K = \frac{C_{ABH} \times C_{BOH}}{C_{salt}}$ or $K = \frac{C_{ABH} \times C_{BOH}}{C^2_{salt}}$, according as the acid is strong or weak.

These equations may be written $K = \frac{C^2_{BOH}}{C_{sult}}$ or $K = \frac{C^2_{BOH}}{C^2_{sult}}$ respectively. If in the above equations we take the ammonia liberated under the conditions

If in the above equations we take the ammonia liberated under the conditions of the experiment as C_{BOR} , we have a means for calculating the hydrolysis constant of the solutions used.

In the following table, the equation $K = \frac{C^2_{\text{BOH}}}{C_{\text{salt}}}$ has been used for the first four acids, whilst for the rest, $K = \frac{C^2_{\text{BOH}}}{C^2_{\text{salt}}}$.

					K ×		$\sqrt{K} \times 10^{\circ}$.		
	Sult,			N.	N/5	. N/25	. N.	N/5.	N/25.
Chloride	1	***		0.00650	0.0069	0.00684	6 2.55	2'62	2.61
Nitrate	an and the second	and the second	10	0.00591	0.0000	5 0.0065	7 2:43	2.46	2.57
Chlorate		***		0.00650	5 0.0070	9 0.00731	2.56	2.66	2.70
Sulphate	and the second			0.103	0.100	0.114	10.15	10.00	10.6
Oxalate .		1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1		7.74	8.51	and the second sec	88.0	92'5	
Succinate		and the second		9.80	10.0	11-0	99.0	100.0	105.0
Formate	a street and	States and	Sec.	12.4	126	and the second	1124	112.5	A series of the
Benzoate	- Harrison -	S.		39.9	34.9	39·8 ·	199.8	189.0	199.5
Acetate	and a starting of the	A State of	· ····	104.0	175.0	172.0	323.0	419.0	41.5.0
Monochloroa	cetate			0.576	And I all		24.0	an <u>al</u> in	
Salicylite		***	····	3.03	3:19	and the second second	65.2	56.5	

In the foregoing table, the values for K are as constant as can be expected from the experimental method. It may be noted that the nitrate and chlorate behave quite normally, and that the formate gives also a satisfactory result.

The value for the normal solution of the acetate is abnormal. This does not seem to be due to experimental error, since two sets of experiments with different solutions gave concordant results. In this respect, attention may be directed to Veley's figures for the acetate. He found that the normal solution gave a little more than half the percentage of ammonia which was given by 0.2 normal and more dilute solutions, and since the acetate is the salt of the weakest acid used, the figures for this salt should be the most accurate. It therefore appears that in concentrated solution the acetate is proportionately less dissociated.

If we take the inverse of the above figures, we ought to find 1/K propertional to the dissociation constants of the acids the salts of which are used, and $\sqrt{1/K}$ proportional to the avidities of the acids obtained by dynamical methods. Since, however, the dissociation constants of the strong acids cannot be used for comparison, we must use the molecular conductivities of their solutions and compare these with $\sqrt{1/K}$. In the following table are given the values for $\sqrt{1/K}$ (hydrochloric acid = 1), also the ratios of the molecular conductivities, and the values for the avidities of the acids obtained from the velocity of decomposition of methyl acetate and the inversion of cane sugar.

	Salt.			<u>иік.</u>	Molecular conductivity.	Inversion of cane sugar.	Decomposition of methyl acetate.
Chloride	Sec. and		***	1.000	1.000	1.000	1.000
Nitrate	100.000	444		1.065	0.991	1.000	0.915
Chlorate	(Been	****		0:985	1.000	1'035	0.944
Salicylate				0.046	0.032		
Formate		••••	0.84	0.023	0.017	0.015	0.013
Benzoate	***			0.013	* 0.008 *		

L

(18)

S 41	t.			/ <u>/1K</u> .	Molecular conductivity.	Inversion of cane sugar.	Decomposition of methyl acetate.
a second and				0.006	0.004	0.004	0.0034
Acetate	etete			0.106	0.049	0.048	0 043
Monochloroac	e ues ue	N. M. S.		0.262	0.625	0.236	0.541
Sulphate			10 10 10 10 10 10 10 10 10 10 10 10 10 1	0.029	0.197	0.185	.0-174
Oxalate	***	Not in the later		0.026	0.006	0.005	0.005
Succinate		•••• 1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1	**				1 will not form

Norr.-In the above table, the conductivities for salicylic and benzoic acids which will not form normal solutions have been calculated from their ratios to acetic acid at lower dilutions.

In discussing the above results, we may first take the monobasic acids. Here we find a very good agreement both in order and magnitude with the figures obtained by any of the other methods. The strong acids are almost equal and the ratio of the four weak acids is the same as that of the conductivities. The agreement here is particularly striking, the ratios being—

or a second s			Salicylic.	Formic.	Benzoic.	Acetic.
			0.032	0.016	,0;0087	0.004
1/K a	***		0.032	0.017	0 0087	0.004
Conductivities)r we may compare	1 / TZ	the	dissociation cons	tants of	these acid	s, in which
)r we may compare	1/h. W101	I ULIO	UIBSUCIERIUM COMP		A	Carl Contractor

ase, again making the values for salicy	tic acid the s	ame, we o	Dreprit		
100, again means	Salicylic.	Formic.	Benzoic	Acetic.	
1/8 ~	102	26.0	8.2	1.8	
$1/K \propto \cdots \qquad \cdots$	102	21:4	6.0	1.8	

Here again the numbers are distinctly of the same order of magnitude. It will be noted in the table, that when hydrochloric acid is taken as the standard for comparison, the weak monobasic acids give slightly higher figures than are given by the conductivities, &c. In this connection it may be suggested that the discrepancy is due to the different temperature-coefficients of strong and weak acids, the conductivities being at 25° and the author's experiments at nearly 100°. It would not appear likely that it is to experimental error, either in the curve for the resistance of ammonia solutions or in the other observations, since the values obtained for Kin the different dilutions are so closely constant.

Dealing next with dibasic acids, we have to remember that, in the hydrolysis of a salt of a dibasic acid, the ammonia neutralising the weaker acid hydrogen is removed first. Thus the method described could not be used to measure the strength of the first hydrogen (or ionisation). That it depends on both the ionisation constants is shown below. With dibasic acids we have—

 $K_1C_{AH_2} = C_{AH'} \times C_{H'}$ and $K_2C_{AH'} = C_{A''} \times C_{H'}$, where K_1 and K_2 are the first and second ionisation constants. Now

$$C_{\rm NH4} + C_{\rm NH4OH} = C_{\rm A''} + C_{\rm AH'} + C_{\rm AH'2} \qquad \dots \qquad \dots \qquad (1).$$

and (positive = negative charges) $G_{\rm NHA}^{*} + G_{\rm H}^{*} = 2C_{\rm A}^{*} + C_{\rm AH}^{*} + C_{\rm OH}^{*}$

where $C_{\rm H'}$ and $C_{\rm OE'}$ are very small and may be neglected, so that

From (1) and (2) we get

But

O

from (4) and (5),

1

$$SH_4 OH = C_A \left\{ \frac{C_{H^*}^2}{K_1 K_2} - 1 \right\},$$

and hence

$$\frac{C_{\mathrm{NH}_{4}\mathrm{OH}}}{C_{\mathrm{NH}_{4}} + C_{\mathrm{NH}_{4}\mathrm{OH}}} = \frac{C_{4''} \left\{ \frac{C^{2}_{\mathrm{H}}}{K_{4}K_{2}} - 1 \right\}}{C_{4''} \left\{ 1 + \frac{C_{\mathrm{H}}}{K_{2}} + \frac{C^{2}_{\mathrm{H}}}{K_{1}K_{2}} \right\}},$$
$$= \frac{C^{2}_{\mathrm{H}} - K_{1}K_{2}}{K_{1}K_{2} + K_{1}C_{\mathrm{H}} + C^{2}_{\mathrm{H}}}.$$

That is, the relative amount of hydrolysis is proportional to a term involving both the first and second ionisation constants.

The Percentage Hydrolysis in Solutions of Ammonium Salts at 100°.—This may be to some degree determined from the above data; thus, in normal ammonium chloride we have 17 grams of ammonia (combined) per litre, and in the laboratory vessel (50 c.c.) we have 0.85 gram. But the free ammonia is 0.000255 \times 1.143 (the inverse of the partition coefficient for ammonia, 0.875).

Thus the percentage hydrolysis is $\frac{100 \times 0.000291}{0.85} = 0.0341$ per cent. similarly, for N/5 acetic acid we get

 $\frac{0.0323 \times 1.141 \times 100}{0.85} = 4.34 \text{ per cent.}$

These values are doubtless too high, since, as ammonia is evolved from the solution, hydrolytic action, to a less degree, continues.

They cannot be compared with values obtained by other methods, as the author is not aware of any determined at so high a temperature.

Conclusions.

1. The hydrolysis of ammonia salts with water is in accordance with the laws of mass action for salts of strong and weak acids.

2. This hydrolytic dissociation is inversely proportional to the "strength" of the acid, that is, to the square of the conductivities of solutions of the acid, or their ionisation constants, in the case of univalent acids only.

3. In the case of bivalent acids, the relation between hydrolytic dissociation of salts and the two ionisation constants of the acids is complicated, and the hydrolysis cannot be used as a direct measure of either of the ionisation constants or the "strength" of either of the acid hydrogen atoms in the acid.

4. Certain maximum values are determined for the degree of hydrolysis at 100°.

The author's thanks are due to the authorities of Magdalen College, Oxford, for a grant which covered laboratory expenses, and to Mr. J. J. Manley, the Daubeny Curator, for kind assistance in making the apparatus used.

MAGDALEN COLLEGE, OXFORD.

APPENDIX B.

OXFORD UNIVERSITY STATUTES.

STATT. TIT. VI. SECT. IV.

October, 1905.

SECTION IV.-OF THE TIMES AND EXERCISES REQUIRED FOR DEGREES IN LETTERS AND IN SCIENCE.

§ 1. Of the Degrees of Bachelor of Letters and Bachelor of Science.

ANY person who has been permitted by the authority and in the manner hereinafter provided to enter on a course of special study or research may supplicate for the Degree of Bachelor of Letters or Bachelor of Science, provided that he has satisfied the conditions prescribed by this Statute. Science shall be taken to include Mathematics, Natural Science, Mental and Moral Science.

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§ 2. Of the Admission of Candidates for the Degrees of Bachelor of Letters and Bachelor of Science, and the Conditions of supplicating for these Degrees.

1. Any person who has been, or is qualified to be, matriculated in the University and is not under the age of twenty-one years, may give notice to the Secretary to the Boards of Faculties of his desire to be admitted as a Caudidate for the Degree of Bachelor of Letters or of Science and thereupon to enter on a course of special study or research. Every such notice shall state in general terms the subject and nature of the proposed course; and no course shall be admissible which does not extend over a complete year. The Secretary shall transmit every such notice received by him to the Chairman of the Board of the Faculty or of Studies which includes the proposed subject for the approval of the Board. Such approval shall not be granted unless the intending Candidate (1) has passed the Examinations required for the Degree of Bachelor of Arts, or has given evidence that he has received a good general education, satisfactory to the Committee hereinafter constituted for the purpose; (2) has satisfied the Board of Faculty or Studies to which his subject belongs of his fitness to enter on a course of special study or research; and that the course of study or research on which he proposes to enter is such as may profitably be pursued under the direction and superintendence of the Board. If the notice given by an intending Candidate is approved by the Board, the Secretary shall notify the fact to him; and he shall pay to the University Chest through the Secretary a fee of £5 within a fortnight of such notification, or, if at the time he is not yet a member of the University, then within a fortnight of his matriculation. He shall thereupon be deemed to have been admitted as a Candidate for the Degree of Bachelor of Letters or of Science; and the Secretary shall register his name, and his notice as approved by the Board; in a book to be kept for the purpose.

2. The Committee appointed to consider whether an intending Candidate has received a good general education shall be composed of one representative of each of the following Boards of Faculty or of Stulies, namely, Theology, Law, Medicine, Natural Science, Literæ Humaniores, Oriental Languages, Modern History, English Language and Literature, and Modern Languages, which representatives shall be elected at the first meeting of each Board after this statute shall come into effect, and shall hold office for two years, at the expiration of which period there shall be a new election, and so on, from time to time, provided that vacancies on the Committee caused otherwise than by lapse of time shall be filled up for the remainder of the biennial period.

3. The Boards of the Faculties shall have authority to direct and superintend the work of Candidates admitted as aforesaid, and to make such general regulations as they shall think fit.

4. The Boards of the Faculties may appoint Committees composed of graduate members of the University, or other competent persons, and may authorize any such Committee to report to them regarding the fitness of an intending Candidate for the course of study or research on which he proposes to enter, and to superintend the work of a Candidate admitted as aforesaid, and to report thereon to the Board of the Faculty to which his subject belongs. A Board shall have power in special cases to recommend to the Vice-Chancellor and Proctors that a remuneration be paid to a person so appointed to superintend the work of a Candidate or to report thereon, and to suggest the amount of such remuneration: provided that (1) the Board shall report to the Vice-Chancellor the circumstances of the case, and that (2) the Vice-Chancellor and Proctors shall determine the amount at their discretion, and that (3) in no case shall such remuneration be paid to a Professor or Reader.

5. Any Candidate who has completed his proposed course of study or research, may at any time not less than twelve months after his admission apply to the Board of the Faculty or Studies for a certificate that so far as proficiency in the subject of his course of special study or research is concerned, he has attained a highstandard of merit. Such application shall be made to the Board through the

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Secretary, and the Candidate shall at the same time pay to the University Chest through the Secretary a fee of £5. On receiving the application and the fee the Secretary shall transmit the application to the Chairman of the Board. On receiving such application, the Board of the Faculty or Studies shall appoint Examiners who shall satisfy themselves as to the merit of the Candidate, and his proficiency in the subject of his course of special study or research, either by examination or by requiring from him such Dissertation, or report of work done, as shall be directed by the Board; provided that if a Discertation be required, notice shall have been given to the Candidate of the intention of the Board, as soon as may be after his admission as a Candidate. Any Candidate who is directed to submit a Dissertation or report of work done shall be further publicly examined in the subject of such Dissertation or report. Before granting a Certificate the Board shall have power to require the publication of the Dissertation or report or of some portion of it in such manner as the Board shall think desirable. It shall be the duty of the Boards of the Faculties or studies to grant Certificates to those Candidates only who are reported to them by the Examiners to have attained a high standard of merit; and to state and publish in the usual manner the ground on which the Certificate has in each case been granted, together with the names of the Examiners who have reported to the Board. Provided that if the Examiners are evenly divided as to the standard of merit attained, the Board of the Faculty or Studies shall be empowered to satisfy themselves in some other way as to the merit of the Candidate, and to grant the Certificate, if they see fit.

6. An entry of the names of those Candidates to whom such Certificates have been granted shall be made in a book to be kept for the purpose. To the name of each Candidate shall be appended a description of the course of study or research which he has completed, together with a statement of the grounds on which the Certificate has been granted. Every entry shall be signed by the Chairman of the Board of the Faculty or Studies, and by the Secretary. This book shall be kept in the custody of the Secretary.

7. The Examiners to be appointed by the Board shall always include one at least of any Professors or Readers who are appointed to lecture and give instruction in the subject or branch of study which includes the subject offered by the Candidate, provided that the Board may, if requested by any such Professor or Reader, appoint an Examiner to act in substitution for him.

8. No Candidate shall be permitted to supplicate for the Degree of Bachelor of Letters or for the Degree of Bachelor of Science, unless he has kept at least eight Terms by residence within one mile and a half of Carfax as a matriculated member of the University. It shall be competent for the Board to allow a Student who has with the consent and under the superintendence of the Board so resided for the purpose of carrying on his proposed course of study or research for a period of forty-two days, not necessarily consecutive, but falling within the same Academical year, to reckon such period of residence as one Term's residence : provided that (1) no day so reckoned which falls within any Term, shall also be reckoned for the purpose of keeping that Term by residence: and (2) no Candidate who has kept by residence the Michaelmas, or the Hilary, or the Easter and Act Terms, shall be allowed to reckon in this manner any day that falls within the eight weeks beginning on the first Monday of Full Term in Michaelmas, or Hilary, or Easter Term, as the case may be: and (3) no Candidate shall be allowed to reckon in this manner more than one such period in the same Academical year: and (4) no Candidate shall be allowed to reckon more than four Terms as being kept by residence in the same Academical year.

It shall be the duty of the Secretary to the Boards of Faculties whenever a Term's residence has been allowed as aforesaid to report the fact as soon as may be to the Society of which the Candidate is a member.

9. The Certificate that a Candidate has, in conformity with the requisitions of the Statute, satisfied the Board of the Faculty of Studies that he has attained a





high standard of merit, shall be signed on behalf of the Board of the Faculty or Studies by the Chairman and Secretary.

The form of the Certificate shall be as follows :--

Board of the Faculty of (or of Studies for

(Signed)

Oxford. (Date.)

This is to certify that A. B., of College (or of Hall, or Non-Collegiate Student), in conformity with the requisitions of the Statutes has completed a course of special study (or research) approved by the Board, and has satisfied the Board that he has attained a high standard of merit.

Signed on behalf of the Board,

C. D., Chairman.

E. F., Secretary.'

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10. The names of the Candidates to whom Certificates in the foregoing form have been granted shall be published in the usual manner.

The list of such Candidates shall be drawn up in the following form :---

Names of Candidates who in Term, A.D. have satisfied the Boards of Faculties or Studies that they have attained a high standard of merit in a course of study or research.

A. B., of	College.
C. D., of	Hall.
E. F., N	on-Collegiate Student.
G. H.,	A Cartoland States

Secretary to the Boards of Faculties.'

To the name of each Candidate in the list shall be appended a notice of the course of study or research which he pursued.

11. Bach elors of Letters and Science shall rank immediately after Bachelors of Civil Law and Medicine; and, among themselves, according to the date of admission to their respective degrees in Letters and Science. Provided always that no such Bachelor of Letters or Science rank before any Master of Arts, unless he himself holds a Master's degree.

§ 3. Of the Admission of Candidates for the Degrees of Doctor of Letters and Doctor of Science, and the C onditions of supplicating for these Degrees.

Candidates may supplicate for these degrees subject to the following conditions:--

(1) A Bachelor of Letters may supplicate for the Degree of Doctor of Letters, provided that he has had his name on the Books of some College or Hall or on the Register of Non-Collegiate Students for twenty-six Terms.

(2) A Bachelor of Science may supplicate for the Degree of Doctor of Science, provided that he has had his name on the Books of some College or Hall or on the Register of Non-Collegiate Students for twenty-six Terms.

(3) A Master of Arts, who has incepted in this University, may supplicate for either of these degrees, provided that he has entered upon the thirty-ninth Term from his matriculation.

(4) Any person who being a Master of Arts of the University of Cambridge or Dublin has been incorporated, and any person who being an Undergraduate or a Bachelor of Arts of the University of Cambridge or Dublin, has been incorporated and has incepted in the faculty of Arts in this University, may supplicate for either of these degrees, provided that he has entered upon the thirty-ninth Term from his matriculation at Cambridge or Dublin.

(5) Any person on whom the Degree of Master of Arts has been conferred by Convocation by decree, other than a degree *honoris causa*, may supplicate for eithen of these degrees, provided that he has entered upon the twelfth Term from his admission to that degree.

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(6) When a Candidate under the provisions of the following clause applies for the approval of a Board of a Faculty or of Studies, the application for approval shall be made through the Secretary of the Boards of Faculties to the Chairman of the Board, and shall be accompanied by a Certificate signed by some officer of or some person deputed by the College or Hall or Body to which he belongs, and showing that his name is on the books of such College or Hall or Body.

(7) Before supplicating, Candidates for either of these degrees must have submitted evidence of their fitness for the degree to the approval of the Board of the Faculty or of Studies to which their subject belongs. Such evidence shall consist of published papers or books, containing an original contribution to the advancement of learning or science, and, where possible, at least two copies of such papers or books shall be submitted. If the Board approves the evidence, a Certificate shall be given to the Candidate describing the evidence approved by the Board, and stating that it is of sufficient merit to entitle him to supplicate for the degree. This Certificate shall be signed by the Chairman and the Secretary, and shall be published in the usual manner: and it shall be the duty of the Registrar, when a Candidate's name is entered for the degree, to ascertain whether the Certificate has been duly granted. One copy of each of the papers and books named in the Certificate shall remain in the possession of the University for deposit in Bodley's Library, provided that no book or paper of which the Library already possesses a copy shall be so deposited except with the consent of the Candidate and of the Librarian, unless the copy submitted by the Candidate shall be of a different issue or shall contain alterations or additions. The Board shall also have power to make and vary from time to time such regulations for carrying out the provisions of this clause as it may deem expedient, provided that all such regulations and any variations in them shall be submitted to the Hebdomadal Council for approval.

APPENDIX C.

Chemical Researches now in progress in Oxford, or completed within the last year.

Lord Berkeley and E. G. J. Hartley, Osmotic Pressure and Vapour pressure of concentrated solutions. Part published in Phil. Trans.

* Prof. H. A. Miers and Miss Isaac, Investigation of Supersolubility. Part published in J. C. S.

* H. L. Bowman. Minerological Researches, Bowmanite, etc. Mineralog. Journal.

T. V. Barker. Parallel Growth of Crystals. Part in J. C. S.

* J. E. Marsh and R. de J. Fleming-Struthers. Organic Compounds of the Metallic Cyanides Part in J. C. S. 05.

J. E. Marsh and G. F. Hood. Study of Iodoso-compounds.

J. E. Marsh, J. G. Burch, and R. de J. Fleming-Struthers. Emission Spectra of Mercury Salts.

J. E. Marsh and F. W. Caton. Synthesis of closed rings.

A. F. Walden. Prozane Derivatives.

B. Lambert. Conductivity of pure Organic Acids.

B. Lambert and G. Lilley. Oxidation of Aluminium by water.

* J. J. Manley. An Accurate Method for determining the Specific Gravities of salt solutions.

V. H. Veley. Action of acids on Methyl-Orange.

* N. V. Sidgwick and T. S. Moore. Calorimetric Investigations of Tautomeric Substances.

T. S. Moore. Tautomerism of Acyl-Phenols.

E. Stokes and H. T. Tizard. Electrolysis of Concentrated Sulphuric Acid with Aluminium Electrodes.

E. G. Hill. The Hydrolysis of Ammonium salts.

* Names marked with an asteriak are those of University or College tutors.



E. G. Hill. The relation between Refractive Indices, Conductivities, Densities, and total Chlorine in Sea water.

H. B. Hartley and N. Garrod Thomas. Solubility of Triphenyl-methane in Organic Solvents, J. C. S.

* H. B. Hartley, N. Garrod Thomas, and M. P. Applebey. Physical Properties of Mixtures of Pyridine and water.

H. B. Hartley, J. P. Hucklebridge, and W. H. Barrett. The Alkaline Sulphites.

H. B. Hartley and N. P. Campbell. Solubility of Iodine in water.

H. B. Hartley, N. Gar rod Thomas, and N. P. Campbell. Mineralogical Investigations.

N. P. Campbell. Rate of Growth of Crystals from Solution.

J. R. Milne. Connection between Optical and Electrical Properties of certain Solutions.

* H. B. Baker. Atomic Weight of Tellurium.

* H. B. Baker. Dissociation and Association of Dry Nitrogen Trioxide.

H. B. Baker and M. H. Godby. The Isomeric Sodium-Potassium Sulphites.

H. B. Baker and G. Lilley. Influence of Pressure on Chemical Reactions.

H. B. Baker and L. C. F. Oldfield. Sulphur Monoxide.

H. B. Baker and H. O. Kershaw. The Metallic Subhalides.

A. Angel. Cuprous Formate. J. C. S.

R. T. Lattey. Vapour Pressures of Binary Mixtures.

G. Leicester. Derivatives of Fluorindene.

F. C. Weedon. Magnetic Alloys.

APPENDIX D.

CHEMISTRY.	Waynflete, Professor of Che-
Chemical Revision, 1850-1860	mistry, W. Odling, M.A.
(The second Course)	J. Watts, M.A.
I moanic Uneillisury (II on our of the	Aldrichian Demonstrator in
Subjects of the Preliminary Examination	Chemistry, W. W. Fisher,
	M.A.
Stereo-chemistry, (Fee, £1)	J. E. Marsh, M.A.
Stereo-chemistry, (Fee, £1) Soils and Organic Chemistry (Forestry Cour	urse)
	B. Lambert, B.A.
(Fee £3) ··· ···	(W. W. Fisher, M.A.
a second seco	J. Watts, M.A. J. E. Marsh, M.A.
Laboratory Instruction. (Fee, £3 or £5)	A. F. Walden, M.A.
Laboratory	N. V. Sidgwick, M.A.
	(B. Lambert, B.A.
	D. H. Nagel, M.A.
Laboratory Instruction: Physical Chemistry	{ D. H. Nagel, M.A. H. B. Hartley, M.A. H. B. Baker, M.A., D. Sc.
Inorganic Chemistry	L. G Killby, B.A.
" Quantitative Analysis	The second second second second
37 F Guillouine	G. B. Cronshaw, M.A.
)),)))) ⁽¹⁾ ⁽²⁾	A. F. Walden, M.A.
	Dr. Lee's Reader in Chemis-
Inorganic Chemistry (Non-metals)	{ Dr. Lee's Reader in Chemis- try, H. B. Baker, M.A. D. Sc.
the standard standard standard standard with the standard standard standard standard standard standard standard	
Organic Chemistry (General Class-reaction	A. F. Walden, M.A.
(Fee, £1) ····	T. S. Moore, M.A.
Electro-chemistry	

* Names marked with an asterisk are those of University or College sutors.

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APPENDIX E.

JOURNALS.

*Journal of the Chemical Society (London).

*Zeitschrift für physikalische Chemie (Leipsig).

* Leibig's Annalen der Chemie (Leipsig).

* Berichte der Deutschen Chemischen Gesellschaft (Berlin).

* Central Blatt (Berlin).

* Zeitschrift für anorganische) Chemie (Leipsig).

Annales de Chimie et Physique (Paris).

Comptes Rendus (Paris).

Journal of Physical Chemistry (London).

Journal of Chemical Industry (London).

Chemical News (London).

Journal of American Chemical Society.

American Chemical Journal.

Bulletin Société Chemique de Paris.

The Analyst (London).

British Association Reports (London).

Monatshefte für Chemie (Vienna).

BOOKS.

History .--- E. Von Meyer.

Thorpe (Essays in Historical Chemistry).

Kopp.

Alembic Reprints.

Inorganic .--- Roscoe and Schorlemmer.

Dammer (Handbuch).

Mendelécff.

Ostwald (Principles of Inorganic Chemistry).

Abeg (Anorganische Chemie).

Physical.-Vant' Hoff. (Lectures on Physical Chemistry) Trans. Lehfeldt.

Ostwald. (Lehrbuch der Allgemeinen Chemie) (in course of publication).

Nernst (Theoretical Chemistry).

Ramsay (series of books on Physical Chemistry).

Whetham. Solutions.

Rutherford. Radio-Activity.

Organic .--- Beilstein (Handbuch and Supplements), 9 Vols.

Richter (Organic Chemistry).

Meyer and Jacobson (Organic Chemistry), New Edition.

The above are all necessary.

* Journals marked with an asterisk are indispensable.

REPORT ON FURLOUGH STUDIES.

BUREAU OF

A comparison of methods in vogue at Oxford and Allahabad as regards the higher teaching of Chemistry, with suggestions for raising Indian standards and for encouragement of research work.

B Y

E. G. HILL, B.A., D.Sc., Professor of Natural Science, Muir Central College, Allahabad.

Report on Furlough Studies, by €. G. Nill, B. A., D.Sc., Professor of Natural Science, Muir Central College, Allahabad.

1. Personal research and study .- Of all branches of Natural Science, that of Physical Chemistry is undoubtedly the one which has been most developed during the last 10 or 15 years. This branch, however, is the one which in India has least attention given to it, because it is the one with which teachers themselves have least acquaintance and with which they have the least opportunity of becoming familiar. It was to Physical Chemistry and especially the practical side of Physical Chemistry that I devoted the greater part of my time, and to get the greatest advantage from my surroundings I entered as a research student in the University of Oxford. This was a somewhat unusual proceeding for one of my university standing, but it brought me into touch with both students and the tutorial staff, among which latter were several of my personal friends. Of the system prescribed for research students, I shall have to speak later. It is not necessary for me to refer to my own research beyond saying that I was eventually awarded the research degree of the University. An account of my work appeared in the Journal of the Chemical Society, August 1906 (appendix A.). In addition to the research just mentioned I went through an advanced course of physical chemistry, one which is somewhat in excess of the requirements of the University for its honours school, and I have prepared an advanced course which may be useful in India, chiefly from the course in use at Balliol College, where the laboratory is specially devoted to the study of physical chemistry.

2. Scope of Report.—My work was not, of course, confined to actual study of chemistry and chemical methods, but was extended to the methods of study and the courses of study in vogue at Oxford. It is with these latter and with their comparison and contrast with Indian methods that this report will largely deal. It will be as well to trace the career of a student from his matriculation to his final school, before attempting to describe the conditions under which he is allowed to begin original work.

3. Preparatory work in Oxford and India compared.—Most, if not all, of the Oxford undergraduates, who intend to make a serious study of Chemistry, have already had a thorough grounding in the subject at school, and are prepared to take the Preliminary scientific examination without further tuition. This examination is held during the first year of residence and is of a considerably higher standard than the Intermediate examination of Indian Universities. A student taking up Chemistry is examined in Chemistry and Physics by both written papers and practical tests. The Chemistry consists of elementary organic and inorganic, and simple inorganic analysis, and preparations, and is but little, if any, lower in standard than that of the Chemistry for the B.Sc. of Allahabad. The Physics is similarly higher than that for the Indian Intermediate examinations and the examination also carries a practical test. There is no examination in Mathematics for the Preliminary Science, but many candidates with a mathematical bent offer themselves for Mathematical Moderations at the end of a year and then continue their chemical studies.

After passing the Preliminary Science, which is strictly a pass as opposed to an honours examination, the student has practically nothing to study except his special subject, *i.e.* Physics or Chemistry. This report deals only with the latter subject. The usual time for the examination is at the end of the 4th year from matriculation, but it may be taken at the end of the 3rd year. The average man has thus three full years after his Preliminary in which he can devote himself to Chemistry in its usual branches, and his course of studies would be more or less as follows. He would attend from three to six lectures a week given by University (as distinct from College) lecturers or by what may be called "privat docents," *i.e.* lecturers who are

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allowed to lecture in the university lecture halls. These lectures are arranged so as to break into the day's practical work as little as possible, and are often given from 9-10 a.M. or 40-11 A.M., or sometimes in the evening. The rest of the morning is given to practical work at either the university or a college laboratory. The afternoon is occupied with some form of recreation, and the evening from 5-7 again with practical work. Dinner is at 7, and the time after dinner is spent in private reading. A diligent student would probably get through his practical course in two years' time after the Preliminary Science if he worked on this plan, and would possibly help in a research for part of his 4th year or spend much of his time in reading original papers, specializing in some particular branch of chemistry. The course given above is the public course open to all members of the university, but Oxford and Cambridge differ from all other universities, in that they consist of system of corporate institutions each of which assumes the responsibility for the tuition of its own undergraduate members. Not all colleges make provision for the study of the Natural Sciences, but those which do so, have a special tutor whose business it is to look after the interests of the science students of his own college. This he does in many ways. He guides the student in his choice of the public lectures, arranges for his practical work, and as a general rule. supplements the university instruction by private tuition in the college. This latter method of instruction is in my opinion the most important feature of the Oxford system, since an enthusiastic tutor certainly stimulates enthusiasm in his pupils, and the system of private tuition gives opportunities for discussion and arousing interest which can never be afforded in public lectures.

The extent of the course, for the honour school is of course much greater than that for the B.A., or B.Sc., degree of Indian universities, and it is generally understood that the M.A., or 2nd D.Sc., examination of Allahabad more or less corresponds to the Oxford B.A. As a matter of fact such a correspondence did exist some six or seven years ago; but whereas Oxford has marched with the times, Allahabad has remained precisely where she was when the new courses were instituted. The reasons for this will appear below.

4. Low Indian Standard.—It must now be conceded that whereas an Oxford honours degree does fairly well fit a student for research work, the same cannot be said so confidently of an Indian Master of Arts. The latter has a good working knowledge of text book chemistry and practical methods up to a certain point, but that point is now decidedly below the level attained by an Oxford graduate. For instance, as was indicated at the beginning of this report, practical physical chemistry is only known in Indian Universities in its most elementary form, but in Oxford one laboratory (Balliol) gives up all other subjects in order to specialize in that branch alone. In organic chemistry much highly important modern work (such as that of Hantzsch on the *Pseudo-acids* to give only one example), has been ignored in India, simply because it has not yet filtered into the text books. Thus it will be seen without further enlargement that both in practical and theoretical work Indian universities have again fallen behind. It is as well to consider whether this is a necessity, and if not so, where the remedy lies.

It has already been stated that after the Preliminary Science the Oxford student has three years of specialized work in Chemistry, and to this may now be added that he works under highly favourable conditions and with the best instruction. But the Indian student on the other hand works at Chemistry as a special subject for only two years after passing an examination of a corresponding standard in Chemistry and Physics (he has or had till recently, it is true, the great advantage of extra mathematics), so that the Oxford man has a clear advantage of a whole year's work. In the present writer's opinion this year must be made up in one way or another, not necessarily for the M.A. examination, but certainly for the doctor's degree which is awarded for original work. This can be done in two ways. The course for the doctorate may be extended by one year, that is to say, a candidate for the degree should be a Master of two years' standing, or the B.Sc. standard may be raised. Either of these courses is perfectly practical.

At present the Intermediate Chemistry course is almost ridiculously easy and it contains no practical work at all. A good teacher can get through the Allahabad Course in one year working three hours a week. The course might thus be extended considerably. Similarly the course for the B.Sc. until last year contained no organic Chemistry. The introduction of this subject will undoubtedly allow a wider and deeper reading of students for the Master's degree, but perhaps the point which is weakest in the whole Chemistry course in Allahabad is the practical work for the B.Sc. (there is none for the Intermediate!).

This includes a very easy set of preparations and ordinary simple qualitative analysis, but no quantitative work of any kind.

It would not be impossible in a properly equipped and properly staffed laboratory to take almost the whole of the B.Sc. practical work and put it in the Intermediate course, certainly all the 'preparations' should be there. Then there would be room (almost a vacuum!) for some quantitative work in the B.Sc. course. It is most essential that a change should be made in the B.Sc. course, for the practical work there is already too light, and the change should be in the introduction of quantitative as distinct from qualitative work. A change on such lines should not be sudden, but on the other hand it should not be too gradual, and in the meantime the research student will find that a year (the minimum time allowed by the Allahabad University) of post-graduate research work is not sufficient for a research degree. These remarks find striking confirmation in Professor Kuchler's Report on Physical Laboratories in Germany (page 10).

5. The Teaching Staff .--- The above is only one reason for the lower standard of the degrees in Indian Universities. A second and equally, if not more, important one lies in the teaching staff. The average Indian student is not stupid or slow to learn the physical sciences, even when he begins them for the first time in College and not in School, but it is lamentably the fact that he is as often as not, badly taught from the beginning, and insufficiently taught as his work becomes more advanced. Now there are very few, if any, colleges which confine their advanced classes to only those students who have received their elementary instruction in their own lower classes, and the consequence is that, in the majority of colleges, a large percentage of the students in B.Sc. (3rd and 4th year) classes are derived from colleges of a lower grade altogether. They have often only just managed to scrape through the Intermediate examination. This fact obviously tends to keep down unduly the standard of the B.Sc. course. Thus the remark that one of the reasons for the low standard of Indian degrees lies in the teaching staff, does not necessarily imply defect in those who are instructors for the degree classes, but it implies a defect in the general average of the teaching staff in all classes from the very beginning. There is no doubt that things are slowly improving, but that so long as chemistry or physics are taught from the book apart from practical work, in whatever class at all, so long will the teacher tend to deteriorate; the converse holds equally true. The extension of practical work to all classes is a necessity.

If we consider the M.A. classes, the highest classes for Chemistry or Physics, we find that the number of affiliated institutions is small indeed. It is so small that for obvious reasons a criticism of the staff is impossible. But a very serious question here arises. If we consider Northern India we find that there are not more than half a dozen institutions which profess to be able to give M.A. instruction, that is to teach up to a standard which is admittedly lower than that of English University degree. In these institutions there is never more than one teacher for the course and he in every case has to assume the responsibility and share in the teaching for all the lower examinations. This defect will be



referred to more fully subsequently. Another even more serious drawback to research, is the fact that teachers do not keep up with the times. In fact they cannot. They lack libraries, periodicals, in many cases materials, and not least they lack absolutely that intercourse with those engaged in similar scientific pursuits, which is the very spirit of progress. The above applies, in its degree to colleges of a lower standard. Those who are teaching up to the B.Sc. standard only, have no stimulus from keep abreast of the times. Our courses vary but little from year to year, and the majority of teachers are quite content to extend their knowledge as the courses are extended. Some suggestions will be made later in this report, for the amelioration of this state of affairs.

6. Laboratories and Accommodation.—Since the introduction of Lord Curzon's Education Bill, with the consequent inspection of all affiliated laboratories, these latter in the United Provinces have undoubtedly enormously improved. The majority of them are quite satisfactory for the work they undertake. There are moreover in India several laboratories of quite as high a standard as a firstclass English one, and they differ from English ones only in their equipment. With the equipment of a research laboratory I shall have some remarks to make subsequently, but as regards a description of the laboratory building itself, there is no need to take up time or space.

7. The Research Course.—Hitherto my remarks have been limited to what I have called preparatory work, that is the period of study which is necessary to fit a student for independent or even assisted research. I now come to the Research work proper.

8. The post graduate course at Oxford .- In appendix B. will be found the regulations which concern the research degree at Oxford. To make the course quite clear this needs a little amplification. After taking his final examination and subsequently his B.A. degree a student wishing to take a research degree must decide on a subject in which he is prepared to carry on some original investigation. As a general rule he is dependent on his college tutor, one of the university professors or readers, or some other official for his subject, and when he has made his choice he sends in an application to the Board to get his subject officially sanctioned. This step is a very useful one, because it prevents waste of time over an unsuitable subject, and at the same board meeting one or two tutors of some standing in the university are appointed as supervisors of the students. Supervisors are selected who have special knowledge in the subject which the student intends to investigate. The supervisors are intended to criticise the student's work from time to time, to offer suggestions and to give advice if any peculiar difficulties crop up in the research, also to see that the whole of the practical work is actually done by the candidate himself. On the completion of his work a thesis embodying all the details of his research is submitted to the board by the student, when examiners are appointed who report on its merits. If it is up to the mark the degree is duly It should be added that the candidate may work in the university awarded. laboratory or in any college laboratory as he wishes, or as he may find convenient.

9. Amount of research at Oxford and its manifold Nature.—The research done by students is of course the least important of that which is going on at Oxford. Every professor or demonstrator, and tutor has his piece of research which he carries on in the time which he can spare from his duties as a teacher, and naturally the field covered by these researches is very wide indeed. Even that of the research students is selected from many different branches of chemistry. While I was in Oxford there were about a dozen students working or preparing for the research degree in chemistry, and the widely divergent natures of the work going on at Oxford may be shown by the list of researches in progress last year (see appendix C.).

10. Specialization at Oxford.—In this respect Oxford is perhaps rather different from German Universities, which tend to concentration more on the (5)

particular subject in which the Professor and his chief assistant are specially interested. It must be remembered, however, that owing to the system of college tutors above described, the total number of teaching experts is much larger proportionately than in German universities, and a wholesome spirit of co-operation and interchange exists between the colleges, which enables them to specialize in particular branches of the science without any detriment to any of their own students whose inclinations may turn to some other branch. The University lecture list for the present year shows the large variety of lecture courses open to students, each of which is in the hands of a specialist, and it will be seen to include some seven different subjects given by fifteen different lecturers (see appendix D.). This does not include the college tuition mentioned above. Most of these courses are in a varying degree in advance of the requirements of the degree examination. To illustrate in some degree the manner in which colleges interchange, and the benefit of the system to specialization, it is enough to say that Balliol takes physical chemistry, Christ Church inorganic, Magdalen quantitative analytical, while most of the organic work is done at the university laboratory.

The feeling for the maintenance of the existing college laboratories as opposed to all work being carried on at the university laboratory is very strong and a new laboratory is in course of construction at Jesus College which will be opened next year, with a Fellow of the college in charge. The great benefit of the system is that it enables a college tutor to specialize in a degree which would be quite impossible if his duties were more general, with the consequent advantages to the students. Thus the specialized inorganic chemist would have little or nothing to do with organic work and the students from his college would get their organic work done at some other laboratory and so forth. Now this specialization is of supreme importance in research and the guidance of research students. While dealing with this point, I should like to call attention to Professor Kuchler's remarks on the guidance of research in German Universities (Occasional Reports, 1905, page 11). It is essential that a supervisor should be "conversant with the literature of all the work that has been done up to date in the special line of research," and it is obviously, as a rule, quite out of the question for a professor or tutor to direct studies in many different lines of research at the same time. Professor Kuchler's remarks on this point deal with Physics, but they apply with equal truth to Chemistry, a science which has developed in the last twenty years into a group of sciences which no single intelligence can master.

11. India and difficulties .- When we turn to Indian Universities we find a different set of conditions. Here each college is independent and instead of being a supplement to other similar institutions it is too often a rival, and specialization in different branches of Chemistry by a college is out of the question. In small colleges, as has been shown, teachers have no opportunities for becoming acquainted with recent work, much less of doing research work on their own account. The large colleges, those in which research work is being carried on for university degrees, are prevented from co-operation by distance, and we are confronted with one real difficulty to research in India which is the limited nature of the laboratory staff, and consequent impossibility of any college keeping abreast of the time in every branch of chemistry. If in Oxford it is recognised advisable for one man not to attempt to even teach all branches of Chemistry it is hardly possible in India for one instructor to stimulate research in all branches. Now, I do not wish these remarks to be understood as a protest that the staff of the laboratories is inadequate for the work which they at present undertake. On the contrary, for my own part, I have always found the Government of United Provinces and Government of India ready and anxious to meet reasonable demands for extra help. But it might be beneficial if colleges which profess to guide research in Chemistry, would agree among themselves to take special interest in different branches of the Science. It might even be advantageous if the different universities did the same, a course of action which to some extent

at any rate holds in German universities. Under some such system it would be possible for a student in, say, Lahore to come to Allahabad for his research course, or for some from Allahabad to go to Bombay or Calcutta, if his professor was of opinion that he would there get better assistance in his special subject than at his own college.

12. Indian Professors and Research.—It is also of the greatest importance that the teachers in colleges which guide research should themselves do research work. Nothing stimulates research like research. A professor's work need not necessarily be of a deeper kind that than of his pupils, but he should always have something going on in which his students can take an interest and share. Every opportunity should be afforded to a science teacher to take either courses in European universities or to go for the purposes of study or actual research. It is astonishing how one research leads to another often of quite a different nature, and a term of work in Europe and the consequent association with others engaged in research is bound to result in a sheaf of new ideas which can be utilized for self and students on return to India. I mention this because I consider it very important that furlough studies should not be limited to pedagogics, but extended so as to include the subject actually taught by the Professor.

13. Libraries .-- If there is one thing more than another which is absolutely essential in a college where research is carried on, it is a good library. In this respect Oxford is particularly well off. The scientific library known as the Radcliffe library adjoins the chemical laboratory, and it contains practically all the modern books on chemistry together with a valuable collection of older works of historical value, and all journals of value bearing on chemistry. This library is a reference library only. No books may be taken away, but tables are provided which may be reserved for a term by students, and the library is largely used by them and professors alike for referring to articles in current literature and for abstracting. This library is largely supplemented by the various college libraries some of which are really excellent. Here again the tendency is for specialization, and the physical literature would be found in the laboratory devoted to physical chemistry, and so on. It must be understood that the literature in any research centre must be as comprehensive as possible; it is otherwise quite impossible to know whether one is repeating work which has already been accomplished or is working in the right direction. In consequence of this German, French, and American as well as English journals and books must be included. I have drawn up a list of books and periodicals which are absolutely necessary in a research laboratory, but it would be a great advantage if a larger central library could be instituted at some central institution, which could be used as a lending library for the whole of India, to supplement the university libraries which would be smaller. For instance, it is not necessary for each research institution to possess complete sets of all the periodicals, but there should be one complete set available in India. Similarly all the American and even English and German journals are not needful, but these again ought to be within a few days' reach. Allahabad would be a suitable spot for such a central library, where there is already a large library under Government control, but of course there are other equally suitable places, and the Tata Institute, or Asiatic Society of Bengal in this scheme (see appendix E.).

14. Scientific Societies.—Undoubtedly one of the most important of all stimuli to research in Europe is the Scientific Society with its Journal. Such societies in Great Britain include the Royal Societies of London and Edinburgh, the Chemical Society of London, the Institute of Chemistry, the Society of Chemical Industry, and similar societies at the new provincial universities. It is in such institutions that chemists meet to read papers on and discuss their work, and in the journals that they publish their researches. In addition to these learned societies we have the more local and less pretentious society or club in Oxford which corresponds exactly to the colloquium or seminarium of the German universities.

(see Kuchler, page 12). Such institutions at Oxford are the Junior Scientific Club and the Alembic Club, the latter of which confines itself to the study of Chemistry, while the former is more comprehensive and includes other sciences. Each of these societies has its Journal in which papers of real value may be published, and in addition to the ordinary meetings there is a grand annual meeting at which some European savant gives a special lecture. The Junior Scientific Club also gives a conversazione with a special display of recent advances in the various branches of science. These two institutions have a very great educational value. The reading of original papers by the students, of the reproduction by a student of some important piece of recent research, together with the free discussions which follow such papers are invaluable, and I cannot express too warmly my entire agreement with Mr. Kuchler's remarks on the advantages of these meetings. (Occasional Reports, page 13). Here again, the distances between centres of learning renders it difficult to found and carry on societies of the kind I have mentioned, but the time has come when some such steps should be taken in each of our research centres. Such a society would be the colloquium of Germany and the larger co-ordinating society must for the present be left as a goal for which to aim. With the introduction of research chemists in Forestry, Agriculture and Mining, its attainment is by no means impossible. Possibly an intermediate step would be the formation of a chemical section to the Asiatic Society of Bengal, whose journal would, even now, form a suitable medium for the publication of chemical notes on indigenous products.

Since my return to India, I have been given to understand that the research chemists from the colleges of Agriculture and Forestry are to meet for discussion and formulation of plans yearly in Calcutta. It would be a great boon to Teachers in the provinces if they might be allowed to join these meetings and share in the discussions.

15. Possibilities for Research in India and its Scope.—I hope that in the above I have made clear that it is practically impossible for Indian Universities to compete with those of Europe in research, and specially that it is impossible for any individual institution to be all embracing in its field of research; also that the average Master of Arts is not thoroughly fitted to embark on original work.

I am very far from meaning by these statements that research should have no place in our Indian Universities. It would seem that for the present at any rate the manner in which such research as that for the Oxford research degree (B.Sc.) or the German Ph.D. can be best helped on, is by the encouragement of somewhat specialized research by the Professors of government institutions, and of research on indigeneous products. The Professors' research is sure to have offshoots which can be handed over to students, while the latter is as a rule work of a comparatively simpler nature, and would be work such as a student might well embark on within a year after his Master's degree. The Agricultural Institute at Pusa and the Forest Department College at Dehra Dun might both give valuable assistance in suggesting indigenous products in which research might advantageously be carried on, and I should suggest that such institutions might also be affiliated to the universities for post-graduate research work.

16. Equipment and grants for research.—That our laboratory buildings are on the whole adequate, I have already mentioned. I am afraid that most institutions are somewhat badly off in the matter of apparatus. Since my return to India I have been informed that any attempt of mine to introduce quantitative work into the B.Sc. course will be opposed by affiliated colleges because of the expense which would be incurred in the puchase of balances. This is typical of the attitude of many of our affiliated institutions towards progress.

On the other hand in Government institutions where the grant for apparatus is liberal, there is too frequently the difficulty which arises from the fact that all large indents *must* go to England and so be delayed for a year at least, and secondly the difficulty arising from the impossibility of getting inexpensive but necessary bits of apparatus and chemicals in India. I am sorry to say that not

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only the Professor's but the student's research suffers in this way, and I cannot urgs too strongly that either a more direct control of all the funds for Science should be given to the Professor, or that he should at any rate be given a special grant for the research department to be spent how, when and where he finds it *necessary*. The recurring expenses need not be large, but in order to avoid delays through having to order through the Secretary of State, I would suggest that an initial sum of say Rs. 1,500 should be put at his disposal with a recurring grant of Rs. 500 per annum. This should be strictly limited to research and at the end of a year any unspent balance above Rs. 1,500 should lapse.

The actual apparatus required for research work varies so much with the nature and conditions of the work that it cannot be discussed here. Any well fitted laboratory is suitable for research work and advanced students gain a great deal from seeing research work carried on, so that the research room should not be isolated from the main laboratory.

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APPENDIX A.

CXXX.-The Hydrolysis of Ammonium Salts by Water.

BY ERNEST GEORGE HILL.

VELEY has recently described (Trans., 1905, 87, 26) a method by which he attempted to measure the amount of hydrolytic dissociation of aqueous solutions of ammonium salts. The method consisted in boiling the solutions in Jena flasks under an inverted condenser and estimating the loss of ammonia at the end of a given time. The results were not very satisfactory, but the conclusion was drawn that three cases are presented: (1) that hydrolysis may be inappreciable, (2) that it may be dependent on dilution, (3) that it may be independent of the dilution beyond a limiting value. Veley also showed that the extent to which various acids retain ammonia is more or less analogous to their avidity, but that the absolute order of magnitude is not the same in the two cases.

Veley's most striking results were those obtained from the nitrate and chlorate, which allowed the escape of comparatively large quantities of ammonia, whereas both nitric and chloric acid, being of the same order as hydrochloric, should hydrolyse to a very slight extent. Thus, taking hydrochloric acid as 100, Veley found the avidity of chloric acid to be 6.9, and he omitted nitric acid, from the discussion on the assumption that at the temperature of the experiment the nitric acid decomposed and caused secondary reactions. Formic acid also gave anomalous results.

It was suggested by Dr. Veley that measurements of the electric conductivity of the solutions of ammonium salts before and after treatment as in his experiments would give a more accurate means of determining the amount of hydrolysis. A few preliminary experiments showed that this was not so, and that in the case, for example, of ammonium sulphate there was very little change, before or after boiling.

The amount of ammonia escaping is so small, and the ionisation in the solution is so great, that the variation in the conductivity of a normal or fifth-normal solution was almost inappreciable, and the method was abandoned. It seemed, however, possible that if the escaping ammonia could be led into pure water, the conductivity of the water might be used to measure the amount of ammonia evolved. This method proved much more satisfactory.

Estimation of very dilute Ammonia by the Conductivity of its solution.— From the conductivity or resistance curve, it is possible to estimate the amount of ammonia which corresponds to any particular conductivity. Accordingly, if precautions are taken to avoid contamination of the water, it should be possible, by aspirating a current of purified air through a solution containing free ammonia, and passing the ammoniacal air into conductivity water, to obtain a solution of ammonia in water, the conductivity of which is a measure of the ammonia dissolved. The method would be specially applicable when the ammonia to be measured is very small. After a number of experiments with various forms of aspirators, flasks, and absorption vessels, it was found necessary to purify the aspirated air from all carbon dioxide, to secure a uniform rate of flow, to avoid transfer of the ammonia solution from one vessel to another, to avoid condensation of water vapour on the limb of the flask containing the ammonium salt solution, and to measure accurately the ammonia solution before taking its conductivity, also the air passing through the whole apparatus.

These conditions were obtained as follows :

The air was supplied from an ordinary gas holder and was purified by passing it through a series of wash bottles containing potassium hydroxide solution, and then through a tube containing glass wool moistened with water. The rate of flow was regulated once for all by placing a constricted capillary tube between the purifiers and the laboratory vessel to be described.



The volume of air passed was measured by collecting it, after it had passed through the absorption vessel over water at 15°, in a graduated 800 c.c. flask with a narrow neck. To avoid condensation of water vapour on any part of the apparatus before the absorption vessel, a special form of vessel was designed for containing the salt solutions, every part of which was kept at the temperature of steam, so that no condensation could take place until the air passing through the apparatus had reached the absorption vessel. And lastly, to avoid transfer of solutions and to obviate the difficulty of measuring the volume of the solution before taking its conductivity, the cell itself was graduated and was designed of such a pattern that it served as the absorption vessel.

The Conductivity Cell and Absorption Vessel.—A tube of about 4 mm. cross section, bent twice at right angles, was constricted at the end D and sealed into the cell E. The constriction was less than 1 mm. the diameter of the cell being about 10 mm. The cell was about 6 cm. long, and at its upper end a tube of 6 mm. diameter was sealed with a slight constriction at the joint. At a distance of 16 cm. from the cell, a small pipette-like bulb was blown as a safety trap for any water forced up the tube, but this was never needed during the experiments. The electrodes were as large as possible and about 5 mm. apart. They were drawn up against the sides of the cell, so as to be quite rigid, and the connecting wire passed into mercury cups ben t upwards and extending well above the cell.

The cell was graduated on the two limbs to hold exactly 20 c.c. (see diagram, p. 1277).

The Laboratory Vessel.—This vessel, used for containing the solution of a salt of ammonium during the passage of 800 c.c. of air, was made as follows:

One of the tubes of a 50 c.c. pipette was lengthened considerably and the other was replaced by a narrow tube with a constriction at the entrance to the bulb. This tube was bent twice at right angles, and the end of it (C) shaped conveniently as in the figure. The wider tube was be nt so as to incline at about 115° to the bulb, and on this was placed a small condenser, the end subsequently being bent downwards parallel to the bulb. The construction is best shown by the figure. The end A was drawn out into a strong, narrow point, which could enter the narrow limb of the conductivity cell. The condenser was kept hot by a supply of steam from a boiler, and the bend of the tube was covered by lengthening the condenser with wide bore rubber tubing cut to shape.

Round the narrow limb of the cell a second steam jacket was placed, so that the latter met the rubber prolongation of the condenser described above. Thus the whole of the limb B B B was kept at the temperature of steam. It was therefore no longer possible for any condensation to take place in this limb (see diagram).

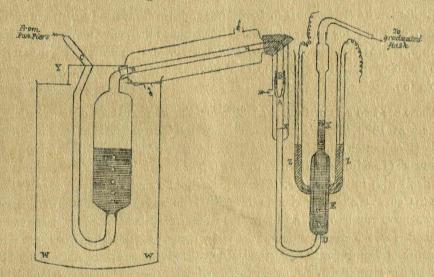
The bulb of the pipette was immersed in a very deep water-bath, and the latter was covered with the usual rings and a small cap, which fitted over the ends of the condenser and the side tube C. In this way the whole of the laboratory vessel was kept at a high and constant temperature. Owing to the shape of the limb BB there could be no spurting of the solution into the cell.

The end of the tube BB was connected with the cell by a small piece of rubber tube, which was wired on to the outside of the narrow limb of the cell, the latter being widened for 10 mm. at its end to allow the tube BB to enter. This joint was so made that the glass of the two tubes just touched and the rubber came into contact with only the outside of the tubes. The point \mathcal{A} entered into the limb of the cell for about 8 mm. The cell was immersed in cold water during the experiment.

Method of Experiment.-At the beginning of an experiment, conductivity water, prepared as subsequently described, was placed in the cell and its conductivity measured. This was found to be slightly diminished by passing the air, purified as above, through the cell for fifteen minutes. No water was considered suitable which had a greater conductivity than 1.5×10^{-6} units.

A solution of the salt was made in conductivity water in a 200 c.c. flask kept for the purpose. Of this solution, 50 c.c. were withdrawn by a pipette, also kept for this purpose but not specially standardised, placed in a small beaker, and immediatety drawn into the laboratory vessel by connecting a rubber tube to BAand aspirating the solution through C. The rubber tube was then removed and the end of the glass tube A rinsed with conductivity water. The laboratory vessel was then placed in the water-bath and joined up with the cell, which contained about 16 c.c. of water at the beginning of an experiment A bent hood fitted over the top of the cell by means of a rubber collar led by a long delivery tube to the 800 c. c. flask inverted over water, in which the air passing through the apparatus was collected and measured. The water was always kept at 15°, and towards the end of the experiment the flask was sponged with water at that temperature.

When the connections were made, the boilers and water-bath were heated, and after a few minutes air regulated as previously described was passed until exactly 800 c.c. had been collected in the measuring flask. This took a little less than an hour. The air was then stopped and the cell disconnected. The cell was filled up to the graduation mark with water directly from the conductivity still and placed in the thermostat, which held several gallons of distilled water. It was



W, water-bath; XX, graduation mark on the cell; Y, copper cap fitting over the water-bath rings, with openings for the limbs of the vessel; ZZ, mercury cups.

heated to little above 18° by a current of steam and allowed to cool slowly. When the temperature reached exactly 18°, the conductivity was measured.

With the apparatus above described, sixteen experiments were made with five different concentrations of animonium sulphate solution. The results were quite satisfactory, the resistances measured differing by less than three per cent. from the mean for a particular concentration. Thus for normal ammonium sulphate the values were 1019, 1027, 1069, 1087, 1083. These were the most discordant results obtained, and a resistance of about 1000 ohms is the least favourable resistance for estimating ammonia by the conductivity method. The reason is that when the resistance is less than 1000 ohms, the nature of the resistance curve is such that only a small difference in resistance is shown by a comparatively large difference in the ammonia present. In these cases, therefore, the ammonia was estimated by titration. For such determinations the laboratory vessel was used in conjunction with a long test-tube containing a measured quantity of standard acid. The tube was fitted with a doubly-bored rabber stopper, which carried a straight tube passing to the bottom, and a short bent tube, which just passed through the stopper. The long tube was connected with the end A of the laboratory vessel, whilst the short end was connected with the delivery tube leading to the collecting flask. The test-tube was rather more than three parts filled with acid. The acid was titrated before and after the passage of 800 c.c. of air, with a very dilute ammonia solution. The latter was standardised for every experiment with standard hydrochloric acid, which also was standardised from time to time with both silver nitrate and sodium carbonate. Experiments were made to ascertain wherther a second absorption tube was required, but it was found that one tube of acid, containing 50 c.c. of acid (1 c.c. = 0.000475 gram HCI), absorbed all the ammonia.

With ammonium acetate, the following values were obtained on different days with different solutions :

Grams of ammonia absorbed in the acid :---

N	N/5.	N/25.
A. 0.033	3 0.00861	0.00169
B. 0.03	2 0.00816	0.00163

To compare the absorption method with the conductivity method in the least favourable cases of the latter, measurments of N/5 salicylate may be quoted.

Two experiments gave 1042 and 1030 for resistances, the mean of these corresponding to 0.00111 gram of ammonia. By the absorption and titration method, the estimated ammonia was 0.001145 gram.

Reduction of Resistances to Percentage of Ammonia.—In order to reduce the numbers obtained for the resistance of the ammonia, solution to percentages of ammonia, it was necessary to plot a curve for the specific resistance of dilute ammonia solution, and read off the values corresponding to the specific resistance of the solution.

These are two sets of figures at 25° for the conductivity of ammonia, and a third set at 18°. The first mentioned are by Ostwald (*Allg. Chem.*, 1893) and Bredig (Kohlrausch and Holborn, *Leitvermogen der Elektrolyte*), and the latter by Kohlrausch (Landolt and Bornstein, *Phys. Chem. Tabellen*). For dilutions such as those dealt with in this paper, these figures do not agree among themselves, and when the curves are plotted side by side it is seen that Kohlrausch's curve and Bredig's curve run parallel, and that when the latter is corrected by the temperaturecoefficient for the dilute ammonia, the two curves differ by about 10 per cent. Kohlrausch's figures for the resistance due to a given percentage of ammonia being about 10 per cent. higher than those of Bredig.

Ostwald's curve almost touches Kohlrausch's at 0.25 per cent. ammonia, but then diverges and cuts Bredig's at the point corresponding to 0.0125 per cent. of ammonia.

The difference between these curves was sufficient to make it necessary for the author to determine a curve of resistance for dilute ammonia, and it was obviously most satisfactory to do this part of the work under conditions as similar as possible to those under which the resistances to be converted were obtained.

The method adopted was to pass air through a solution of ammonia in the laboratory vessel, absorb the issuing ammonia in conductivity water in the cell, and determine the resistance. It was found, as will be shown, that the ratio of the escaping ammonia to the total ammonia in the laboratory vessel was constant, and for the conditions of the experiments was $87\cdot5$ per cent.

The ammonia solution was prepared by mixing pure ammonium nitrate and a solution of freshly prepared potassium hydroxide in conductivity water in a Jena distilling flask. The arm of the flask passed into an ordinary Jena flask fitted with a doubly-bored rubber stopper, the second hole of which carried a potash tube. A current of washed hydrogen was then passed through the two flasks for several



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minutes and the distilling flask gently warmed. The ammonia dissolved in the conductivity water, and the distilling flask was removed. The latter was replaced by a burette fitted with a potash tube, and the ammonia solution was drawn up into the burette. It was then titrated against N/100 hydrochloric acid. To perform an experiment, a few c.c. of the titrated ammonia solution were run into a small graduated flask containing conductivity water, and the volume was made up to 100 c.c. Fifty c.c. were then introduced into the laboratory vessel, and the other experimental conditions were precisely similar to those already described. During these experiments care was taken to keep the air of the laboratory as free as possible from carbon dioxide.

Two series of experiments with different ammonia solutions were performed. The agreement was satisfactory.

SERIES	I. The second second	SERIE	s II.
Ammonia in laboratory		Ammonia in laboratory	
on antipation and a state of the second	Resistance in cell.	The second second second second second	Resistance in cell.
vessel.		vessel.	
0.000391	2056	0.000759	1321
0-000860	1216	0.001518	939
0.0001955	2990	0.000555	1880
0.0000977	4200	0.001897	840
0.0003333	2311		
0-000489	6601	One c.c. of the ammon	is solution contained
0.0001075	1077	0.0000759 gram of amm	onia.

One c.c. of the ammonia solution in the burette contained 0.0000782 gram of ammonia.

From these values a curve of resistances of the ammonia in the cell was plotted and used for converting the other resistances into percentages of ammonia. The porportion of free ammonia passing from the laboratory vessel into the cell was stated above to be 87.5 per cent. This was shown as follows :--

A solution of ammonia free from carbon dioxide, prepared in the manner previously described, was titrated against standard acid. Of this solution, a measured quantity was run from the burette into a graduated flask and the volume made up to 200 c.e. Fifty c.c. were now drawn into the laboratory vessel and 800 c.c. of air aspirated through it in the usual manner. The issuing air passed through standard acid which was titrated before and after the experiment.

The following experiments were performed :---

The original ammonia solution contained 0.001643 gram per c.c.

The standard acid used for absorption was titrated against the orginal ammonia solution before and after the experiment. Thus the difference between the two values gave the amount of ammonia absorbed by the acid.

ammonia introduced into the vessel in c.c.	Ammonia passing into the acid in c.c.	Mean.
15-9	13:25 13:15 18:15	13.18
10'0	8·70 8·70	8.70
5.0	4·35 4·40	4-375
2.50	2:20 2:15 2:20	2.163
125	1:10	1.10

The ratio of ammonia in the vessel to the escaping ammonia absorbed by the acid is consequently-

1:0.879, 1:0.870, 1:0.875, 1:0.873, 1:0.880.

The ratio may thus be considered constant, and it may be assumed that 87.5 per cent. of the ammonia passes from the laboratory vessel into the cell under the conditions of the experiments.

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Effect of Dissolved Salts on the Escape of Ammonia.—In the hydrolysis of ammonium salts with water, the amount of free ammonia in the salt solution is small compared with that of the total salt dissolved. It was necessary to ascertain what influence the dissolved salt had on the rate of escape of ammonia under the conditions of these experiments. Raoult (Ann. Chim. Phys., 1874, [v], 1, 262), who used strong solutions, states that ammonium chloride decreases the solubility proportionally to the amount present, but that ammonium nitrate has no effect. The latter statement was confirmed by Gaus (Zeit. amorg. Chem., 1900, 25, 236).

Perman (Trans., 1902, 81, 482) gives details of two series of experiments, from which he concludes that ammonium chloride may form a complex molecule with ammonia and that the effect of this is to decrease the vapour pressure of the ammonia. He, however, was working with very strong solutions of ammonia (12-15 per cent. NH³), and his conclusions were derived from a comparison with an ammonia solution containing the same percentage of ammonia and water. If the comparison is made with a solution containing the same mass of ammonia in unit volume, it is seen that the effect of the ammonium chloride is to increase the vapour pressure, or to decrease the solubility to the ammonia. Perman's figures also seem to show that the alteration in vapour pressure increases with the amount of salt in solution.

It was necessary, therefore, to de termine what happened with such concentration of salt as the author was using.

To ascertain the effect of ammonium salts on the rate of escape of ammonia from its solutions under the conditions of the author's work the following experiments were made :---

A dilute solution of pure ammonia was prepared, 50 c.c. of this introduced into the laboratory vessel, which as in all cases was heated in the water-bath and S00 c.c. of air passed through it, the issuing air and ammonia passing through a tube of standardised acid. The conditions of this experiment were in all respects similar to those previously described. The acid was subsequently titrated with dilute ammonia. In another experiment, a gram-molecular solution of ammonium nitrate was made up in some of the ammonia solution and 50 c.c. of this used in the laboratory vessel, and in a third case ammonium chloride was used.

Two series of experiments with different ammonia solutions, which, accidentally, were of the same strength, gave-

SERIES A.

Fifty c.c. of each solution used,	requ	Standard ammonia required for neutralis- ing the acid after passing the air.			
Ammonium chloride (10.7 grams in 2 of ammonia solution)	00 c.c.	1 	44:75 c.c,		
Ammonium nitrate (18.0 grams)		••	44.70 "		
Ammonia solution alone	· ···	•••	44.70 "		
The amount of ammonia required passing air was	before		52.70 "		
Series I	3,				
Ammonium chloride as above		14	44.70 c.c,		
Ammonium nitrate 33 33	7	1	44.75 "		
Ammonia solution alone			44:70 "		

(15)

It may thus be concluded that the dissolved salts do not exert any influence on the escape of ammonia when the amount of the latter is small compared with that of the dissolved salt.

There seems no doubt, therefore, that the ammonia evolved under the conditions of the author's experiments is a measure of the relative hydrolysis of the salts used.

The Conductivity Water.—The water used in these experiments, both for preparing the solutions of the salts and for the absorption of the ammonia, was made by distilling tap-water (which had been well boiled for ten minutes) through a dilute solution of permanganate acidified with dilute sulphuric acid and then through a solution of permanganate made alkaline with potassium hydroxide. The two permanganate solutions were contained in Jena flasks of 1000 c.c. capacity and were kept about one-third full.

The issuing steam passed through a trap and was finally condensed in a specially kept Jena flask. With this apparatus it was easy to get a sufficient supply of water with a conductivity not greater than 1.5×10^{-6} at 18° .

The cells were standardised by comparison with solutions of potassium and sodium chloride at 18.0°, and the following values were obtained :--

Solutio	D				Cell 1.	Cell 2,
(1) N/50 Sodium chloride	9 9,99	996		-	0.09041	0.06609
(2) N/50 Sodium chloride	8	***				0.06609
(3) N/500 Sodium chlorid	le				0.09025	0.06549
(4) N/500 Sodium chlorid	10			0.97	0.09029	
(5) N/500 Sodium chlorid	le	***	100 ALS		0.09020	
(6) N/100 Potassium chief	oride			500 844	0.09031	0.06597
					-	A Contraction of the second
Mean		0,00			0.09024	0.06291

Hence the ratio of the cells to one another was 0.09024 to 0.06591, or 1.369 to 1.000. The first three values were determined before the commencement of the work, but the values in experiments (4), (5), and (6) were obtained during the research (6) being taken on the completion of the experimental portion. The value of the cells had, consequently, not changed during the work.

The Salts.—The salts used were the chloride, chlorate, nitrate, sulphate, oxalate, salicylate, succinate, citrate, benzoate, acetate, and formate. Of these the organic salts were kindly supplied by Dr. Veley, whilst the others were recrystallised from good specimens in the laboratory. An exception must be made in the case of the chlorate, which was prepared from barium chlorate in the usual manner. It gave no trace of chloride after two crystallisations. The organic salts were all recrystallised with the exception of the citrate, and had all been supplied originally by Kahlbaum.

The ammonium acetate was dried over solid potassium hydroxide in an atmosphere containing ammonia gas after the crystals had been dried as far as possible on blotting-paper.

In addition to the above, fine crystalline specimens of the ammonium salts of monochloroacetic and trichloroacetic acids were prepared. Unfortunately both decomposed under the conditions of the experiment, the former yielding a considerable amount of hydrochloric acid and the latter chloroform.

The Solutions.-The solutions were made by weighing out exact quantities of the salts in a weighed beaker and making up to 200 c.c. with conductivity water. The strengths used were normal, fifth-normal, and twenty-fifth normal. The



solutions were always used immediately after being prepared, and the following

 Salt.
 O'2 normal.
 O'4 normal.

 Salt.
 Call 1. Cell 2.
 Cell 1. Cell 2.

 Chloride
 ...
 3550
 (2595)
 - 3470
 - 5549

 Nitrate
 ...
 State
 Cell 1. Cell 2.
 Cell 1. Cell 2.

 Nitrate
 ...
 3470
 - 5549

 Nitrate
 ...
 3577
 7314
 (5559)

Cintoricie	4 50	00-0U	6000000	164 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 - 1941 -	The second second second second second second		Contraction of the second second	
		and the second second	2420	antern	3577	7814	(5345)	
Nitrate		8428	(2495)	5198	(3796)	7611	(5559)	
A		and the second	2638	-	3602		5443	
Chlorate	tes		2495	Sandalli .	3569	7156	(5227)	
Salicylate	***		-		1030	3172	(2317)	
			an a	1427	(1042)	1997 - Anna 19	2223	
Succitate			and and a second	and the second	\$80	2399	(1752)	
		and the second second	and a start	A AND A A		-	1639	
Formate				preside in the	and stars	anna)	1345	
Sulphate			1048	2298	(1678)		2081	
Suparo	1485		in and		1662	and the second	2780	

The numbers in brackets are the values for cell 1 divided by 1.369, and hence would be the resistances of the solution in cell 2.

As previously stated, the conductivity method was not accurate when the resistance in the cell was less than 1,000 ohms, but in such cases the titration method already described could easily be applied. As an example of two experiments, we have-

Ammonium acetate, N/1 solution, 50 c.c. acid used for absorption.

Ammonia solution used for titration, 1 c.c. = 0.00087 gram ammonium hydroxide.

Before absorption, 50 c.c. acid = 114.00 c.c. ammonia, after absorption = (a) 77.30, (b) 76.50, mean = 76.90; hence ammonia absorbed = 37.1×0.00087 = 0.0323 grams.

By using the above method as a supplement to the conductivity method, the following table was obtained. In it the resistances are converted into ammonia, which is given as the actual amount passing over from the laboratory vessel.

In all cases except that of the chlorate, the values are the mean of at least two concordant results. In the case of the chlorate, the values are for singleexperiments :---

CHIROTROS			and the second second second	STIP	NIOF
Salt.			N/1.	N/5.	N/25.
Chloride	10		0.000255	0.000118	0.0000523
Nitrate			0.000243	0.000111	0.0000520
			0.000356	0.000119	0.0000559
		Sec. 1	0.001015	0.000443	0.000218
Sulphate	•••		0.00552	0.00113	0.000301 *
Salicylate	The first		0.01998	0.00878	0.000798
Benzoate	-			0.00838	0.00166
Acetate		10 (1946 9	0.03230	and the second	0.000640 *
Formate			0.01151	0.00225	
Succinate	-	1 000	0.00380	0.00200	0.000420
Oxalate		100	0.0088	0.00185	and the second
Citrate			0.01217	0.00574	0.00272
Monochloroacetate			0.0024		An and a second second

*Values high; obtained by conductivity method; probably slight decomposition and evolution of tarbon diexide, hence lowering the resistance in the cell.

In the case of dibasic acids, half molecular weights were dissolved in a litre of normal solution.

In the preceding table we have several sets of cases. There are monobasic, dibasic, and tribasic acids, and the two former contain both weak and strong acids.

Monobasic Acids.—These form only one simple salt, and consequently only one type of hydrolysis is possible. According as the acid is strong or weak, the equation for the hydrolysis constant will be

$$\frac{C_{\rm AH} \times C_{\rm BOH}}{C_{\rm salt}} = K, \text{ or } \frac{C_{\rm AH} \times C_{\rm BOH}}{C^2_{\rm salt}} = K.$$

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Dibasic Acids.-In the case of the salts of dibasic acids, hydrolysis may take place in two ways :---

- (1) $A''B'_2 + H_2O = A''BH + BOH.$
- (2) $A''B'_2 + 2H_2O = A''H_2 + 2BOH$,

Where the amount of hydrolysis is small, as in the above experiments, it may be assumed that the first of these equations holds, and the equation for the hydrolysis constant becomes $K = \frac{C_{ABH} \times C_{BOH}}{C_{salt}}$ or $K = \frac{C_{ABH} \times C_{BOH}}{C^3_{salt}}$, according as the acid is strong. or weak.

These equations may be written $K = \frac{C^{2}_{BOH}}{C_{salt}}$ or $K = \frac{C^{2}_{BOH}}{C^{2}_{salt}}$ respectively. If in the above equations we take the ammonia liberated under the conditions

If in the above equations we take the ammonia liberated under the conditions of the experiment as C_{BOH} , we have a means for calculating the hydrolysis constant of the solutions used.

In the following table, the equation $K = \frac{C^2_{BOH}}{C_{salt}}$ has been used for the first four acids, whilst for the rest, $K = \frac{C^2_{BOH}}{C_{BOH}}$.

				K×	$\sqrt{K} \times 10^4$.				
	Salt.			N.	N/5	. N/25	N.	N/5.	N/25.
Chloride	A SAME	A State of		0.00650	0.00690	0.0068	1 2.55	2.62	2.61
Nitrate				0.0059)	0.0000		AND STATES	2.46	2.57
Chlorate	***			0.00658	5 0.0070	3 0.0073	ALC: NOT THE REAL	2.66	2.70
Sulphate	and the second second	Alexandress and the second		0.103	0.100 .	0.114	10.15	10.00	10.6
Oxalate	19 - 19 - 19 - 19 - 19 - 19 - 19 - 19 -	100 ···		7.74	8.51	-	88.0	92.5	100
Succinate	an encount	and the second		9:80	10.0	11-0	99.0	100.0	105.0
Formate	See		ves	12.4	126		112.1	112.5	
Benzoate				39.9	34.9	39.8	199.8	189-0	199.5
Acetate	1.1.1		•••	104.0	175.0	172.0	323.0	419.0	415.0
Monochloroac	etate	1.110		0.576	-		24.0		
Salicylate	A Section		•2•	3.03	3.19		65.2	56.5	And Address of Control

In the foregoing table, the values for K are as constant as can be expected from the experimental method. It may be noted that the nitrate and chlorate behave quite normally, and that the formate gives also a satisfactory result.

The value for the normal solution of the acetate is abnormal. This does not seem to be due to experimental error, since two sets of experiments with different solutions gave concordant results. In this respect, attention may be directed to Veley's figures for the acetate. He found that the normal solution gave a little more than half the percentage of ammonia which was given by 0.2 normal and more dilute solutions, and since the acetate is the salt of the weakest acid used, the figures for this salt should be the most accurate. It therefore appears that in concentrated solution the acetate is proportionately less dissociated.

If we take the inverse of the above figures, we ought to find 1/K proportional to the dissociation, constants of the acids the salts of which are used, and $\sqrt{1/K}$ proportional to the avidities of the acids obtained by dynamical methods. Since, however, the dissociation constants of the strong acids cannot be used for comparison, we must use the molecular conductivities of their solutions and compare these with $\sqrt{1/K}$. In the following table are given the values for $\sqrt{1/K}$ (hydrochloric acid = 1), also the ratios of the molecular conductivities, and the values for the avidities of the acids obtained from the velocity of decomposition of methyl acetate and the inversion of cane sugar.

	Salt.			//IK.	Molecular conductivity.	Inversion of cane sugar.	Decomposition of methyl acetate.
Chloride	Sec. Street			1.000	1.000	1:000	1.000
Nitrate			840	1.065	0.991	1.000	0.915
Chlorate		· · · · · · · · · · · · ·		0.985	1.000	1:035	0'944
Salicylate			S. CARRO	0.046	0.032		
Formate				0.033	0.017	0.015	0.013
Benzeate	***	and the second s	. In.	0.013	0.008		www

SI

(18)

8.1	t.	√/1K.	Molecular conductivity.	Inversion of cane sugar.	Decomposition of methyl acetate.
Acetate		 0.006	0.004	0.004	• 0.0034
Monochloroace		0.106	0.049	0.048	0 0 4 3
Sulphate		 0.262	0.625	0.236	0.541
Oxalate		0.029	0.197	0.185	,0.174
Succinate	***	 0.026	0.006	0.005	0.005
Ducernace	060				

Norr. -- In the above table, the conductivities for salicylic and benzoic acids which will not form normal solutions have been calculated from their ratios to acetic acid at lower dilutions.

In discussing the above results, we may first take the monobasic acids. Here we find a very good agreement both in order and magnitude with the figures obtained by any of the other methods. The strong acids are almost equal and the ratio of the four weak acids is the same as that of the conductivities. The agreement here is particularly striking, the ratios being—

noto 15 Farren à			Salicylic.	Formie.	Benzoic.	Acetic,
1117 -		 	0.032	0.016	0.0087	0.004
$\sqrt{1/K} \propto \cdots$	1		0.032	0.017	0 0087	0.004
Conductivities	400				11	a in mhich

Or we may compare 1/K with the dissociation constants of these acids, in which case again making the values for salicylic acid the same, we obtain --

ase, again musing one case	Salicylic.	Formic.	Benzoic	Acetic.
1/K a	 102	26.0	8.2	1.8
Dass. const. $\times 10^8$	 102	21.4	6.0	1.8

Here again the numbers are distinctly of the same order of magnitude. It will be noted in the table, that when hydrochloric acid is taken as the standard for comparison, the weak monobasic acids give slightly higher figures than are given by the conductivities, &c. In this connection it may be suggested that the discrepancy is due to the different temperature-coefficients of strong and weak acids, the conductivities being at 25° and the author's experiments at nearly 100°. It would not appear likely that it is to experimental error, either in the curve for the resistance of ammonia solutions or in the other observations, since the values obtained for Kin the different dilutions are so closely constant.

Dealing next with dibasic acids, we have to remember that, in the hydrolysis of, a salt of a dibasic acid, the ammonia neutralising the weaker acid hydrogen is removed first. Thus the method described could not be used to measure the strength of the first hydrogen (or ionisation). That it depends on both the ionisation constants is shown below. With dibasic acids we have—

 $K_1C_{AH_2} = C_{AH'} \times C_{H'}$ and $K_2C_{AH'} = C_{A''} \times C_{H'}$

where K_1 and K_2 are the first and second ionisation constants. Now

$$C_{\rm NH4} + O_{\rm NH40H} = C_{\rm A''} + C_{\rm AH'} + C_{\rm AH'3} \qquad \dots \qquad (1).$$

and (positive = negative charges)

 $C_{\rm NH4'} + C_{\rm H'} = 2C_{\rm A''} + C_{\rm AH'} + C_{\rm OH'},$

From (1) and (2) we get

But

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$$\begin{aligned} a_{14} + C_{NH_{4}OH} &= C_{A'} + C_{AH'} + \frac{C_{A''} + C_{H'}}{K_{1}}, \\ &= C_{A'} + C_{AH'} \left\{ 1 + \frac{C_{H'}}{K_{2}} \right\}, \\ &= C_{A'} + \frac{C_{A''} \times C_{H'}}{K_{2}} \left\{ 1 + \frac{C_{H'}}{K_{1}} \right\}, \\ &= C_{A'} \left\{ 1 + \frac{C_{H'}}{K_{2}} + \frac{C^{2}_{H'}}{K_{1}K_{2}} \right\} \dots \dots \dots \dots \dots \dots \dots \dots \quad (5); \end{aligned}$$

(19)

from (4) and (5);

CN

$$T_{4}$$
 OH = $C_{A'} \left\{ \frac{C_{H'}}{K_1 K_2} - 1 \right\},$

and hence

$$\frac{C_{\mathrm{NH}_{4}\mathrm{OH}}}{C_{\mathrm{NH}_{4}} + C_{\mathrm{NH}_{4}\mathrm{OH}}} = \frac{C_{\mathrm{A}''} \left\{ \frac{C^{2}_{\mathrm{B}'}}{K_{1}K_{2}} - 1 \right\}}{C_{\mathrm{A}''} \left\{ 1 + \frac{C_{\mathrm{B}'}}{K_{2}} + \frac{C^{2}_{\mathrm{B}'}}{K_{1}K_{2}} \right\}},$$

$$= \frac{C^{2}_{\mathrm{B}'} - K_{1}K_{2}}{K_{1}K_{2} + K_{1}C_{\mathrm{B}'} + C^{2}_{\mathrm{B}'}}.$$

That is, the relative amount of hydrolysis is proportional to a term involving both the first and second ionisation constants.

The Percentage Hydrolysis in Solutions of Ammonium Salts at 100°.—This may be to some degree determined from the above data; thus, in normal ammonium chloride we have 17 grams of ammonia (combined) per litre, and in the laboratory vessel (50 c.c.) we have 0.85 gram. But the free ammonia is 0.000255×1.143 (the inverse of the partition_coefficient for ammonia, 0.875).

Thus the percentage hydrolysis is $\frac{100 \times 0.000291}{0.85} = 0.0341$ per cent. similarly, for N/5 acetic acid we get

$\frac{0.0323 \times 1.141 \times 100}{0.85} = 4.34 \text{ per cent.}$

These values are doubtless too high, since, as ammonia is evolved from the solution, hydrolytic action, to a less degree, continues.

They cannot be compared with values obtained by other methods, as the author is not aware of any determined at so high a temperature.

Conclusions.

1. The hydrolysis of ammonia salts with water is in accordance with the laws of mass action for salts of strong and weak acids.

2. This hydrolytic dissociation is inversely proportional to the "strength" of the acid, that is, to the square of the conductivities of solutions of the acid, or their ionisation constants, in the case of univalent acids only.

3. In the case of bivalent acids, the relation between hydrolytic dissociation of salts and the two ionisation constants of the acids is complicated, and the hydrolysis cannot be used as a direct measure of either of the ionisation constants or the "strength" of either of the acid hydrogen atoms in the acid.

4. Certain maximum values are determined for the degree of hydrolysis at 100°.

The author's thanks are due to the authorities of Magdalen College, Oxford, for a grant which covered laboratory expenses, and to Mr. J. J. Manley, the Daubeny Curator, for kind assistance in making the apparatus used. MAGDALEN COLLEGE,

OXFORD.

APPENDIX B.

OXFORD UNIVERSITY STATUTES.

STATT. TIT. VI. SECT. IV.

October, 1905.

SECTION IV.-OF THE TIMES AND EXERCISES REQUIRED FOR DEGREES IN LETTERS AND IN SCIENCE.

§1. Of the Degrees of Bachelor of Letters and Bachelor of Science.

Any person who has been permitted by the authority and in the manner hereinafter provided to enter on a course of special study or research may supplicate for the Degree of Bachelor of Letters or Bachelor of Science, provided that he has satisfied the conditions prescribed by this Statute. Science shall be taken to include Mathematics, Natural Science, Mental and Moral Science.

§ 2. Of the Admission of Candidates for the Degrees of Bachelor of Letters and Bachelor of Science, and the Conditions of supplicating for these Degrees.

Any person who has been, or is qualified to be, matriculated in the 1. University and is not under the age of twenty-one years, may give notice to the Secretary to the Boards of Faculties of his desire to be admitted as a Candidate for the Degree of Bachelor of Letters or of Science and thereupon to enter on a course of special study or research. Every such notice shall state in general terms the subject and nature of the proposed course, and no course shall be admissible which does not extend over a complete year. The Secretary shall transmit every such notice received by him to the Chairman of the Board of the Faculty or of Studies which includes the proposed subject for the approval of the Board. Such approval shall not be granted unless the intending Candidate (1) has passed the Examinations required for the Degree of Bachelor of Arts, or has given evidence that he has received a good general education, satisfactory to the Committee hereinafter constituted for the purpose; (2) has satisfied the Board of Faculty or Studies to which his subject belongs of his fitness to enter on a course of special study or research ; and that the course of study or research on which he proposes to enter is. such as may profitably be pursued under the direction and superintendence of the Board. If the notice given by an intending Candidate is approved by the Board, the Secretary shall notify the fact to him; and he shall pay to the University Chest through the Secretary a fee of £5 within a fortnight of such notification, or, if at the time he is not yet a member of the University, then within a fortnight of his matriculation. He shall thereupon be deemed to have been admitted as a Candidate for the Degree of Bachelor of Letters or of Science; and the Secretary shall register his name, and his notice as approved by the Board, in a book to be kept for the purpose.

2. The Committee appointed to consider whether an intending Candidate has received a good general education shall be composed of one representative of each of the following Boards of Faculty or of Studies, namely, Theology, Law, Medicine, Natural Science, Literæ Humaniores, Oriental Languages, Modern History, English Language and Literature, and Modern Languages, which representatives shall be elected at the first meeting of each Board after this statute shall come into effect, and shall hold office for two years, at the expiration of which period there shall be a new election, and so on, from time to time, provided that vacancies on the Committee caused otherwise than by lapse of time shall be filled up for the remainder of the biennial period.

3. The Boards of the Faculties shall have authority to direct and superintend the work of Candidates admitted as aforesaid, and to make such general regulations as they shall think fit.

4. The Boards of the Faculties may appoint Committees composed of graduate members of the University, or other competent persons, and may authorize any such Committee to report to them regarding the fitness of an intending Candidate for the course of study or research on which he proposes to enter, and to superintend the work of a Candidate admitted as aforesaid, and to report thereon to the Board of the Faculty to which his subject belongs. A Board shall have power in special cases to recommend to the Vice-Chancellor and Proctors that a remuneration be paid to a person so appointed to superintend the work of a Candidate or to report thereon, and to suggest the amount of such remuneration : provided that (1) the Board shall report to the Vice-Chancellor the circumstances of the case, and that (2) the Vice-Chancellor and Proctors shall determine the amount at their discretion, and that (3) in no case shall such remuneration be paid to a Professor or Reader.

5. Any Candidate who has completed his proposed course of study or research, may at any time not less than twelve months after his admission apply to the Board of the Faculty or Studies for a certificate that so far as proficiency in the subject of his course of special study or research is concerned, he has attained a high standard of merit. Such application shall be made to the Board through the

Secretary, and the Candidate shall at the same time pay to the University Chest through the Secretary a fee of £5. On receiving the application and the fee the Secretary shall transmit the application to the Chairman of the Board. On receiving such application, the Board of the Faculty or Studies shall appoint Examiners who shall satisfy themselves as to the merit of the Candidate, and his proficiency in the subject of his course of special study or research, either by examination or by requiring from him such Dissertation, or report of work done, as shall be directed by the Board; provided that if a Dissertation be required, notice shall have been given to the Candidate of the intention of the Board, as soon as may be after his admission as a Candidate. Any Candidate who is directed to submit a Dissertation or report of work done shall be further publicly examined in the subject of such Dissertation or report. Before granting a Certificate the Board shall have power to require the publication of the Dissertation or report or of some portion of it in such manner as the Board shall think desirable. It shall be the duty of the Boards of the Faculties or studies to grant Certificates to those Candidates only who are reported to them by the Examiners to have attained a high standard of merit; and to state and publish in the usual manner the ground on which the Certificate has in each case been granted, together with the names of the Examiners who have reported to the Board. Provided that if the Examiners are evenly divided as to the standard of merit attained, the Board of the Faculty or Studies shall be empowered to satisfy themselves in some other way as to the merit of the Candidate, and to grant the Certificate, if they see fit.

6. An entry of the names of those Candidates to whom such Certificates have been granted shall be made in a book to be kept for the purpose. To the name of each Candidate shall be appended a description of the course of study or research which he has completed, together with a statement of the grounds on which the Certificate has been granted. Every entry shall be signed by the Chaisman of the Board of the Faculty or Studies, and by the Secretary. This book shall be kept in the custody of the Secretary.

7. The Examiners to be appointed by the Board shall always include one at least of any Professors or Readers who are appointed to lecture and give instruction in the subject or branch of study which includes the subject offered by the Candidate, provided that the Board may, if requested by any such Professor or Reader, appoint an Examiner to act in substitution for him.

8. No Candidate shall be permitted to supplicate for the Degree of Bachelor of Letters or for the Degree of Bachelor of Science, unless he has kept at least eight Terms by residence within one mile and a half of Carfax as a matriculated member of the University. It shall be competent for the Board to allow a Student who has with the consent and under the superintendence of the Board so resided for the purpose of carrying on his proposed course of study or research for a period of forty-two days, not necessarily consecutive, but falling within the same Academical year, to reckon such period of residence as one Term's residence : provided that (1) no day so reckoned which falls within any Term, shall also be reckoned for the purpose of keeping that Term by residence : and (2) no Candidate who has kept by residence the Michaelmas, or the Hilary, or the Easter and Act Terms, shall be allowed to reckon in this manner any day that falls within the eight weeks beginning on the first Monday of Full Term in Michaelmas, or Hilary, or Easter Term, as the case may be: and (3) no Candidate shall be allowed to reckon in this manner more than one such period in the same Academical year: and (4) no Candidate shall be allowed to reckon more than four Terms as being kept by residence in the same Academical year.

It shall be the duty of the Secretary to the Boards of Faculties whenever a Term's residence has been allowed as aforesaid to report the fact as soon as may be to the Society of which the Candidate is a member.

9. The Certificate that a Candidate has, in conformity with the requisitions of the Statute, satisfied the Board of the Faculty of Studies that he has attained a

high standard of merit, shall be signed on behalf of the Board of the Faculty or Studies by the Chairman and Secretary.

The form of the Certificate shall be as follows:--

Board of the Faculty of (or of Studies for

Oxford. (Date.)

This is to certify that A. B., of College (or of Hall, or Non-Collegiate Student), in conformity with the requisitions of the Statutes has completed a course of special study (or research) approved by the Board, and has satisfied the Board that he has attained a high standard of merit.

Signed on behalf of the Board,

C. D., Chairman.

E. F., Secretary.'

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10. The names of the Candidates to whom Certificates in the foregoing form have been granted shall be published in the usual manner.

The list of such Candidates shall be drawn up in the following form :----

'Names of Candidates who in Term, A.D. have satisfied the Boards of Faculties or Studies that they have attained a high standard of merit in a course of study or research.

	A. B.,	of College.
	C. D.,	of Hall.
	E. F.,	Non-Collegiate Student.
(Signed)	G. H.,	all an and a probability of the

Secretary to the Boards of Faculties.'

To the name of each Candidate in the list shall, be appended a notice of the course of study or research which he pursued.

11. Bach elors of Letters and Science shall rank immediately after Bachelors of Civil Law and Medicine; and, among themselves, according to the date of admission to their respective degrees in Letters and Science. Provided always that no such Bachelor of Letters or Science rank before any Master of Arts, unless he himself holds a Master's degree.

§ 3. Of the Admission of Candidates for the Degrees of Doctor of Letters and Doctor of Science, and the C onditions of supplicating for these Degrees.

Candidates may supplicate for these degrees s ubject to the following conditions:--

(1) A Bachelor of Letters may supplicate for the Degree of Doctor of Letters, provided that he has had his name on the Books of some College or Hall or on the Register of Non-Collegiate Students for twenty-six Terms.

(2) A Bachelor of Science may supplicate for the Degree of Doctor of Science, provided that he has had his name on the Books of some College or Hall or on the Register of Non-Collegiate Students for twenty-six Terms.

(3) A Master of Arts, who has incepted in this University, may supplicate for either of these degrees, provided that he has entered upon the thirty-ninth Term from his matriculation.

(4) Any person who being a Master of Arts of the University of Cambridge or Dublin has been incorporated, and any person who being an Undergraduate or a Bachelor of Arts of the University of Cambridge or Dublin, has been incorporated and has incepted in the faculty of Arts in this University, may supplicate for either of these degrees, provided that he has entered upon the thirty-ninth Term from his matriculation at Cambridge or Dublin.

(5) Any person on whom the Degree of Master of Arts has been conferred by Convocation by decree, other than a degree *honoris causa*, may supplicate for either of these degrees, provided that he has entered upon the twelfth Term from his admission to that degree. (6) When a Candidate under the provisions of the following clause applies for the approval of a Board of a Faculty or of Studies, the application for approval shall be made through the Secretary of the Boards of Faculties to the Chairman of the Board, and shall be accompanied by a Certificate signed by some officer of or some person deputed by the College or Hall or Body to which he belongs, and showing that his name is on the books of such College or Hall or Body.

(7) Before supplicating, Candidates for either of these degrees must have submitted evidence of their fitness for the degree to the approval of the Board of the Faculty or of Studies to which their subject belongs. Such evidence shall consist of published papers or books, containing an original contribution to the advancement of learning or science, and, where possible, at least two copies of such papers or books shall be submitted. If the Board approves the evidence, a Certificate shall be given to the Candidate describing the evidence approved by the Board, and stating that it is of sufficient merit to entitle him to supplicate for the degree. This Certificate shall be signed by the Chairman and the Secretary, and shall be published in the usual manner: and it shall be the duty of the Registrar, when a Candidate's name is entered for the degree, to ascertain whether the Certificate has been duly granted. One copy of each of the papers and books named in the Certificate shall remain in the possession of the University for deposit in Bodley's Library, provided that no book or paper of which the Library already possesses a copy shall be so deposited except with the consent of the Candidate and of the Librarian, unless the copy submitted by the Candidate shall be of a different issue or shall contain alterations or additions. The Board shall also have power to make and vary from time to time such regulations for carrying out the provisions of this clause as it may deem expedient, provided that all such regulations and any variations in them shall be submitted to the Hebdomadal Council for approval.

APPENDIX C.

Chemical Researches now in progress in Oxford, or completed within the last year.

Lord Berkeley and E. G. J. Hartley, Osmotic Pressure and Vapour pressure of concentrated solutions. Part published in Phil. Trans.

* Prof. H. A. Miers and Miss Isaac, Investigation of Supersolubility. Part published in J. C. S.

* H. L. Bowman. Minerological Researches, Bowmanite, etc. Mineralog. Journal.

T. V. Barker. Parallel Growth of Crystals. Part in J. C. S.

* J. E. Marsh and R. de J. Fleming-Struthers. Organic Compounds of the Metallic Cyanides Part in J. C. S. 05.

J. E. Marsh and G. F. Hood. Study of Iodoso-compounds.

J. E. Marsh, J. G. Burch, and R. de J. Fleming-Struthers. Emission Spectra of Mercury Salts.

J. E. Marsh and F. W. Caton. Synthesis of closed rings.

A. F. Walden. Prozane Derivatives.

B. Lambert. Conductivity of pure Organic Acids.

B. Lambert and G. Lilley. Oxidation of Aluminium by water.

* J. J. Manley. An Accurate Method for determining the Specific Gravities of salt solutions.

V. H. Veley. Action of acids on Methyl-Orange.

* N. V. Sidgwick and T. S. Moore. Calorimetric Investigations of Tautomeric Substances.

T. S. Moore. Tautomerism of Acyl-Phenols.

E. Stokes and H. T. Tizard. Electrolysis of Concentrated Sulphuric Acid with Aluminium Electrodes.

E. G. Hill. The Hydrolysis of Ammonium salts.

* Names marked with an asterisk are those of University or College tutors.



E. G. Hill. The relation between Refractive Indices, Conductivities, Densities, and total Chlorine in Sea water.

H. B. Hartley and N. Garrod Thomas. Solubility of Triphenyl-methane in Organic Solvents, J. C. S.

* H. B. Hartley, N. Garrod Thomas, and M. P. Applebey. Physical Properties of Mixtures of Pyridine and water.

H. B. Hartley, J. P. Hucklebridge, and W. H. Barrett. The Alkaline Sulphites.

H. B. Hartley and N. P. Campbell. Solubility of Iodine in water.

H. B. Hartley, N. Garrod Thomas, and N. P. Campbell. Mineralogical Investigations.

N. P. Campbell. Rate of Growth of Crystals from Solution.

J. R. Milne. Connection between Optical and Electrical Properties of certain Solutions.

* H. B. Baker. Atomic Weight of Tellurium.

* H. B. Baker. Dissociation and Association of Dry Nitrogen Trioxide.

H. B. Baker and M. H. Godby. The Isomeric Sodium-Potassium Sulphites.

H. B. Baker and G. Lilley. Influence of Pressure on Chemical Reactions.

H. B. Baker and L. C. F. Oldfield. Sulphur Monoxide.

H. B. Baker and H. O. Kershaw. The Metallic Subhalides.

A. Angel. Cuprous Formate. J. C. S.

R. T. Lattey. Vapour Pressures of Binary Mixtures. G. Leicester. Derivatives of Fluorindene.

F. C. Weedon. Magnetic Alloys.

APPENDIX D.

CHEMISTRY.		TT a Defense of Che
Chemical Revision, 1850—1860	•••	Waynflete, Professor of Che- mistry, W. Odling, M.A.
Q : Chamistry (Honours Course)		J. Watts, M.A.
Organic Chemistry (Honours Course) Subjects of the Preliminary Examination		Aldrichian Demonstrator in
Subjects of the freihinary intermediate		Chemistry, W. W. Fisher,
		M.A.
		J. E. Marsh, M.A.
Stereo-chemistry, (Fee, £1)		
Soils and Organic Chemistry (Forestry Cour	useg	B. Lambert, B.A.
(Fee £3)		(W. W. Fisher, M.A.
		J. Watts. M.A.
		TE Marsh M.A.
Laboratory Instruction. (Fee, £3 or £5)	•••	A.F. Walden, M.A.
		N. V. Sidgwick, M.A. B. Lambert, B.A.
		J D. H. Nagel, M.A.
Laboratory Instruction: Physical Chemistry	•••	H. B. Hartley, M.A. H. B. Baker, M.A., D. Sc.
" Inorganic Chemistry		L. G Killby, B.A.
" " Quantitative Analysis		T T TT - DE A
" " Quantitative Analysic		(G. B. Cronshaw, M.A.
35 97 35 ³ 7		A. F. Walden, M.A.
		(Dr. Lee's Reader in Chemis-
Inorganic Chemistry (Non-metals)		try, H. B. Baker, M.A. D. Sc.
		(D. Sc.
Organic Chemistry (General Class-reaction	ons)	Martin and All Martin and
(Fee, £1)	•12 •	
Electro-chemistry		T. S. Moore, M.A.
Enecoro-cholinsony		the on College Intons

* Names marked with an asterisk are those of University or College tutors.

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APPENDIX E. JOURNALS.

*Journal of the Chemical Society (London).

*Zeitschrift für physikalische Chemie (Leipsig).

* Leibig's Annalen der Chemie (Leipsig).

* Berichte der Deutschen Chemischen Gesellschaft (Berlin).

* Central Blatt (Berlin).

* Zeitschrift für anorganische) Chemie (Leipsig).

Annales de Chimie et Physique (Paris).

Comptes Rendus (Paris).

Journal of Physical Chemistry (London).

Journal of Chemical Industry (London).

Chemical News (London).

Journal of American Chemical Society.

American Chemical Journal.

Bulletin Société Chemique de Paris.

The Analyst (London).

British Association Reports (London).

Monatshefte für Chemie (Vienna).

BOOKS.

History.-E. Von Meyer.

Thorpe (Essays in Historical Chemistry).

Kopp.

Alembic Reprints.

Inorganic .-- Roscoe and Schorlemmer.

Dammer (Handbuch).

Mendelécff.

Ostwald (Principles of Inorganic Chemistry).

Abeg (Anorganische Chemie).

Physical .--- Vant' Hoff. (Lectures on Physical Chemistry) Trans. Lehfeldt.

Ostwald. (Lehrbuch der Allgemeinen Chemie) (in course of publication).

Nernst (Theoretical Chemistry). -

Ramsay (series of books on Physical Chemistry).

Whetham. Solutions.

Rutherford. Radio-Activity.

Organic.-Beilstein (Handbuch and Supplements), 9 Vols.

Richter (Organic Chemistry).

Meyer and Jacobson (Organic Chemistry), New Edition.

The above are all necessary.

* Journals marked with an asterisk are indispensable.