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R. Henry V. Pickering

# THE SCIENTIFIC WORK

OF THE LATE

# SPENCER PICKERING, F.R.S.

BY

PROF. T. M. LOWRY, F.R.S.

AND

SIR JOHN RUSSELL, F.R.S.

WITH A BIOGRAPHICAL NOTICE BY

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# THE SCIENTIFIC WORK OF THE LATE SPENCER PICKERING.

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## PERCIVAL SPENCER UMFREVILLE PICKERING—1858–1920.

SPENCER PICKERING, who died at the age of 62, on December 5, 1920, after a long illness, was a fine example of the sturdy and independent-minded type of Englishman. Free by the accident of birth to choose his own career, he devoted himself to science, and produced work which, although concerned with various widely different branches, was throughout characterised by a disregard of authority and reliance on his own judgment, based on the results of carefully-planned and well-executed experiments.

He was born in 1858, and was the son of Percival Andree Pickering, Q.C., Recorder of Pontefract, and Anna Maria Wilhelmina Stanhope, granddaughter of Coke, of Norfolk, the celebrated agriculturist, who was created Earl of Leicester in 1837. He felt much pride in his descent, and made elaborate inquiries into the history of the various branches of his ancestry. Both his father and mother were representatives of distinguished and ancient families, concerning which his surviving younger sister Wilhelmina (Mrs. A. W. W. Stirling) has written several fascinating volumes. He was educated at [illegible], and entered Balliol on January 19, 1877, where he remained until the Lent term 1880. He became Brackenbury Natural Science scholar, and took the Final Honours in Natural Science in 1879. Even as a school boy he had been devoted to chemistry, and it was whilst experimenting in the laboratory provided for him by his father at his home in Bryanston Square that, as the result of an explosion, his eye received the serious injury which ultimately resulted in its removal. Before he left Oxford he had published several papers in the Journal of the Chemical Society. In the following year he took up the only academic appointment he ever held, becoming Lecturer in Chemistry at Bedford College, a position which he retained until 1887. He continued to work in the private laboratory at Bryanston Square, first pursuing the subjects which had already attracted his attention at Oxford. Gradually he became interested in the problem of the nature of solutions, until the whole of his energy was devoted to the experimental study of this subject. After 1896, probably disappointed at the reception accorded to his views by the scientific world, he ceased to work on these lines. The almost innumerable determinations of density, freezing point, conductivity, etc., involved in this work were carried out single-handed with a high degree of accuracy, and the results were embodied in a long series of more than 70 papers published between 1887 and 1896, in which, in the face of much criticism, he steadfastly maintained the hydrate theory of solutions. From this subject Pickering turned to an entirely different branch of investigation, which he approached with his characteristic disregard for all conventional ideas. How this came about is well told in

an article in *Nature* (19.9.95) on the establishment of the Woburn Experimental Fruit Farm, which is quoted in the preface of "Science and Fruit Growing" (Macmillan & Co., London, 1919), the book in which the Duke of Bedford and he summed up their joint experience of 25 years. "The object of this institution, which, under the above somewhat unpretentious title, has been established by the joint action of the Duke of Bedford and Mr. Spencer Pickering, F.R.S., in order to supply what has hitherto been a great national want, is to provide an experimental station where all matters connected with horticulture, and especially with the culture of hardy fruits, may be investigated both from the scientific and practical point of view.

"The origin of such an enterprise is always a matter of some interest, and it becomes all the more so in after years, when, too often, the details of its conception and evolution are irretrievably lost. In the present instance, we may trace the origin to an accident in a chemical laboratory. It was owing to such an accident some years ago that Mr. Pickering, whose work in physical chemistry is well known, was driven to seek health in a partial existence in the country. Not having the means, however, to procure this in the orthodox manner without abandoning his scientific work, he resorted to the somewhat unusual means of getting air and exercise by becoming an agricultural labourer at Rothamsted. From an agricultural labourer to a small farmer and landowner the steps were not so tedious as is generally the case, and for some years past Mr. Pickering has turned his attention, after the manner of many landowners, to horticulture and practical fructiculture. To anyone of a scientific turn of mind the unsatisfactory basis on which the culture of fruit depends cannot fail to be apparent. Its present condition is little better than that of agriculture some fifty years ago. It rests mainly on the hard-earned and often one-sided experience of practical men, gardeners for the most part, or nurserymen.

"But the pressure of business will rarely allow a nurseryman to indulge in anything approaching to systematic research, and even when he does obtain any important results they are liable to be looked on askance, as being possibly tinctured by mercenary considerations. Moreover, even amongst the highest practical authorities there is hardly a single point in the cultivation of fruit on which unanimity of opinion prevails; indeed, on some of even the most elementary processes there seem to be as many opinions as there are so-called authorities.

"The desirability of having some station where such matters might be patiently investigated, and from which results might issue free from any taint of commercial expediency, was evident to Mr. Pickering, and not having himself the capital or land necessary for such an undertaking, he applied for assistance to a former college friend, the Duke of Bedford. The Dukes of Bedford have during generations past identified themselves with the progress of agriculture

and horticulture, the present holder of the title showing no tendency to be eclipsed by his predecessors in these matters. As was probable, such a scheme met with the hearty approval of the Duke, and the result was the establishment of the present institution, conducted jointly by himself and Mr. Pickering.

"The fruit farm is on the Duke's land near Ridgmont station, and almost adjoins the land which is given up to the use of the Royal Agricultural Society as an experimental agricultural station. About twenty acres have been devoted to the purpose, and of this some fifteen have already been planted."

At the experimental farm all aspects of fruit growing were carefully investigated—nothing being taken for granted—and the results were published in a series of reports, the 17th of which appeared in 1920, and were summarised in the work quoted above.

The fruit farm was admirably planned, and the results of the experiments were in many cases obvious and striking to the eye. The writer well remembers the convincing picture presented by the experimental plots some ten years after their establishment, and there is no doubt that this ocular demonstration was of great value in spreading among fruit growers the new and often startling information derived from the experiments. His association with Harpenden was strengthened by the purchase of a house in 1885, which became his permanent home in 1902, in which year he gave up his London house. Here he found congenial society in the presence of Gilbert, Lawes, Warrington and Lyddeker, and in later years of Hall and Russell. He was a member of the Athenæum, and in 1890 was elected a Fellow of the Royal Society. He married, in 1897, Ethel Wilmot, whom he had thanked in his 1890 paper on 'Solution' as "a little girl who had devoted all her spare time to the laborious calculations involved in the present work." They became inseparable companions in the home and in the walks to which at one time he was devoted. Though austere in manner, Pickering was endowed with a strong infusion of that artistic and romantic temperament which showed itself so markedly in his sisters, one of whom, Evelyn, a distinguished artist, married William de Morgan, whilst the second, Wilhelmina (Mrs. Stirling), is a well-known authoress, to whose works allusion has already been made. This revealed itself throughout his life in his love of music and his taste in art and literature, and found final expression in the romantic instructions for his burial on the Devon coast. He left no children, and placed his private fortune, subject to his widow's life interest, in the hands of the Royal Society for the promotion of research in science.

His views on solution are to be found fully expounded in an article in the Muir-Morley revision of Watt's 'Dictionary of Chemistry' (vol. 4, pp. 492–6), following one by Arrhenius, in which the views of the Van't Hoff school of physical chemistry were expressed. His contention that hydrates exist in solution is now generally accepted, whereas his deduction of the composition of these hydrates from discontinuities in the first or even second differentials

of his curves of densities, etc., which led him to believe in the evidence of highly complex hydrates such as $H_2SO_4$, 5,000 $H_2O$, has never been generally admitted as convincing.

Pickering was not only firmly convinced of the existence and preponderating importance of hydrates in solution, but was also strongly opposed to Arrhenius' theory of electrolytic dissociation, seeking to explain the phenomena on which this theory was based on grounds of residual affinity and increased freedom of motion of the atoms in the molecule.

In the event his views were overwhelmed by the rising flood of physical chemistry, and it was only after a considerable interval that hydration of molecules and ions in aqueous solutions became generally recognised.

Among the many and important results arising from the work at the experimental fruit farm two or three may be selected as being typical of his methods, as well as of intrinsic interest. The first concerns the method of planting fruit trees and was at first received with incredulity and the most hostile criticism. The orthodox method of planting was to spread the roots well out, trimming them when necessary carefully with a knife, and then replacing the soil and making it firm, avoiding as far as possible any injury to the root. The results of the Woburn experiments led to a procedure which was the exact antithesis of this. It was found that even when the roots were huddled into a small hole and the soil rammed tightly round them by the aid of a rammer, regardless of mechanical injury, in the great majority of cases the trees grew better, usually even in the first year after planting—more certainly in the second year. Nearly 1,500 trees were used in these experiments which were extended to a variety of soils and situations throughout the country. So opposed to general practice were the conditions that it was difficult to ensure the proper carrying out of the experiments by independent observers trained in the orthodox methods, but the results clearly showed that, except in very light soils and in the London clay, planting the tree "in gatepost fashion" undoubtedly benefited it.

Of considerable interest are the observations and experiments on the effect of grass on the growth of fruit trees, which were extended to the more general problem of the toxic effect of one crop on another. This work arose from the observation that the growth of the trees of certain of the experimental plots which had been grassed over was seriously affected. This difficult question was investigated in the most careful manner, the various possible factors such as changes in nourishment, aeration, and water supply, temperature, the physical and chemical conditions of the soil, etc., being separately examined, often by extremely ingenious methods. The final result was to establish beyond all reasonable doubt that the deleterious effect which is exerted by a large number of plants on others growing in association with them is due to a toxic substance probably excreted by the roots. There is still some mystery as to the nature of the toxin, for it cannot be detected in the soil in which the grass is grown or in the washings from soil in which grass is growing.

Another subject to which a considerable amount of attention was paid at Woburn was the composition and proper use of insecticides and fungicides. This led Pickering back to the subject of basic salts, which had occupied him in his early days, and he published from 1907–1917 a long series of papers on the basic salts of copper, in which a large number of such compounds, which are present in the mixtures used for spraying plants, were described and an attempt made to represent their constitution by chemical formulæ. The study of insecticides also led to work on emulsification, and he succeeded in obtaining remarkable semi-solid true emulsions, containing as much as 99 per cent. of paraffin oil dispersed in only 1 per cent. of a 1 per cent. solution of soap. He also found that insoluble precipitates, such as the basic sulphates of iron and copper, could replace the soap usually employed as emulsifier, yielding extremely stable emulsions, admirably adapted for use as insecticides or fungicides.

The work at Woburn is generally regarded, in the words of Sir Daniel Hall, "as the most substantial contribution of the last hundred years to the study of fruit tree development." Its importance resides not only in the value of the actual results obtained, striking as these are, but in the example afforded of the strict application of scientific principles to the investigation of horticultural problems.

A. H.

# THE SCIENTIFIC WORK OF THE LATE SPENCER PICKERING.

## Introduction.

Mr. Pickering's work extended over two main fields of investigation—in pure and in applied science. His researches in Agricultural Science are described by Sir John Russell in the second part of this volume; the present section of the volume is therefore limited to a description of his physical and chemical researches, together with a discussion of some of the larger issues raised by these researches.

(*a*) For the purpose of preparing this Memoir I have received two bound volumes of "Scientific Papers":—

(i) Vol. 1, 1878–1889, contains 29 reprints of papers, from the *Journal of the Chemical Society*, the *Philosophical Magazine*, and the *Reports of the British Association*. Excluding one paper, to which Pickering had written only an appendix, the volume includes about 390 pages of text.

(ii) Vol. 2, 1889–1893, contains some 37 reprints covering about 420 pages; these are taken from the same journals, together with reprints of papers from the *Proceedings of the Royal Society*, the *Chemical News*, the *Berichte* of the German Chemical Society, and the *Zeitschrift für physikalische Chemie*.

In addition to these two volumes of reprints, I have received—

(iii) A bundle of reprints representing papers published since 1893. This includes 22 papers published up to 1897 in the *Transactions of the Chemical Society*, the *Berichte* of the German Chemical Society, and the *Philosophical Magazine*, and covering about 260 pages; and a series of 21 papers published in the *Transactions of the Chemical Society* from 1907 onwards, with 2 papers published in the *Proceedings of the Royal Society* in 1917 and 1918, covering about 290 more pages.

(iv) A file of some 36 contributions to the *Chemical News* and to *Nature*, covering a period of 41 years from 1878 to 1919.

Finally, I have obtained permission to copy a paper on "Valency" in the *Archives* of the Chemical Society.

For the loan of these reprints I am indebted to Mrs. Pickering, and to the Librarian of the Rothamstead Experimental Station. If they had not been available, the task of extracting Pickering's work from the scores of heavy bound volumes in which it is contained would have been extremely laborious, and the completion of this Memoir would have become a very difficult problem for any author still actively engaged in research.

(*b*) The Bibliography given below includes the titles of 162 communications as follows :—

*Proceedings of the Royal Society*, 3 memoirs.

*Journal of the Chemical Society*, 55 papers published in full in the *Transactions*, in addition to a contribution of two pages to a paper by W. H. Perkin, senr., 11 abstracts or preliminary notes published in the *Proceedings* and not corresponding precisely with the titles of papers in the *Transactions*, 1 paper preserved in the Archives of the Society, and 1 obituary notice.

*Philosophical Magazine*, 25 papers, including one note commenting on a paper by another author and immediately following the text of that paper. Many of these papers are also noted in the *Proceedings of the Physical Society of London.*

*British Association Reports*, 1 report.

*Transactions of the Faraday Society*, 1 note contributed to a Discussion on "Hydrates in Solution."

*Berichte der Deutschen Chemischen Gesellschaft*, 20 papers.

*Zeitschrift für physikalische Chemie*, 1 paper.

*Chemical News*, 31 articles, letters and notes.

*Nature*, 11 articles, letters and notes.

Pickering also wrote in 1908 the obituary notice of Robert Warington (1838–1907) in the *Transactions of the Chemical Society* (vol. 93, pp. 2258–69).

Throughout the whole period of his active work Pickering continued to publish his most important researches in the *Transactions of the Chemical Society*. Less important communications were made in the form of articles contributed, or of letters sent, to the *Chemical News ;* but from about 1890 these minor communications were usually sent to *Nature*. During the decade from 1886 to 1895 a series of 25 papers was published in the *Philosophical Magazine*, but this series was interrupted when Pickering turned over from pure science to agriculture, and was not resumed again. The five years from 1890 to 1894 were also marked by the publication of a similar series of 21 papers in German, mainly in the *Berichte* of the Chemical Society of Berlin.

(*c*) The titles of the papers indicate the various scientific appointments held by their author. From 1878 to 1880 he appears as "Brackenbury Scholar of Balliol College, Oxford." One paper, dated August, 1881, refers to him in the dual rôle of "Assistant Master at Highgate School," and "Lecturer in Chemistry at the Bedford College." The next few papers describe him under the latter title only, but in January, 1886, this is changed to "Professor of Chemistry at Bedford College." This title disappears after 1887, when he appears as M.A., F.R.S., with no other professional description.

T. M. L.

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# PART I.—CHEMISTRY AND PHYSICS.

## CHAPTER I.

### SCOPE OF THE WORK.

Although Pickering is best known as a physical chemist of a very independent type, his earliest work, covering a period of about five years from 1878 to 1883, was in the field of inorganic chemistry, dealing with subjects such as the action of sulphuric acid on copper (1878), of hydrochloric acid on manganese dioxide (1879), and of iodine on sodium thiosulphate (1880). He also wrote papers on the basic sulphates of iron (1880), the sulphides of copper (1881), the oxides of manganese (1881), the sulphates of aluminium (1882), a basic ammonio-copper sulphate (1883), and the basic sulphates of copper (1883). Abstracts of these papers are given on pp. 119 to 123. Attention may also be directed to a very early note on "Ammonium Nitrate" in the *Chemical News* of December 6, 1878 (not recorded as an original paper in the Royal Society's Catalogue), in which he showed that this salt does not melt at 108°, as stated in all the contemporary publications, since when dried at 100° it invariably melted at 165 to 166° C., whether it had been recrystallised from water or from alcohol. Pickering's value for the melting-point was generally accepted for nearly half a century, and is substantially correct for the air-dried salt, which melts at 167°; but when the salt is dried by sealing in an exhausted flask connected with a bulb of phosphoric oxide, so that the powder no longer "cakes" on cooling, the melting-point can be raised to 169·6° C. (Early and Lowry, *J.C.S.*, vol. 115, p. 1387 (1919)).

Whilst, however, Pickering retained throughout his career a special interest in inorganic chemistry, he began at a very early period to develop physical methods of investigation, to supplement the chemical or analytical methods which he had at first employed. Thus in 1884 he published his first thermochemical paper; his first paper on valency appeared in 1885, and his first communication "On the Nature of Solutions" was published in 1886. The latter subject kept him busily occupied for nearly 12 years, from 1886 to 1897, and during this period he carried on a vigorous discussion with his critics at the Chemical Society, at the British Association, and in the pages of the *Philo-*

*sophical Magazine.* It was also during this period of acute controversy that he sent the series of papers to the Chemical Society of Berlin, to which reference has already been made.

A sheet, inserted in his own file of reprints, serves to explain the gap in Pickering's chemical publications during the 10 years from 1897 to 1907. This sheet is an announcement of a series of thirteen reports, dated from 1897 to 1911, by the Duke of Bedford, K.G., F.R.S., and Spencer U. Pickering, M.A., F.R.S. Pickering's work as Director of the Woburn Experimental Fruit Farm, which formed the subject of these reports, is described fully in another section of this volume. It is referred to here, in part as accounting for the sudden cessation of his activity as a physical chemist, but also as an explanation of the type of work which formed the principal subject of his chemical papers when he resumed publication in 1907. Thus an early paper of the new series was on emulsions (1907), which he had studied in connection with their application to fruit-trees. In the same way, a series of some 12 papers on cupric compounds, in the *Transactions of the Chemical Society*, was obviously related to a paper on " Copper Fungicides " which appeared in the *Journal of Agricultural Science* in 1912 ; and the papers on metallo-compounds of cobalt and nickel (1915) and of iron, manganese, lead, etc. (1916), represented a further extension of his work on the fungicidal preparations of iron and copper. A paper on the " Detergent Action of Soap "(1917) was related to the use of soap in the preparation of paraffin emulsions.

Two papers on " Problems Bearing on Residual Affinity " (1917) and on " Flocculation " (1918) appeared in the *Proceedings of the Royal Society* during the later part of the war period, and there were also two post-war contributions to *Nature*. One of these, a letter in the issue of September 4, 1919, recorded that the actual sound of the explosion of a munition dump at Bailleul had been heard at Harpenden ; the other, in the issue of October 23, 1919, drew attention to the influence of the size of the bulb on the readings of a thermometer, of which the temperature is raised or lowered above or below that of the surrounding air by radiation. The bearing of this observation in the problem of protecting orchards from frost belongs to the other section of this Memoir.

## CHAPTER II.

### CHARACTERISTICS OF PICKERING'S WORK.

(*a*) A mere glance at the bibliography is sufficient to reveal one of the most striking characteristics of Pickering's work, namely, its intensely personal character. This bibliography is indeed surely almost unique in the history of modern chemistry in that out of nearly 170 entries there are only half a dozen in which the title includes the names of two authors. The most important of these joint publications are a short experimental paper with Miss Emily Aston (No. 19*a*) in the early group of papers "On Multiple Sulphates," and two highly specialised papers (Nos. 103 and 104) with Dr. Horace Brown on the thermochemistry of mutarotation in sugar solutions and of carbohydrate hydrolysis. A brief note (No. 24*a*) in the *Chemical News* with Miss E. M. Farrer on "Hydration of Salts," and two notes (No. 24*b*) on "The Composition of Hydrated Salts" with P. G. Sandford, complete the series of joint publications.

For Pickering, indeed, research had much more the character of a hobby than of a profession. In particular his keenness for developing a personal skill in manipulation, and then undertaking researches in which this superior skill was essential, is much more characteristic of the enthusiastic English amateur than of the professional chemist or physicist, since the latter is generally only too glad to delegate to others the more laborious part of his work, whilst the former finds a pleasure in his labour, and may even shrink from putting forward data for which he cannot give a direct personal guarantee.

(*b*) Pickering's readiness to undertake the most arduous labour, in order to establish beyond dispute the final results of his work, can perhaps be illustrated best by quoting, from Paper No. 20, his own account of the effort incurred in one of his early thermochemical researches. In this particular case he was anxious to prove, or finally to disprove, the existence of a number of minute sinuosities in the curves showing the influence of temperature on the heat of dissolution of salts, on the heat of hydration of salts, and on the heat of formation of double salts. These sinuosities were not very much larger than the recognised errors of experiment, and a less dogged worker would certainly have dismissed them at once on the ground that they could have no real physical meaning, and must therefore be due to experimental errors of rather larger magnitude than those already known to exist. Pickering, however, was too honest in his outlook, and too little prejudiced by theoretical considerations.

to adopt this easy method of avoiding inconvenient facts. He therefore repeated his observations, and finding that the sinuosities reappeared in much the same form as before, began to think that they must be real, and so went on and on until he had a complete assurance of their reality. The way in which this assurance was reached is described in the following passage (*J.C.S.*, vol. 49, pp. 275 and 290 (1886)) :—

> "It is impossible by a mere description in outline, or by the synoptical view presented by experiments massed together in tables or diagrams, to convey any adequate conception of the strength of this assurance: of how the few experiments which first had exhibited any irregularity were repeated over and over again, after long intervals of time, with different instruments and with different samples; of how often the work, after being laid aside as complete, would slowly assume the appearance of a phantom conjured up by imperfections in the instruments, and of how often, having been begun all over again, such an idea would be dispelled, and conviction in the accuracy of the results enforced with double power. And now, it is only after having fully investigated all the imperfections of thermometers themselves, having obtained some more delicate and more perfect instruments than any yet produced, and having devised a method of using them which obviates the greater part of the experimental error, that I venture to bring the results before this Society" (p. 275).

> "It would indeed have been more satisfactory to have examined a greater variety of salts, and this would have been done had not the work been begun with a different object in view, and had it not progressed a considerable way towards its conclusion before its more important bearings became apparent. It is my hope, however, to extend the work at some future time, though the laborious and trying nature of it may prevent my doing so for some time; no form of apparatus has at present been devised whereby such experiments as these would not suffer in accuracy by being performed at temperatures other than that of the surrounding air, and the absolute dependence of one's work on the atmospheric conditions of a changeable climate, the great waste of time which its changes entail, together with the hardship of working for days together at temperatures but a few degrees above zero, and on other occasions in an atmosphere superheated some 20 or 25° by burning gas, and the constant attention requisite in maintaining these temperatures for a long period of time, render the work of a most laborious and unenviable description." (*Ibid.*, p. 290.)

These two quotations are all the more interesting in view of the fact that this arduous research was largely fruitless, since in a paper published in the following year Pickering felt himself obliged to withdraw unreservedly the conclusions at which he had arrived after so much labour, and to admit that the sinuosities in question had no real existence (see pp. 57 and 129).

It is not necessary to discuss in detail at this stage the evidence which would lead a modern physical chemist to dismiss these sinuosities as "theoretically impossible," since many critics would be quite ready to impose a similar arbitrary veto on the discontinuities in the properties of solutions with changing concentration, which the present writer regards as being established beyond dispute. It would perhaps be more just to say that we regard these sinuosities as impossible largely because Pickering, who thought he had found them, was obliged to admit finally that they did not exist. If his experiments had led to a different result, our theories would long since have been modified in such a way as to "explain" and perhaps even to "predict" these "theoretically impossible" observations.

(*c*) Another feature of Pickering's work, which is too characteristic to be passed over in any complete review of his scientific activity, was his habit of including in his numerical results one or more surplus figures beyond those which he regarded as trustworthy.

This curious mannerism was developed at a very early stage. Thus, in 1879, in the second paper cited in the Royal Society's *Catalogue of Scientific Papers*, we find an analysis of a sample of peroxide of manganese in which two duplicate determinations of the percentage of $MnO_2$, differing by two units in the first decimal, were averaged to three decimals (85·259, 85·039, mean 85·149). In the same way, in Paper No. 10, where the weighings which record the progressive hydration of a precipitate are expressed to six significant figures, the average of results which differ in the integer are given to two decimal places. Again, the basic ammonio-copper sulphate, described in 1883 (Paper No. 11), was said to have given on analysis the numbers CuO 66·946, $SO_3$ 16·987, $NH_3$ 4·561, $H_2O$ 11·506 per cent., as compared with the calculated figures CuO 67·691, $SO_3$ 17·116, $NH_3$ 3·646, $H_2O$ 11·548 per cent. These results are recorded to a larger number of significant figures than the atomic weights which must have been used in calculating them; and results are given to three decimals which appear to be uncertain in the first decimal, since the discrepancy between the found and calculated values in the last four analyses amounted to 0·745, 0·129, 0·915 and 0·042 per cent.

The same curious habit appears again in the early thermochemical papers,

*e.g.*, on the first page of Paper No. 15, where data which cover a range of 246 calories (on a total of 6,000 calories) are averaged, and the result is given to the last unit, *i.e.*, the calculation is carried two significant figures beyond the point at which differences first appear. His temperatures are also given to a thousandth of a degree, but with a probable error of a twentieth, *e.g.*, 22·793° C. ± 0·05°. In such a case as this all the data are given and the reader can see for himself the limits of accuracy that are claimed, or can estimate those that are probable; but Pickering preferred to give the actual average of his numbers, or the direct reading of his thermometer, rather than to replace a meaningless figure by an equally meaningless 0.

A similar relentless logic is seen in Paper No. 23, where an attempt is made to trace the relative influence of the various sources of error in calorimetric work by a mathematical analysis of his own experimental results. On the hypothesis that the recorded measurements, and the observed discrepancies between them, could be treated as exact data for such an analysis, he worked out in hundredths of a calorie the distribution of various types of error which between them had led to discrepancies of 30 to 50 calories. For instance, where one thermometer was employed, the average difference in duplicate experiments was 26·6 cal., on a total of about 7,000 calories, *i.e.*, a deviation of ± 13·3 cal. from the mean value; but with two different thermometers the figures were 41·9 or ± 20·95. By comparing these errors with those obtained under other conditions, he divided them as follows:

| | | |
|---|---|---|
| Error of reading .. .. .. | ± 5·71 | ± 11·42 cal. |
| Error of manipulation .. .. .. | ± 7·59 | ± 9·53 „ |
| | ± 13·3 | ± 20·95 „ |

Errors of 30 to 50 calories were thus analysed to two places of decimals, giving results which can scarcely have had more than a distant relation to the original experiments on which they were based.

In this case again there can be no doubt that Pickering himself was familiar with the limitations of mathematical analysis, but perhaps regarded it as more honest to give his results in the precise form in which he had calculated them rather than to trim off the decimals on the ground that fractions of a calorie can have no experimental significance in measurements of this type.

Pickering's habit of retaining the meaningless figures at the end of his data had the unfortunate effect of conveying to casual readers of his papers the

impression that he was claiming a much greater degree of accuracy than that which was justified either by the precision of the measurements themselves or by the degree of concordance reached in duplicate determinations. The accusation, that Pickering's measurements were untrustworthy because the precision of his data obviously exceeded the possibilities of the methods of measurement then available, was actually made, in a most uncompromising form, by Lunge (*Journ. Soc. Chem. Ind.*, p. 1017 (1890)), in reference to Pickering's *magnum opus* on sulphuric acid. The data in reference to which this accusation was made included a long series of measurements of the densities of aqueous solutions of sulphuric acid over the range from 0 to 100 per cent. These measurements were made with a care and accuracy that have, perhaps, never been excelled; and, after the lapse of nearly 40 years, they are still the best data that are available in reference to this particular property of the solutions. The dilution of the stock solution was carried out with such care that Pickering was able to claim that the *relative* concentrations were subject only to an error of the order of 0·001 per cent. The *absolute* concentrations were only known to 0·01 per cent.; but the chief novelty of the work, and its principal claim to recognition to-day, are to be found in the fact that, instead of relying on the traditional analytical methods for determining the concentration of the stock solution, Pickering attained a new standard of accuracy by employing a physico-chemical method of standardisation. This novel method of standardisation was based upon the process of crystallising out the acid from its concentrated solutions, until its purity was established by the constancy of its physical properties; it did not involve any analytical process, and was even independent of the atomic weights of the relevant elements. In practice, the form of the freezing-point curve was plotted for a series of acids containing a small excess or deficit of $SO_3$, and the concentration of the stock acid was determined by measuring its exact freezing-point. This concentration was checked by titration, but merely in order to show that it was concordant with that deduced by the rougher conventional methods of analysis. This careful and accurate work was criticised by Lunge in the following terms:

> "The enormous amount of his observations, and the seemingly stupendous accuracy of those, indicating *thousandths* of a per cent. of $H_2SO_4$ in the acid, may possibly make them appear more trustworthy than ours to those who have not worked in the same field. But I cannot for one moment acknowledge this conclusion. Hundreds of tests made by myself with the greatest possible care and calibrated vessels and corrected weights, with constant checkings and re-checkings, have proved to me

that estimations of strong sulphuric acid are already *very* good if they do not differ from one another by more than one unit in the first decimal per cent., and that the utmost accuracy attainable, but most certainly not attained by the majority of workers, is $\pm 0{\cdot}05$ per cent. If Prof. Pickering maintains . . . that his percentages are accurate to $\pm 0{\cdot}001$, this *impossible* assumption is to my mind from the outset a reason for distrusting the accuracy of his figures altogether, and I believe that this impression will be conveyed to others as well who take the trouble of looking at the very tottering foundations of that seemingly stupendous accuracy. . . . All his hundreds of observations are founded upon the analysis of a sample of pure sulphuric acid. . . . The fundamental analyses were not made by Prof. Pickering himself, but by Mr. Crompton. . . . *Now these estimations of Mr. Crompton's vary between* 99·704 and 99·962 *per cent., that is, to the amount of* 0·26 *per cent.*, and yet Prof. Pickering does not hesitate to assert that the percentages of two acids . . . are accurately known to the third decimal per cent."

Lunge's attack was unfortunate in that he does not appear to have read the paper against which his criticisms were directed. Thus, whereas he suggests that Pickering claimed an accuracy of 0·001 per cent. in his concentrations, Pickering in his paper had stated in three places that the limit of accuracy was $\pm$ 0·01 per cent. Again, Lunge suggests that Pickering's data were based on Crompton's titrations, whereas the main feature of the work was the use of a physical method of analysis which gave a degree of concordance at least five times better than that which Lunge stated to be the best that could be attained by chemical analysis, even in the hands of a highly skilled worker. Pickering protested against this gross misrepresentation of his work, and justified the strength of his protest by saying (Paper No. 65*a*) that "there is certainly much excuse for irritation when one finds a critic condemning a most laborious piece of work on the grounds that the very thing had been done which one had taken the greatest pains to point out to readers had not been done." Lunge replied to Pickering's protests, but in his further letter to the *Chemical News* Pickering complained that "Prof. Lunge seems fated to misrepresent me, for even in his communication to your journal he states that the method adopted by me for ascertaining the strength of the acid was 'founded upon the hypothetical basis that the pure (acid) must have the lowest freezing-point.' This would, indeed, be an hypothetical basis! What my method was founded on was that a pure substance has a *higher* freezing-point than an impure one, and this statement is based, not upon hypothesis, but upon fact. Out of the

many thousands of cases which have been investigated, there are only one or two in which the addition of impurity has been found to raise the freezing-point of a liquid, and the nature of the results with sulphuric acid can leave no doubt but that this substance does not form another instance of such abnormal behaviour."

Although Lunge's criticisms were wholly unfounded, they were typical of the impression made upon many other readers by Pickering's practice of retaining all the significant figures that were given by his experimental readings, without adopting the usual process of pruning away those figures on which no reliance could be placed. In practice, this unconventional method of presenting the results of his work had the disadvantage that the data given in Pickering's papers could not be quoted with safety apart from a careful study of the original text, since it was not possible by a casual glance at the tables to distinguish between those figures which were trustworthy and those which had no real meaning. It also had the indirect effect of depriving a worker, whose supreme passion was for accurate measurement, of much of that reputation for exact experiment to which his careful, precise and pertinacious work entitled him.

In this connection a personal reminiscence may perhaps be permitted. The writer of this Memoir recalls, with an impression that is still vivid, his first contact with this particular aspect of Pickering's work. In collaboration with Mr. W. R. Bousfield he had been engaged for many months in determining the densities of aqueous solutions of sodium hydroxide, from 0 to 50 per cent. NaOH, in the hope of being able to assign valid numbers to the fourth decimal in the densities. The method of working depended on weighing out, with special precautions to avoid oxidation, 150 grams of metallic sodium at a time, and converting the whole of it quantitatively to sodium hydroxide by a series of carefully devised operations. After a large number of concordant data had been obtained, we discovered in a " Dictionary of Chemistry " a series of data quoted from one of Mr. Pickering's papers, in which the densities were given to six places of decimals, but differed from our own in the third decimal. Only one conclusion seemed possible, namely, that, in spite of the great care that we had taken, we had only reached a beggarly accuracy of 1 part in 1,500, instead of 1 part in 15,000, as we had hoped. It was with mingled feelings that we discovered, on looking up the text of Pickering's original paper, that the strength of his stock solutions had been determined by titration against a standard acid, by a method much inferior to our own, so that an error in the third decimal could easily occur, and an error in the fourth decimal was absolutely unavoidable. After this disconcerting experience it was perhaps natural to associate

Pickering's name with the citation to six decimals of data which were incorrect in the third decimal; but for this citation no blame could be attached to Mr. Pickering, who was concerned only with the *relative* densities of solutions of different concentrations, and not with the *absolute* values of the densities or concentrations, and who had made use of methods which were entirely suitable to the work in which he was engaged. On the other hand, it was an unfortunate error of judgment which led to the citation, in a standard work of reference, of Pickering's table of relative densities as absolute values, to a degree of accuracy far beyond anything that was justified by the methods of standardisation that had been used, or could have been used, when the measurements were made.

As a further illustration of the lurid possibilities of misapplied mathematics, it is of interest to notice that, prior to 1883, *i.e.*, 10 years before the publication of Pickering's table, the generally accepted tables of physical constants gave the densities of aqueous solutions of sodium hydroxide, from 40 to 50 per cent. NaOH, to *four* places of decimals, on the basis of measurements made at the beginning of the century by Dalton to *two* places of decimals only.* The remarkable performance of adding two additional decimals to Dalton's densities, without the assistance of a single new experiment, was accomplished in two stages: (i) The existing data of Dalton (1810) and of Tünnermann (1827) were used by Schiff in 1858 in order to deduce an interpolation formula, with the help of which it was proposed to calculate, by extrapolation to 100 per cent. NaOH, a theoretical value for the density of liquid sodium hydroxide at atmospheric temperatures; (ii) the formula of Schiff was used by Gerlach in 1867 in order to calculate the densities for each exact per cent. of $Na_2O$ and NaOH. These interpolated densities were worked out to four decimals and the source from which the data were derived was so far forgotten that the validity of the two fictitious decimals does not appear to have been questioned.

A revision of this series of densities was attempted by Hagen in 1883, but his list of densities is even less accurate than the table of Gerlach which it was intended to replace, and data given to four places of decimals are still found to be incorrect in the second decimal. The table of densities which Pickering published in 1893, although only based upon a titration of the stock solution, was therefore a real advance on all those that had preceded it, since it was

* From 0 to 40 per cent. a series of measurements made by Tünnermann in 1827 was available. These were given to four decimals, and the citation of a fourth decimal in the interpolated values over this range of concentrations was therefore legitimate; but the measurements were, in fact, no more accurate than Dalton's, since they contained errors in the second decimal place, where Dalton's data are usually correct, and the last figure at least must have been entirely fictitious.

only in the case of the strongest solutions that the third decimal was incorrect, whereas all previous tables had contained errors in the second decimal. It may be regretted that Pickering did not apply in this case the method, which had proved so successful in his determinations of the density of sulphuric acid, of freezing out a hydrate of definite composition and using this in the preparation of his solutions. If this had been done, the data would probably have been exact up to the limit of accuracy of the relevant atomic weights, and a comparison with the results afterwards obtained by weighing out large masses of metallic sodium, where the atomic weights are again a limiting factor, would have been of great interest and value.

## CHAPTER III.

### Methods and Principles of Thermochemistry.

Pickering's first calorimetric work arose out of his study of the simple, double and basic sulphates, which he had selected as suitable compounds on which to investigate the properties of molecular compounds in general and of basic and double salts in particular. His general conclusions from this work were summarised in his paper on "Atomic Valency" (R.S. 17); but already a year earlier, in December, 1884, a paper (R.S. 13) was published, in which heats of dissolution were used as a test for the existence of different modifications of sodium sulphate.

(*a*) *Thermometers and Calorimeters.*—Pickering's work on thermochemistry, which forms the subject of the second half of his first volume of reprints, as well as of the first few papers of the second volume, includes six papers on calorimetric apparatus and thermometers. Three of these, R.S. 22, 23 and 24, were published in the *Philosophical Magazine* in March and April, 1886, followed by two more (R.S. 32 and 33) in May, 1887, and by another pair of papers (R.S. 52 and 53) in March, 1890.

It was unfortunate that Pickering's calorimetric work preceded the experiments of Callendar and Griffiths on platinum thermometry. In the absence of these more easily-controlled devices for measuring temperature, Pickering could only make use of mercurial thermometers. Some of the limitations of these instruments were already familiar, and the technique of calibration had been worked out in detail. But in seeking to secure a maximum of accuracy in his measurements, Pickering developed his instruments to the extreme limit of practical manipulation, and so stirred into intense activity a long series of latent sources of error. There can be little doubt that the origin of many of the unsuspected errors which Pickering found so troublesome may be looked for in the inherent vices of the mercurial thermometer, and that later workers may indeed be grateful for being delivered from the necessity of using so treacherous a device.

The "Delicate Calorimetric Thermometers" described in these papers were huge instruments, *e.g.*, 746 mm. long, with a graduated scale of 565 mm., covering only 3·4° C., giving a range of 166 mm. per degree. Such an instrument could be read to one-twentieth of the millimetre scale divisions, *i.e.*, to 0·0003° C. An interesting point noted by Pickering is that "besides practice,

and uniformity in the lines themselves, nothing conduces so much to accuracy in estimation as a just proportion between the breadth of the mercurial column and the distance between the divisions. I find the best proportion to be 1 : 10 ; 1 : 15 is too great and 1 : 5 too small. Different ratios, however, might suit different observers" (footnote, p. 327). These large, and perhaps oversensitive, thermometers proved to be troublesome instruments to use, and Pickering himself raised the question "whether we have not pushed thermometric delicacy beyond the limits compatible with accuracy" (p. 338). For instance, "As is well known, the bulb of a thermometer does not expand regularly when heated. . . . To obtain a state of equilibrium the thermometer must be tapped on the top with the finger, or some such means adopted to overcome the inertia of the bulb before each reading. The larger the bulb and the finer the bore of the tube, the more apparent does this inertia become : with instruments such as the less delicate ones here mentioned a dozen or less taps are sufficient to overcome it, but with No. 62839 it was found that continuous tapping for two or three minutes was absolutely necessary. The extent to which error from this source may accumulate may be drawn from the fact that this instrument, when the mercury is *rising* to the temperature of the bath in which it is placed, will register 6 mm. lower than when *falling* to the same temperature, however long it be left in the bath, if it be not tapped" (pp. 332-33).

A much more serious source of error was described as follows : "Now, besides the inertia of the bulb, which may be overcome by a sufficient amount of tapping, there appears to be another and more serious imperfection, due to what may be termed a permanent alteration in size, as opposed to the other, which may be called temporary, and one which no amount of tapping will overcome. It would seem that the bulb of this, and every thermometer, has two different shapes, one when the column is rising, the other when it is falling" (p. 333). Thus these very delicate thermometers gave different readings for a bath of liquid at constant temperature, according as the thermometer rose or fell to this temperature.

This difference, which amounted in some cases to nearly 1 mm. of the scale, was at first attributed to direct variations in the size of the bulb, but this was disproved in a further paper (R.S. 32) "On Delicate Thermometers." In this investigation different bulbs were sealed on to the same stem, and it was found that a progressive reduction in the size of the bulb was accompanied by an exaggeration of this source of error until, finally, "no accurate measure could be made," because "the column of mercury in

the tube kept breaking off when the instrument was tapped" (p. 403). A suggestion of Lord Rayleigh (p. 401) "that these differences should be attributed to the capillarity of the tubes acting on the expansibility of the bulbs, and not to the action of the bulbs only," was disproved by experiments which showed that the magnitude of the effect did not even run parallel with the much more minute variations in the diameter of the bore.

Finally, it was evident "that the cause of these differences in the readings did not lie in the bulbs of the instruments, but in the stems, that each time the instrument was opened, and air admitted into the stem, the defect was increased, till the tube eventually became entirely ruined. The moisture and gases present in the air, no doubt, affect the glass and adhere so strongly to it that the heating to which the stem is subjected is quite incapable of removing it, and the interior of the tube remains coated with an elastic covering, which destroys the working capabilities of the instrument" (p. 403).

> "To settle this question, and to ascertain whether it was possible to make instruments of such delicacy entirely free from this defect, two other thermometers were manufactured, Nos. '08 and '61. The delicacy of these was somewhat less than in the former instruments, owing to the impossibility of procuring sufficiently fine tubes; the size of the bulbs, however, was increased, that of '61 containing as much as 46 grams of mercury. An estimation-figure, 0·05, represented about 0·0005° C. On examining these instruments, in the same manner as previously, it was found that they worked perfectly, the mercury registering exactly the same temperature whether the column had risen or fallen to the point of rest, equally satisfactory results being obtained whatever portion of the stem was examined. Instruments of this excessive delicacy are therefore perfectly workable; it is, however, only by observing the utmost precaution in making them that success can be obtained. The tube must on no account be opened till the last minute, when the bulb is finished and ready to be attached without a moment's delay; the bulb, as soon as it is attached, must be warmed so as to fill the tube with mercury and prevent the access of air through the upper end. If any failure occurs in the attachment of the bulb at the first trial, the stem must be rejected; a second attempt would be attended with the same results as putting on a second bulb after the instrument had been made up. When once the stem is filled with mercury, the tube may apparently be opened several times at the top without damage being done, and the bulb itself may be made 24 hours

before it is attached to the stem without being injured by exposure to air for that time" (p. 405).

"It is a common practice of thermometer-makers to examine the bore of a tube before it is made into a thermometer by passing a thread of mercury along it, and often, indeed, the stems are divided and fully calibrated before the bulb is attached and the tube closed. From what has been ascertained as to the effect of the air on the interior of the tube, it is obvious that a tube which has been treated in such a manner will be utterly useless for any really delicate instrument" (p. 405).

In a third thermometric paper, No. 53, "On the Effect of Pressure on Thermometer Bulbs," it was shown that the action of the bulb under pressure was often not regular, *i.e.*, the rise of the meniscus was not proportional to the external pressure. This effect, and the irregularities in it (which were regarded as indications of faultiness in the instrument), were found to be greater in thermometers with blown bulbs than in those made from cylindrical glass. Pickering concludes that "Although it seems probable, *prima facie*, that a blown bulb, however well constructed, would not be so uniform as a cylinder bulb, these facts of course do not prove that such is necessarily the case, as the thickness of the walls of the bulbs was not known; but it does prove that, by ordering a thermometer with a cylinder bulb, we should in all probability get an instrument possessing nearly twice the strength of one with a blown bulb" (p. 409).

"I may mention one source of error in thermometric work which attains considerable dimensions when dealing with tubes of very fine bore. These tubes, even when of the most perfect description obtainable, generally possess a few points at which the mercury column experiences a difficulty in passing: the mercury, when it has reached such a point, sticks there an appreciable time, and then passes it suddenly with a jerk; sometimes, even, the mercury sticks so persistently that the column will separate sooner than pass it. These points do not indicate any contraction which is sufficient to affect the results of calibration, and are probably due to some difference in the nature of the glass, for they may be developed by heating the thermometer tube externally with a very small flame up to about 400°. The error of taking a reading while the mercury is sticking at such a point may, I estimate, amount sometimes to as much as 0·5 mm. All delicate thermometers should be carefully examined in

order to ascertain the position of such points, and they should be avoided, if possible, in any work with the instrument" (p. 411).

It is of interest to notice that Pickering was not alone in his experience of the extreme difficulty of controlling a hypersensitive mercurial thermometer. The freezing-point determinations of H. C. Jones, which are referred to below (p. 35), were made with an even more sensitive thermometer.

> "Mr. Jones states that his thermometer could be read with certainty to 0·0001°, and that the greatest difference ever noticed between duplicates was 0·0004° . . . ; but the average error is, undoubtedly, much larger . . . ; putting all the estimates together, one must conclude that the mean error cannot be much less than 0·001°."
>
> "Mr. Jones's determinations were made on a scale six or seven times larger than mine, and his thermometer, comparing the values of equal lengths of scale, was three times more delicate than mine, and it is instructive, as far as thermometry is concerned, to note that this increase of delicacy does not seem to have produced any appreciable increase in the accuracy of the results, . . . for the mean error of '10 of my series of determinations . . . gave 0·00103°, a value practically identical with the error above mentioned" (*J.C.S.*, vol. 65, pp. 295, 296, 297 (1894)).

Pickering was able to show that the wavy freezing-point curves, which Jones had obtained for solutions of alcohol and of urea in water, where Pickering, Raoult and Loomis had obtained smooth curves, were "just what Mr. Jones might have obtained had he forgotten to calibrate his thermometer, or if he had trusted to the rough calibration sometimes performed by the maker before the instrument is completed" (p. 303). The conclusion, that the waviness of Jones's curves had its origin in thermometric errors, was established by a detailed comparison with other data; but when similar corrections were applied to his curves for dilute sulphuric acid, the effect was to develop even more clearly the "breaks" already recorded by Pickering in these solutions.

Pickering invented in 1886 (R.S. 20, p. 264) an adjustable thermometer, with an auxiliary reservoir at the top of the stem, into which some of the mercury could be transferred when it was desired to use the instrument over a range of temperatures above that for which it was normally adopted.

> "In any thermochemical work in which the effect of temperature on a given reaction is being studied, many of the sources of error inherent in the use of thermometers may be avoided by using the same portion of the stem of the instrument, whatever the actual temperature may be.

To effect this, the zero-point is altered in each experiment by removing some of the mercury into the upper chamber of the thermometer. Formerly I removed the requisite amount of mercury by the application of a very small flame to a point just below this chamber; but I now adopt a method which is much safer, more expeditious, and equally exact. A fine tube, somewhat wider than the stem of the thermometer, is affixed to the upper end of the stem, and in this tube there is a small contraction or 'knife-edge,' sufficiently wide to permit of the mercury passing it either upwards or downwards, but yet so narrow that a slight shaving of the instrument will cause the column of mercury to break off at it, that portion of the mercury which is above the knife-edge passing up into the upper chamber. By this means any point on the stem may be adjusted with ease to within 0·02° of any given temperature" (R.S. 32, p. 411).

Thermometers of this type are now used extensively for measuring small differences of temperature, as in determining molecular weights from the rise of the boiling-point or fall of the freezing-point of a solution. They are generally known as "Beckmann thermometers," but the device which they embody is clearly due to Pickering, who described it in 1886, whereas Beckmann's paper in the *Zeitschrift für physikalische Chemie* (vol. 2, p. 644 (1888)) did not appear until two years later. In a paper published in 1886 (No. 20, p. 264) Pickering mentions that Crafts had used a similar device, but no reference is given, and I have not been able to trace any prior publication of this useful invention.

The "New Form of Mixing Calorimeter," which Pickering described in Paper No. 52, consisted of an oblong platinum vessel (14 by 8 by 10 cm. deep), with a frame in the middle, against which small folding doors closed, dividing the vessel into two equal compartments.

"The stirring apparatus . . . consists of a fan-screw with three blades revolving at the bottom of the liquid, and worked by means of an electro-motor. This apparatus was doubled, so that each half of the mixing calorimeter should have a separate stirrer, and in each half also one of the most delicate thermometers is suspended, these being tapped continuously on the upper end by a clockwork-tapper."

"In working this calorimeter it is first of all put in position with the doors closed, and the thermometers and stirrers in their places. The two liquids are then measured or weighed out from flasks into the two compartments, the temperature of each being slightly below that selected for the initial temperature of the experiment. The stirrers and tappers are then

started, and the temperature of two liquids raised to the required temperature by touching the outside of the calorimeter with some heated object. The temperatures of the two liquids are in this way easily and quickly brought to within 0·02° of each other."

"The rate of cooling is then determined . . . ; after which the doors of the calorimeter are opened without stopping the stirrers; the thermometers are again read, and the readings repeated at intervals of one minute, as before, in order to determine the correction for cooling at the final temperature" (p. 249).

The calorimeter failed with dense salt solutions, which required in extreme cases up to 30 minutes to mix completely with water, and these were therefore investigated by the methods used to determine the heat of dissolution of solids.

(*b*) *Heat of Dissolution.*—Pickering's first big calorimetric paper, on "The Influence of Temperature on the Heat of Chemical Combination" (R.S. 20) raises in an acute form the most controversial aspects of his work and methods. We have seen that almost from the beginning he had a peculiar passion for the appearance as well as for the reality of minute exactness. Thus, on the experimental side, we have seen him developing his technique until he could obtain a close concordance in his duplicate determinations; but, coupled with this, we have seen him unable to resist the temptation to work out calculations in reference to his errors to a hundredth of a calorie, where the errors themselves were of the order of 10 calories, even when no exceptional discrepancies were present.

We now see him firmly convinced that physical and physico-chemical properties, such as the specific heat of a salt or its heat of dissolution in water, instead of varying in a regular manner with the temperature, *e.g.*, according to some simple linear or parabolic law, vary in a curiously erratic way, exhibiting perhaps three maxima and two minima within a range of some 20°. Where a less conscientious worker would have assumed that a ripple on his experimental curve was the result of a mere temporary intrusion of some known error, Pickering insisted on repeating the experiment over and over again, with new refinements; and when these failed to smooth out the curve, he found himself compelled to admit the real existence of the local hummock. The problem of discontinuity opens up, however, a very wide field for discussion, and a full consideration of this difficult problem must be postponed to a separate section of this report (p. 57).

(*c*) *Heat of Neutralisation.*—Pickering's work "On the Thermal Phenomena of Neutralisation" (R.S. 31) was frankly controversial. It provides one of the earliest examples of the clash of opinions as to the nature of the process of

solution, which resulted from the total incompatibility of Pickering's views on the formation of hydrates in aqueous salt solutions with Arrhenius's theory of electrolytic dissociation in the somewhat crude form in which it was broadcast by its more dogmatic supporters.

The paper cited above was in the first instance a reply to Nicol (*Chem. News*, vol. 54, 53-192; *J.C.S.*, vol. 51, 396 (1887), etc.), who had asserted that "the thermal phenomena attending the heat of neutralisation of acids with alkalies" were of such a character as to "prove his views as to the dissolution of a salt being a physical and not a chemical action." As a final conclusion from his study of the heat of neutralisation, Pickering asserted "that the dissolution of a salt in water is a chemical and not a physical action" (p. 601).

The facts derived from Thomsen's thermochemical experiments were not in dispute, namely that an aqueous hydroxide, when neutralised by an aqueous acid, usually, gives rise to a liberation of 13,800 calories for each molecule of water formed:

$$MOH + HA = MA + H_2O + 13{,}800 \text{ calories.}$$

Some acids, *e.g.*, $H_2SO_4$ (15,580 calories) and $(HF)_x$ (16,270 calories) gave higher values, and others gave lower figures; but even insoluble hydroxides gave the same heats of neutralisation when dissolved in hydrochloric acid and in nitric acid; and the heat of neutralisation by sulphuric acid was always 1,750 calories higher, precisely as in the case of the soluble hydroxides. The followers of Arrhenius explained the constant value of 13,800 calories as being the heat of neutralisation of a hydrogen ion by a hydroxyl ion

$$\overset{+}{H} + \overset{-}{O}H = H_2O + 13{,}800 \text{ calories,}$$

the other two radicals being supposed to be in the same condition of dissociation both before and after neutralisation, *e.g.*,

$$\overset{+}{K} + \overset{-}{O}H + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{K} + \overset{-}{Cl} + H_2O + 13{,}800 \text{ calories.}$$

The "abnormal" heats of neutralisation were then ascribed to incomplete dissociation of the acid or base, giving rise to a larger evolution of heat if the dissociation were exothermic, and to a smaller evolution of heat if the dissociation were endothermic. Alternatively, incomplete neutralisation might give rise to low values, when the salt formed was partially hydrolysed in solution. Pickering had no difficulty in accepting the view that the abnormally low heats of neutralisation observed in the case of certain weak acids might be due to the formation of "salts which are more or less dissociated in solution"

(p. 599), and in a later paper (R.S. 41, p. 323) he expresses the same conclusion in other words, as follows :—" Those cases where the values are abnormally low present no great difficulties, for they are confined chiefly to weak acids where the salts are partially dissociated and neutralisation is, therefore, not complete." In the present paper, however, he disputes the correctness of the main proposition that the constant heat of neutralisation of strong acids and bases is due to electrolytic dissociation, and seeks to show that the results can be explained by ordinary chemical rules, without making use of Arrhenius's theory. He shows that the constant heat of neutralisation can be reduced to a statement of the facts that " there is a constant difference between two metals, independent of the negative radicle with which they are combined, and there is a constant numerical difference between any two negative radicles, independent of the metal with which they are combined, *provided*, always, the compounds are in presence of excess of water " (p. 595).

Pickering concludes that " the fact that a large number of acids give the same heat of neutralisation with bases " can be explained by the theory of *residual affinity* which had been developed independently by himself and by certain other workers (especially Armstrong), but only on the assumption that the hydration of the salt in solution depends on the residual affinity of *one* of the radicals only. The limitation of residual affinity to one radical was not supported by any experimental evidence, and has not been accepted by later workers. Moreover, although Pickering found it easy to explain by means of his theory both the normal heats of neutralisation and the exceptionally high heats of neutralisation of certain acids, this explanation was withdrawn in a subsequent paper " On the Heat of Neutralisation of Sulphuric Acid " (R.S. 41) on the ground that " the heat of neutralisation of these acids is *not* abnormally high," since they gave normal values for the heat of neutralisation when greater dilutions were employed.

For this purpose Pickering calculated the heats of neutralisation at *infinite dilution.* " Any constancy observed in the heat of neutralisation is dependent, as I have shown, on the saturation of the residual affinity of the molecules concerned by the water present, and, hence, this water must be present in large excess, and should, theoretically, be infinite in quantity " (p. 324).

The heats of neutralisation of the three mineral acids by sodium hydroxide when both were diluted with 100 $H_2O$ per equivalent were as follows :—

| | |
|---|---|
| HCl | = 13,740 cal. |
| $HNO_3$ | = 13,680 cal. |
| $\frac{1}{2}H_2SO_4$ | = 15,690 cal. |

With hydrochloric acid the water present was sufficient to complete for all practical purposes the thermal effects of dilution, but this was by no means the case with sulphuric acid. Extrapolation to infinite dilution (with the help of the measured heats of dilution of the acid, base and salt) gave the following values:

$$\begin{aligned} HCl &= 13{,}708 \text{ cal.} \\ HNO_3 &= 13{,}134 \text{ cal.} \\ \tfrac{1}{2}H_2SO_4 &\begin{cases} = 15{,}238 \text{ cal. (Thomsen).} \\ = 14{,}098 \text{ cal. (Pickering).} \end{cases} \end{aligned}$$

The difference between Thomsen's extrapolated values and those given by Pickering was due to the fact that "there is a sudden change in the direction of the curve at about 0·3 per cent., and as Thomsen's last determination was made with a 0·67 per cent. solution, his results cannot take this change into account; had I deduced the correction from my own experiments, taking only the same points as Thomsen took, I should have got 29,825 cal. for $N_\infty$, a value still 2,200 cal. above that of hydrochloric acid" (p. 325).

Pickering concludes: "There can be little doubt but that the heat of neutralisation of sulphuric acid, and probably also that of selenic, hypophosphorous and hydrofluoric acids,* is normal, under perfect conditions. . . . Under these perfect and unattainable conditions, the value would be constant only because we should be measuring the *same* quantity in every case, namely, the difference between (*a*) the heat of combination of H with (OH) and the union of the water molecules with each other, and (*b*) the heat of combination of M with (OH) and the union of the hydroxide formed with excess of water, which latter quantity is the same whatever metal M may be, for it represents in each case the perfect satisfaction of the affinity of the same radical—hydroxyl."

It is not clear whether the break at 0·3 per cent. solution is real (this point will arise again in connection with Paper No. 49), but it is interesting to notice—

(i) That Pickering's evidence that abnormally high heats of neutralisation are fictitious, arising from the use of insufficiently dilute solutions, is also in complete harmony with the theory of electrolytic dissociation.

(ii) That according to the theory of electrolytic dissociation, the ions of sulphuric acid, being a dibasic acid, should dissociate in two stages, and that the second stage of electrolytic dissociation should require more dilution than in the case of a strong non-basic acid. This paper can therefore be regarded

* There are no data for calculating the corrections in these cases.

as an experimental vindication of Arrhenius's theory, in at least the same degree as it supports the alternative view (p. 326) that the heat of combination of a hydroxide with water is independent of the metal because " it represents in each case the perfect satisfaction of the affinity of the same radical—hydroxyl "(see *J.C.S.*, vol. 53, p. 878 (1888) ).

Pickering's controversy with Nicol led to an interesting investigation on " The Heat of Dissolution of Substances in Different Liquids " (R.S. 36).

It must be remembered that the " physical " theory of solution was supposed to require the absence of all combination between solvent and solute, so that the solvent could not affect the heat of dissolution. Pickering's explanation of the constant value of the heat of neutralisation had led him to a very similar conclusion. Thus, "According to my explanation of the heat of neutralisation, the residual affinity of one of the radicles composing any salt molecule becomes entirely saturated when it is dissolved in excess of water, and it appeared probable at first sight that, since the amount of residual affinity is independent of the nature of the solvent, the heat of dissolution of a salt must be the same whatever the solvent be" (p. 871).

Experimental determinations of the heat of dissolution of 15 salts in alcohol and water showed that, although the general order to magnitude of these heats was similar for the two solvents, the actual numbers differed widely, so that Pickering's theory needed modification, just as did the theory discussed by Dr. Nicol. A further investigation of the heats of dissolution of three elements, iodine, bromine and sulphur, where no question of electrolytic dissociation could arise, showed the same wide variation between the values in different solvents, as set out in the following tables :—

| *Iodine.* | | *Bromine.* | |
|---|---|---|---|
| Benzene .. .. .. | — 3,057 cal. | Water .. .. .. | — 754 cal. |
| Chloroform .. .. | — 3,007 „ | Chloroform .. .. | — 323 „ |
| Carbon tetrachloride .. | — 2,891 „ | Carbon tetrachloride .. | — 265 „ |
| Carbon disulphide .. .. | — 2,504 „ | Carbon disulphide .. | — 7 „ |
| Ammonium chloride sol. .. | — 1,538 „ | Water (Thomsen) .. | + 539 „ |
| Alcohol .. .. .. | — 857 „ | Potassium bromide sol. | +1,090 „ |
| Ether .. .. .. | — 768 „ | | |
| Potassium iodide sol. .. | — 546 „ | | |

*Sulphur.*

| | |
|---|---|
| Water .. .. .. .. .. | —1,499 cal. |
| Chloroform .. .. .. .. | — 697 „ |
| Benzene.. .. .. .. .. | — 690 „ |
| Carbon tetrachloride .. .. .. | — 624 „ |
| Carbon disulphide .. .. .. | — 469 „ |

Pickering, however, regarded the results as "strongly in favour of the conclusion that the heat of dissolution of an elementary body in a solvent of simple constitution is a constant quantity, as must be the case if the heat evolved is due to the complete saturation of residual affinity" (p. 878).

It is difficult to see the experimental justification for this view, and at the present time no chemist would feel it necessary to admit that the residual affinity of an element or compound must have a fixed thermal value. Expressed in physical language, this conception represents every substance as lying at an energy-level situated at a fixed distance above that of complete saturation. There is, however, no evidence for the existence of a fixed level of complete saturation, since the energy set free by a given substance in the process of chemical combination also depends on the other partner in the process, and varies with the character and tastes of that partner in a way that precludes the idea of a fixed reserve of residual affinity in any element or compound.

(*d*) *Thermochemistry of Mutarotation and of Hydrolysis.*—In conclusion, attention may be directed to Pickering's collaboration with H. T. Brown in a thermochemical investigation of the mutarotation of the sugars and of the hydrolysis of starch and cane-sugar (Papers 103 and 104).

(i) *Mutarotation.*—The thermal changes recorded were as follows :—

| Sugar (anhydrous). | Specific rotatory power as $[\alpha]_D$. | | Concurrent thermal change. | |
|---|---|---|---|---|
| | Unstable $\alpha$. | Stable $\beta$. | Per gram. | Per gram-molecule. |
| | ° | ° | Cal. | Cal. |
| Dextrose | 107·0 | 52·5 | + 0·588 | + 106 |
| Maltose | 117·5 | 138·0 | 0 | 0 |
| Levulose | ? | — 92·0 | — 4·64 | — 835 |
| Milk-sugar | 88·9 | 55·2 | + 0·19 | + 34 |

The authors adopt "the hypothesis that multirotation is intimately connected with the formation of an aldehydrol in contact with water" (p. 773). "It is, of course, open to explain the change in the optical properties of their solutions in another way, by supposing them to be correlated with intramolecular transpositions which produce a change of sign in the asymmetric carbon atoms. A remarkable series of such intramolecular changes has been brought about in some of the sugars by Lobry de Bruyn (*Rec. Trav. Chim.*, vol. 14, p. 203 (1895)) by acting on their solutions with large quantities of alkali at the ordinary temperature, or by heating them with smaller quantities of alkali. We have, however, no reason to believe that such changes of configuration can be produced at ordinary temperatures by mere contact with water, and until some well-marked case of this kind can be adduced, we shall be justified in rejecting this as a *vera causa* of multirotation" (Paper 103, *J.C.S.*, vol. 71, p. 774 (1897)).

In an addendum, values are given for the heat of hydration of aldehyde and of the formation of aldehyde-ammonia, as follows :—

| | Per gram-mol. | Per gram of aldehyde. |
|---|---|---|
| $CH_3COH$ + aq. = | 4598 cal. | 104·5 cal. |
| $CH_3COH$, aq. + $NH_3$, aq. = | 5617 ,, | 127·6 ,, |

"The value for the hydration of aldehyde is much larger than the corresponding values with the sugars (the hydration of dextrose, for instance, gave 106 cal. per gram-molecule), but such a difference does not militate against the view that the actions are similar in their nature. The heat of combination of soda with dextrose—about 3,800 cal. per gram-molecule—does not fall far short of the heat of formation of aldehyde-ammonia" (*ibid.*, p. 778).

(ii) *Hydrolysis of Starch.*—"In starch-hydrolysis by diastase the heat liberated is sensibly proportional to the amount of hydrolytic work done, or, what is the same thing, to the amount of water fixed, and that this is independent of whether we commence with starch bodies of a high or of an intermediate degree of complexity" (pp. 788–789).

"The mean value of our five determinations is + 2·60 cal. per gram of amylin transformed into maltose, when malt-extract is the hydrolysing agent" (Paper 104, *J.C.S.*, vol. 71, p. 789 (1897)).

(iii) *Hydrolysis of Cane-Sugar by Invertase.*—"The results of two concordant

experiments . . . lead to a value of 11·21 cal. per gram of cane-sugar inverted. This is five times larger than the heat of hydrolysis of starch" (*ibid.*, p. 792).

"The heat of inversion of cane-sugar to the bi-rotatory α-forms of dextrose and levulose is $11 \cdot 21 - (0 \cdot 588 - 4 \cdot 64)\ 0 \cdot 526 = + 13 \cdot 34$ cal. as against + 11·21 cal. for the inversion to the stable β-forms" (*ibid.*, p. 793).

## CHAPTER IV.

### On the Nature of Solutions.

Pickering's early work in inorganic chemistry very soon took definite shape in a number of investigations of "molecular" compounds—hydrates, basic salts, and double salts. It was therefore by a natural sequence that he passed on to a series of physico-chemical investigations of the same group of compounds, with special reference to the thermal changes produced on dissolving simple or double salts in water, on converting the anhydrous salts into hydrates, or on converting a pair of simple salts into a double salt. These investigations again assumed immediately a definite aspect, in view of the indications which Pickering obtained of discontinuous variations in properties which had generally been regarded as varying only in a simple and perfectly continuous manner. The possibility of discontinuities of this kind, and the theoretical considerations raised by them, are vital features of Pickering's later work, and will be referred to again in a later section of this Memoir. It will therefore be sufficient at this point to direct attention to the fact that, at the time when the modern theory of dilute solutions was being worked out, Pickering had already acquired a wide experience of the properties of aqueous solutions, and had developed definite opinions in reference to their essential character. Under these conditions it was almost inevitable that he should have played a leading part in the vigorous controversies which ensued; and it was entirely appropriate that, 20 years later, when these controversies were at last drawing to a close, he should have been selected to preside over a General Discussion on "Hydrates in Solution," which was held under the auspices of the Faraday Society on June 25, 1907.

(*a*) *The Hydrate Theory of Solution.*—The report (Paper No. 18) "On the Nature of Solution," in which Pickering described the "hydrate" theory of solutions, was read before the British Association at Birmingham in 1886. Since it preceded the period of controversy, it is entirely impersonal in character. It is a delightful document, so fresh and vivid in its presentation of the relevant facts, and so sound in its deductions from them, that it is as pleasant to read to-day as it must have been when it first appeared nearly 40 years ago.

In opposition to the views expressed by Nicol (*Phil. Mag.*, vol. 1, p. 453, and vol. 2, p. 295 (1885)) and others, Pickering's "hydrate" theory of solutions asserted that dissolution depends on the existence, in a stable or partially

dissociated condition, of definite liquid compounds of the solute and solvent, and the mixing of these compounds with excess of the solvent. This view is admitted by every one to be correct in cases such as the formation of sulphuric acid as a product of the hydration of sulphur trioxide ; but it was not generally accepted in the case of mineral salts. Pickering therefore urged that copper sulphate, potassium hydroxide, etc., with their intense affinity for water, cannot be supposed to exist in an anhydrous condition in the presence of an unlimited amount of water. This conclusion is entirely rational, and Pickering was obviously right in asserting that, in cases where a solid hydrate was already in existence, there was no known chemical force which would account for its supposed decomposition into an anhydrous salt and water by the mere addition of a large excess of water. Indeed, all chemical experience goes to show that the presence of an excess of one of the products of dissociation of a compound always tends to repress the dissociation of the compound. The point that the addition of an excess of one of the products of dissociation must increase, and not diminish, the amount of a compound present in a given solution was driven home by Pickering in a very emphatic way in a later paper (No. 86) on " The Hydrate Theory of Solutions," as may be seen by referring to the relevant quotation from this paper which is printed on p. 35 below.

In further support of his theory, Pickering cited the fact that, when an anhydrous salt (such as $MgSO_4$) is dissolved in water, a considerable evolution of heat occurs, whereas, when the hydrated salt is used, less heat is evolved. The difference is obviously due to the hydration of the anhydrous salt in the process of dissolution. The evolution of heat becomes less and less as the salt taken is more and more highly hydrated ; but, even when the salt is taken in its most highly hydrated condition, the evolution of heat on dissolution is often considerable, especially when an allowance is made for the latent heat of fusion of the solid salt. Pickering argued that this further evolution of heat was due to a further hydration in solution of the fully hydrated solid salt, and that not only do hydrates exist in solution, but that they are often of a higher order than the highest known in the solid condition.

Against this conclusion the argument was advanced that the molecular volumes of dissolved salts are found to be the same for the anhydrous and hydrated forms of the salt ; but this is precisely the result that would be expected from Pickering's theory, and could not be accepted as an argument against it. Of much greater interest, therefore, is Pickering's attitude in regard to the physical properties of salt solutions, many of which were already known to be additive functions of the properties of the component radicals of

the salt, *e.g.*, the solution volumes (Valson, *Comptes Rendus*, vol. 75, p. 1000 (1875)) the capillarities (Valson (1870)) and the freezing-points (Raoult, *Ann. Chim. Phys.* [v], vol. 28, p. 133 (1883); [vi], vol. 2, p. 66 (1884); [vi], vol. 4, p. 401 (1885)). In commenting on these phenomena, Pickering regarded it as "surely not surprising" "that atoms and molecules which are undoubtedly united may retain their individuality so far as to act towards certain agents as if they were free" (p. 4). The argument thus advanced by Pickering 40 years ago is still used whenever it is desired to maintain a semblance of chemical combination in cases where the components of a complex are found to behave as if they were quite free.

(*b*) *The Theory of Electrolytic Dissociation.*—The idea that the radicals of a dissolved salt not only "act towards certain agents as if they were free," but that they really become free on dissolution in water, was first put forward in a concrete numerical form by Arrhenius in 1887, in a paper "Ueber die Dissociation der in Wasser gelösten Stoffe." Arrhenius's paper was published in the first volume of the newly founded *Zeitschrift für physikalische Chemie* (vol. 1, p. 631). It is noteworthy that this volume contains, not only the classical papers of Arrhenius and van't Hoff on the theory of Electrolytic Dissociation, but also a paper by Mendeléef, in which he sought to establish the existence of a series of hydrates of sulphuric acid by a method which he had already used in the case of alcohol, namely, the discovery of discontinuities in the density-concentration curves. Both points of view were therefore represented in the earliest issues of the journal; but by a natural process of development the *Zeitschrift* became the principal medium for the propagation of the doctrines of Arrhenius and van't Hoff,* whilst the most important papers on the hydrate theory were published in the *Journal of the Chemical Society.*

The theory of Arrhenius postulated that electrolytic conduction depends on a reversible decomposition into ions of the electrically neutral molecules of a salt, *e.g.*, $NaCl = Na^+ + Cl^-$. The advocates of this theory made an unfortunate mistake in assuming that, even in the case of a hydrated salt, the products resulting from the dilution of the salt solutions with water consisted of naked anhydrous ions. This illogical conclusion was all the more unnecessary since the original idea of Arrhenius, in 1883, when he first found it desirable to postulate the existence of an active and an inactive form of an electrolyte, was that the electrolytically active form, which was produced in maximum amount in

* Prof. Walker described it in 1891 as "the recognised organ of the 'dissociationists'" (*Phil. Mag.*, vol. 32, p. 361 (1891)).

presence of a large excess of water, *might be a hydrate.* Thus, in his Swedish paper, "Recherches sur la Conductibilité galvanique des Electrolytes," Mémoire présenté à l'Acad. des Sciences de Suède le 6 juin 1883 (*Abstr.*, *B.A. Report*, Birmingham, p. 363 (1886)), Arrhenius cited two possible alternatives as follows: "How the inactive and active portions differ is not certain, perhaps only physically; perhaps the active part is a compound of the [solute] and solvent." It was therefore only in 1887 that, in presenting his theory to a wider circle of readers, he suggested that the active portion of the electrolyte was formed by a reversible dissociation into ions of the inactive molecules of the solute, *i.e.*, by a process in which the solvent played no essential part beyond that of a mere diluent.

The writer can claim to look upon this controversy with some measure of personal interest since, whilst still at school, he was first attracted to the study of chemistry by the fascination of the theory of electrolytic dissociation, and in particular of its dramatic correlation of the conductivity of an electrolyte with the freezing-point of the solution. Soon afterwards, as a student of Prof. Armstrong—then, as now, a consistent critic of the "new" theory of solutions,—he was faced with the necessity of finding for his own use a scheme which should be compatible with the two rival points of view. This he found in the idea that *both* views were correct, that their incompatibility was imaginary and not real, and that the hydration of the ions not only provided a way of reconciling the two theories of solution, but also supplied a motive for the electrolytic dissociation of a salt, which (as Armstrong had pointed out) was conspicuously absent from the original "naked" theory of electrolytic dissociation.

It is difficult to say exactly where this reconciling theory originated. Arrhenius himself in 1889 concluded that "the simplest and likeliest assumption is that the ions of the salts, and consequently the salts themselves, exist in solution without water of hydration" (*Phil. Mag.*, vol. 28, p. 32 (July, 1889)). This conception of "naked" anhydrous ions was also accepted by Ramsay as a correct description of the theory of electrolytic dissociation in the discussion on the "Theory of Solutions" at Leeds in 1890. Thus, even when suggesting "that it might well be the case that complex molecular aggregates were capable of existence alongside of dissociated molecules where ions are present," he formulates the process of dissociation as one in which "compounds of acid and water, such as $H_2SO_4 2H_2O$, etc., might exist along with the ions of dissociated sulphuric acid 2H and $SO_4$, or more probably H and $HSO_4$" (*B.A. Report*, p. 325 (1890)). This one-sided hydrate theory, which represented

the limit to which the "dissociationists" were prepared to go in admitting the existence of hydrates in solution, certainly gave no clue to the function of water in promoting ionisation in dilute solution, since, according to the laws of mass action, the addition of water would tend to convert the anhydrous ions into hydrated molecules, instead of actively promoting the electrolytic dissociation of the acid. Arrhenius (*Phil. Mag.*, vol. 28, p. 32 (1889)) ascribes to G. Wiedemann the view that a hydrated salt may dissociate into hydrated ions containing the same total number of molecules of water; but even this would leave the water as a helpless spectator of the dissociation of the acid, unable either to retard or to promote the process of ionisation. In the opinion of the writer of this Memoir, the reconciling theory was, by the persistent inquisition of Pickering, extorted finally from the "dissociationists," who were more ready to admit the hydration of their ions than Pickering was to admit the ionisation of his hydrates. It was therefore natural that the first adequate enunciation of this theory, which the writer of this Memoir has been able to find, should have come from one of Pickering's fellow-countrymen, Mr. Whetham, who, when compelled to admit the validity of Pickering's proof of the real existence of hydrates in solution, suggested that "although there is strong evidence to show that the opposite ions are free from *each other*, there is nothing in the facts of electrolysis inconsistent with the view that they are united with solvent molecules, and that solution is essentially a chemical process" (*Nature*, vol. 55, p. 151 (December 17, 1896)). In a subsequent letter (*Nature*, vol. 56, pp. 29–30 (May 13, 1897)) he maintained that even if we admit "that combination does occur when sulphuric acid is dissolved in water," we need not abandon the dissociation theory, although this result provided a strong argument for modifying the theory in the manner which he advocated.

Whetham's modified theory postulated that hydration and electrolytic dissociation can occur simultaneously; it therefore provided a clear basis for regarding these two phenomena as cause and effect, as urged subsequently by the writer in conjunction with Mr. W. R. Bousfield (*Phil. Trans.*, vol. 204, p. 254 (1904); *Trans. Faraday Soc.*, vol. 1, p. 197 (1905); vol. 3, p. 123 (1907)). According to the view thus advanced, "the ionisation of an aqueous electrolyte consists essentially in a further process of hydration, whereby the fully hydrated molecule combines with an additional quantity of water to form two or more hydrated ions. The process of ionisation might thus be compared with the biological process of karyokinesis, whereby the growth of a cell leads ultimately to the fission of the individual and its resolution into two or more separated cells" (*Trans. Faraday Soc.*, vol. 1, p. 197 (1905)). Since the heat of hydration

of the ions may not be very large,* this picture of the function of water in promoting the electrolytic dissociation of a salt is even more convincing when it is assumed that the ions exist ready-made in the salt, and only require to be pushed apart by the growth of a "watery atmosphere" around them (Kohlrausch, *Sitz. ber. Preuss. Akad.*, Berlin, vol. 26, p. 579 (1902)), than ft was when electrolytic dissociation was supposed to involve the creation of ions from neutral molecules of the salt.

(c) *Arguments in Favour of the Theory of Electrolytic Dissociation.*—The most conclusive argument in favour of Arrhenius's theory depended on the fact that the degree of electrolytic dissociation could be calculated by two entirely independent methods, as follows :—

(i) *From the Conductivity of the Solution at Different Dilutions.*—On the assumption that the undissociated molecules of a salt had no conductivity, the proportion of "free ions" in the solution could be expressed by the familiar equation $\alpha = \lambda_v/\lambda_\infty$, where $\alpha$ is the degree of dissociation of the electrolyte and $\lambda_v$, $\lambda_\infty$ are the molecular conductivities of the solution at volume $v$ and at infinite dilution respectively.

(ii) *From the Osmotic Properties of the Solution,* or from one of the thermodynamically related properties, such as the depression of the freezing-point or the elevation of the boiling-point. Since Raoult had found that the radicals of a salt in a dilute aqueous solution behaved as separate molecules in their influence on the osmotic pressure of the solution, the direct or indirect measurement of the osmotic pressure afforded a duplicate method of estimating the proportion of free ions in the solution.

Since these two methods gave results which could be claimed as concordant, it was clear that no theory of solution could be accepted as complete unless it gave an equally good interpretation of this unforeseen numerical coincidence. Since this could not be done, the theory of electrolytic dissociation, although profoundly modified in its details, has remained impregnable in its main propositions, and has long since been admitted to the canon of orthodox physico-chemical doctrine.

Later work, culminating in the careful experiments of Whetham and Griffiths, showed that the numerical agreement referred to above is only complete in dilute solutions, and that in practice this term must be limited to

* Fajans, however, has estimated the heat of hydration of a naked hydrogen ion or proton as 262,000 calories (*Verh. Deutsch. phys. Ges.*, vol. 21, p. 709 (1919)).

concentrations from about M/100 downwards. Arrhenius himself regarded solutions containing 5 to 10 per cent. of the solute as "strong" solutions (see Pickering's written reply in the *Chemical News* to the points raised in the discussion at Birmingham on the Theory of Solution, Paper No. 48); and, in the same discussion, Walker claimed that the observed freezing-points agreed within the limits of experimental error with the theoretical values "so long as the concentration is less than 1 per cent" (*B.A. Report*, p. 324 (1890). Again, in criticising the data issued from Ostwald's laboratory by H. C. Jones (*Zeitschr. phys. Chem.*, vol. 11, pp. 110, 529 (1893); vol. 12, p. 623 (1893)) to illustrate the concordance between the percentages of dissociation calculated from the freezing-points and conductivities of various solutions, Pickering pointed out (in R.S. 94) that "the differences increase more or less regularly with the strength of the solution, and that it is only in the case of solutions of the extremest dilution, where the total depression is less than a hundredth of a degree, that the differences are within the 0·0001° which Mr. Jones assigns as his experimental error; with a depression of about 0·3°, the difference is 65 times greater than this error, and, if he had carried his calculations further, he would, no doubt, have found, as I did, that the differences increase at a rapidly increasing rate" (*J.C.S.*, vol. 65, pp. 294–95 (1894).

As a result of observations such as these, the theory of electrolytic dissociation became, at least in its quantitative aspects, a theory of dilute solutions. On the other hand, the hydrate theory of Mendeléef and Pickering was based upon experiments which covered the whole of the available range of concentrations; but since the peculiarities which pointed most clearly to the intervention of hydrates were generally observed at higher concentrations, the validity of the hydrate theory was established most firmly in the case of strong solutions. Indeed, one of Pickering's papers (R.S., 89) was described as "A Study of the Properties of some Strong Solutions." A curiously illogical position was, therefore reached, in which the existence of hydrates was widely admitted in strong solutions, but denied in the case of weak solutions—as if water were, in fact, a dehydrating agent for mineral salts and other electrolytes. The illogical character of the position was described by Pickering in a later paper (No. 86) as follows:—

> "The supporters of the physical theory, certainly, do not seem at present very inclined to dispute that in strong solutions hydrates may exist, and they are content either with ignoring or denying their existence in weak solutions only, attributing the behaviour of these solutions not only to purely physical causes, but to an absolute dissociation of atoms

which is the very antipodes of the existence of complex hydrates and similar compounds. But any proof of the existence of hydrates in strong solutions must render such explanations of the behaviour of weak solutions highly improbable, for, once we have a hydrate present in a strong solution, how are we going to get rid of it by further dilution? According to our knowledge of the ordinary laws of dissociation, the addition of the excess of either of the components of a composite fluid which is partially dissociated into its components must do one of two things: either (1) it must increase, and not diminish, the amount of the compound (hydrate) present, or (2) it must lead to the formation of new compounds, higher or lower hydrates, as excess of water or of substance is added. That the addition of excess of water should lead to the disunion of the dissolved substance and the water, and even (in the case of electrolytes) the disunion of the atoms with each other, is a view which is directly opposed to our knowledge of the effect of mass on dissociating fluids, and requires some explanation on the part of those who advocate it" (*J.C.S.*, vol. 63, p. 194 (1893)).

(*d*) *The Hydrates of Sulphuric Acid.*—The year 1890 was a very important one in the history of the "hydrate" theory of solution, and nearly half a volume is occupied by reprints of papers published by Pickering in that year. His monumental paper (No. 49) on "The Nature of Solutions, as elucidated by a study of the Density, Electric Conductivity, Heat Capacity, Heat of Dissolution, and Expansion by Heat of Sulphuric Acid Solutions" had been communicated to the Chemical Society in the preceding year, but was not published until March, 1890. In this paper, of which an abstract is given on p. 133, Pickering claimed to have established (by the analysis of eight series of measurements of various properties of the solutions) the existence of discontinuities at 17 different concentrations. Each of these discontinuities was attributed to a hydrate of corresponding composition, so that 17 hydrates were postulated in all, ranging from $36H_2SO_4$, $H_2O$ at one end of the series to $H_2SO_4$, $5182H_2O$ at the other end.

Eight months before its appearance *in extenso*, this paper "had been honoured by an adverse criticism from Prof. Arrhenius" (*Phil. Mag.*, vol. 28, p. 36 (1889)). Arrhenius's main attack was based on the view that the discontinuities which Pickering had detected would have disappeared if he had "smoothed" his curves "properly," and that Pickering's discontinuities and his hydrates were therefore alike imaginary. Pickering made a spirited reply to this premature and ill-informed attack in the *Philosophical Magazine* of May, 1890 (Paper No. 54); but since the immediate purpose of the controversy

was to determine whether the observed discontinuities were real or not, a review of the arguments used will be postponed to a later section of this Memoir, in which this problem is discussed specifically.

(*e*) *Isolation of Predicted Hydrates.* (i) *Sulphuric Acid.*—More important from many points of view than the controversy with Arrhenius was the publication in the *Journal of the Chemical Society* of May, 1890, of a paper (No. 50) on "The Nature of Solutions, as elucidated by the Freezing-Points of Sulphuric Acid Solutions." At this time it was generally admitted that a hydrate which could be frozen out from a liquid must have a real existence in that liquid*; and Pickering now had the immense satisfaction of describing how he had been able to freeze out a new hydrate, the existence of which he had already postulated from a study of the properties of aqueous solutions of the acid at atmospheric temperatures. Thus, in a letter to the *Chemical News*, dated July 31, 1889 (R.S. 39), he writes:—

> "I beg to announce that I have this day succeeded in isolating in the solid crystalline form one of the hydrates of sulphuric acid, the existence of which in solutions I had lately predicted from a study of the densities and heat of dissolution of sulphuric acid solutions of different strengths (*Proc. Chem. Soc.*, vol. 88 (1889); and *Chemical News*, vol. 59, p. 249). The new hydrate is $H_2SO_4$, $4H_2O$, containing 57·66 per cent. of acid. The proof of its existence depends on its having a definite melting-point at — 25°, which is lowered (as far as about — 70°) by the addition of excess of either water or sulphuric acid, and on other evidence which it is not convenient to give in the present place. The isolation of one of the hydrates with either 2, 4, 5, or $9H_2O$ had been rendered probable by a study of the freezing-points of sulphuric acid solutions, and the nature of the curves representing the freezing-points of solutions from which the tetrahydrate crystallises renders it highly improbable that any other hydrate will be obtained in the solid form except, of course, the monohydrate, which has long been known. Such an absolute proof of the conclusions which I have drawn from other sources must place those

* Prof. Walker, however, took an opposite point of view. "That such a hydrate as $H_2SO_4,H_2O$ can be crystallised is no proof that it has previously existed as such in solution. All experiments, for instance, have gone to show that racemic acid and racemates do not exist in aqueous solution, although they are always obtained on evaporation. Again, although ammonium chloride may be sublimed unchanged, yet it does not exist in the vaporous state. The fact, therefore, that certain hydrates can be obtained as crystalline solids in no wise proves their existence in solutions from which they separate" (*Phil. Mag.* [v.], vol. 32, p. 360 (1891)).

conclusions beyond doubt, and must establish as an incontestable fact the existence of hydrates in solution " (p. 68).

In his preliminary experiments Pickering did not succeed in obtaining any crystallisation of solutions between 76 and 38 per cent., but since the curves for ice and for the monohydrate $H_2SO_4$, $H_2O$, looked as if they would never meet, he anticipated that the gap must be bridged by one of the two hydrates indicated by his former work, namely, $H_2SO_4$, $5\frac{1}{2}H_2O$, or $H_2SO_4$, $4H_2O$. Actually it was the latter compound that crystallised out (fig. 1). Pickering was therefore

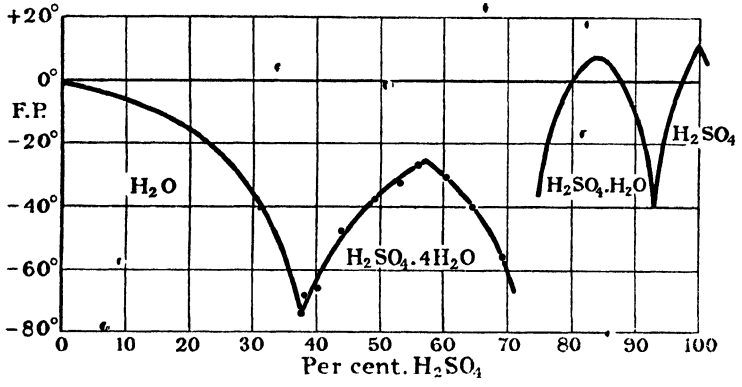


FIG. 1.

able to claim that " the isolation of this hydrate would in any case afford considerable weight to my previous conclusion that it existed in solution; for I recognised it *first* in solution, and *subsequently* proved, by isolating it, that it did exist " (*J.C.S.*, vol. 57, p. 340 (1890)).

(ii) *Nitric Acid.*—Three years later Pickering was even more fortunate in his " Isolation of two Predicted Hydrates of Nitric Acid " (Paper No. 87). In this case he was able to detect, in the published data for the densities and heats of dissolution of acids of various concentrations, breaks at three points only (two on each curve); and, by cooling the solutions, he was actually able to isolate two of the three predicted hydrates, and no others (fig. 2). The hydrates thus isolated were the *monohydrate* and the *trihydrate:*

$HNO_3$, $H_2O$ = 78·0 per cent. $HNO_3$, f.p. — 37°.
$HNO_3$, $3H_2O$ = 53·8 per cent. HNO3, f.p. — 18°.

In reference to the isolation of these hydrates Pickering writes as follows:—

" The two hydrates isolated here are the second and third instances of hydrates isolated owing to their existence having previously been recognised in solutions by means of breaks in various properties examined.

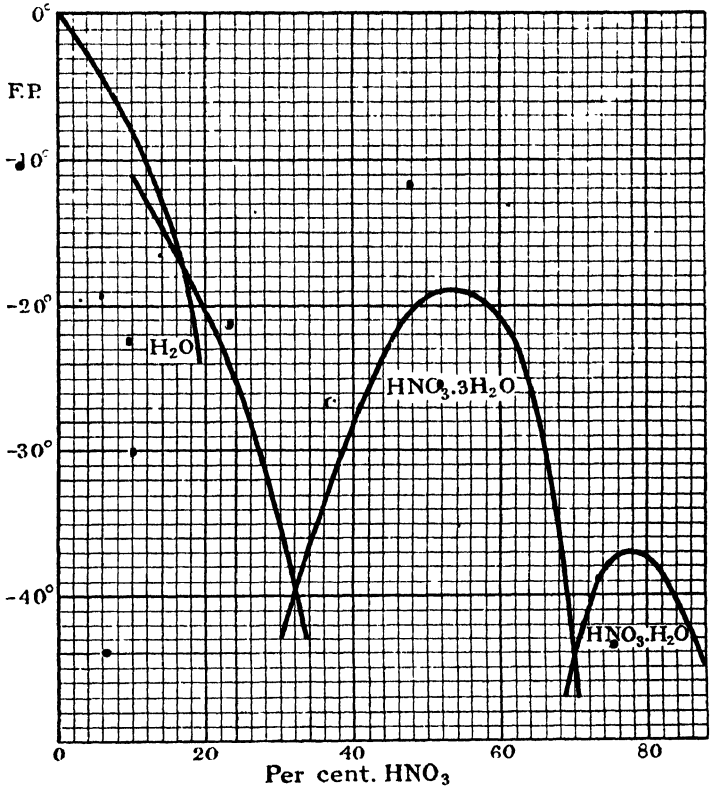


FIG. 2.

. . . In the present instance . . . only two breaks representing hydrates of a sufficiently low order to render their existence in the solid condition probable were recognised, and both these, and these only, have been isolated. It is difficult to imagine how more conclusive evidence could be obtained as to the reality of breaks, and the existence of hydrates in solution, than by the isolation of the very hydrates indicated by the breaks" (*J.C.S.*, vol. 63, pp. 441–42 (1893)).

(iii) *Hydrochloric, Hydrobromic and Hydriodic Acids.*—Similar success attended Pickering's work on aqueous hydrochloric, hydrobromic and hydriodic acids. These solutions had the disadvantage that they could only be studied up to the limit of solubility of the gases in water at the temperature of experiment. Later workers, by making use of high pressures, have been able to plot a complete equilibrium-diagram for mixtures of hydrogen chloride and water over the whole range from 0 to 100 per cent.; but in practice Pickering was limited to the study of the general properties (densities, etc.) of solutions

saturated at atmospheric temperatures, with a substantial extension in the case of the freezing-points, where the solutions could be saturated at the temperature of a freezing-mixture. It is, however, remarkable that Pickering was able to isolate all the hydrates of the following series :

| | | | | |
|---|---|---|---|---|
| R.S. 80. | $HCl \cdot 2H_2O$ | m.p. | $-17{\cdot}4°$ | Fig. 3. |
| | $HCl \cdot 3H_2O$ | m.p. | $-24{\cdot}8°$ | |
| R.S. 92. | $HBr \cdot 2H_2O$ | m.p. | $-11{\cdot}2°$ | Fig. 4. |
| | $HBr \cdot 3H_2O$ | m.p. | $-48°$ | |
| | $HBr \cdot 4H_2O$ | m.p. | $-55{\cdot}8°$ | |
| R.S. 83. | $HI \cdot 2H_2O$ | m.p. | $-43°$ | Fig. 5. |
| | $HI \cdot 3H_2O$ | m.p. | $-48°$ | |
| | $HI \cdot 4H_2O$ | m.p. | $-36{\cdot}5°$ | |

The dihydrate of hydrochloric acid, which melts at $-17{\cdot}7°$ (calc. 50·35 per cent., obs. 49·5 per cent. HCl) had already been isolated and analysed by Pierre

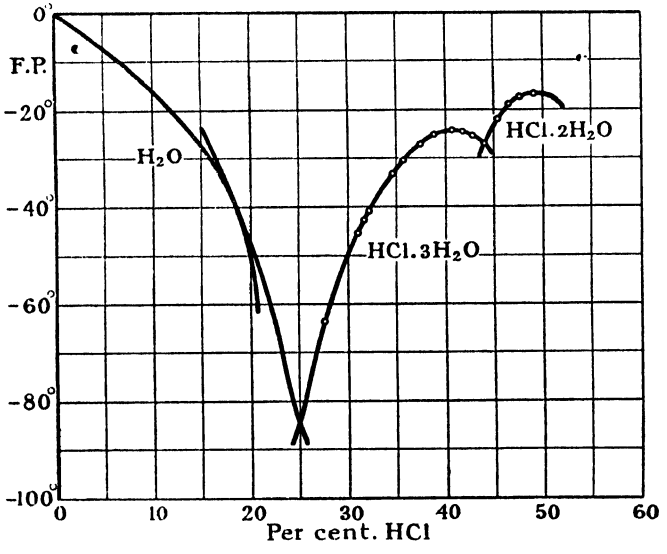


FIG. 3.

and Puchot (*Comptes Rendus*, vol. 82, p. 45 (1876)), and a monohydrate melting at $-15{\cdot}35°$ has since been prepared ; but since solutions of the corresponding concentrations cannot be kept at atmospheric temperatures and pressures, the existence of these hydrates could not be predicted from a study of the physical properties of the solutions. The density curve for aqueous hydrochloric acid, however, which is almost linear up to 39·5 per cent. HCl, bends rapidly at

higher concentrations; and if allowance is made for a small curvature at about 25 per cent. HCl, the main break corresponds exactly with the composi-

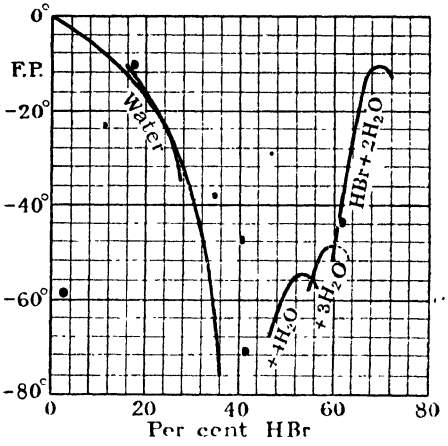


FIG. 4.

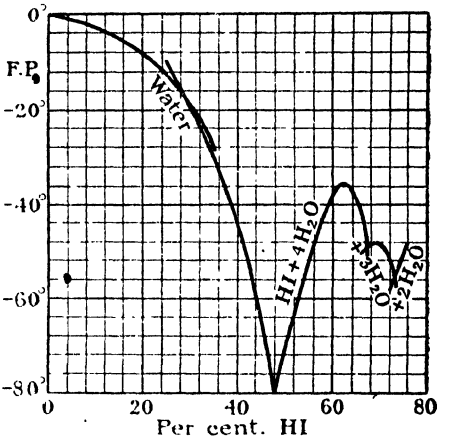


FIG. 5.

tion of the trihydrate, $HCl \cdot 3H_2O$ (40·8 per cent. obs., 40·33 per cent. calc., HCl), isolated by Pickering.

The existence of a further hydrate of hydrogen chloride has been the subject of much speculation. The mixture of maximum boiling-point at atmospheric pressure, which contains 20·24 per cent. HCl, has the composition of an octahydrate $HCl \cdot 8H_2O$ (20·2 per cent. HCl); but since this percentage rises to 23·2 per cent. at low pressures, Mendeléef supposed that the compound contained in the dissociating mixture might be the hexahydrate ($HCl \cdot 6H_2O$ = 25·24 per cent. HCl). Both Mendeléef and Pickering detected a slight break in the density curve at 25 per cent. HCl, but no indications of the existence of the corresponding hydrate were obtained from the freezing-point curve, which passes through a eutectic at this composition. On the other hand, Pickering represents the temperatures at which ice separates from the weaker solutions by means of two distinct curves intersecting at 16·9 per cent. This percentage corresponds with the composition of a decahydrate $HCl \cdot 10H_2O$. Although, therefore, there are many indications of hydrate formation in the region of the high-boiling mixtures, the evidence is not concordant as to the composition of the principal hydrate, since hydrates with $6H_2O$, $8H_2O$, and $10H_2O$ are indicated by the study of different properties of these solutions.

The dihydrate of hydrogen bromide, containing 69·23 per cent. HBr, had been obtained by Berthelot (*Ann. Chim. Phys.* [v.], vol. 14, p. 369 (1878)) and examined by Roozeboom (*Rec. Trav. Chim.*, vol. 4, p. 331 (1885)), who gave its

melting-point at $-11\cdot3°$; but since the crystals could not even be melted without giving off a small amount of gas, it was not possible to deduce the existence of this hydrate in the liquid state from discontinuities in the physical properties of the solutions. The examination of solutions containing rather less of the acid "suggested the existence of two breaks at 52 and 60 per cent. respectively, neither of which, however, were at all well marked (p. 114).

> "Although the breaks thus indicated were of a minor character only, it was deemed advisable to investigate the freezing-points of the solutions, to see whether hydrates corresponding to them could be isolated, and, as a matter of fact, both the hydrates indicated were isolated" (p. 115).
>
> "The two new isolated hydrates here described form the fifth and sixth instances of hydrates isolated in cases where the only grounds for regarding their existence as probable were that they were indicated by changes of curvature in the figures representing the properties of the solutions. The isolation of so many predicted hydrates would, even if no other arguments existed, be sufficient to place the reality and significance of these breaks beyond doubt, and the two special instances here described are of particular importance in that neither of the breaks were of at all a marked character, thus showing that minor breaks have the same significance as the more marked ones" (R.S. 92, *Phil. Mag.*, vol. 36, p. 117 (July, 1893)).

The hydrates of hydrogen iodide contain a very high percentage of the acid, and their existence had not been predicted from a study of the physical properties of the solutions. Pickering, however, represents the temperatures at which ice separates from solutions containing less than 44 per cent. HI by means of two curves intersecting at 30 per cent. HI, corresponding with the composition of a hydrate of the formula $HI \cdot 17H_2O$.

(iv) *Hydrates of Bases and of the Alkalis.*—It will be convenient at this point to deviate from the strict historical sequence in order to refer to later work on the isolation of definite hydrates from aqueous solutions of *bases* and of *alkalis*.

The isolation of a long series of "Compounds of the Alkylamines and Ammonia with Water" (R.S. 86) is of interest as establishing the existence of a number of unknown hydrates; but these had not been predicted from the study of the solutions, and were therefore not evidence of the same value as in the case of the predicted hydrates of the acids. The paper illustrates

again, however, Pickering's contention that a "break," or rapid change of curvature, in a freezing-point curve could occur without any alteration in the nature of the solid phase, as a result of alterations in the nature of the compounds existing in the liquid phase, since he claimed to have detected "breaks" in the ice-curves of several of these solutions. This view was contested by Meyerhoffer in a paper under the title "Die Knicke der Hydrattheorie" (*Ber.*, vol. 26, p. 2475 (1893)), and led to a brief reply (R.S. 93) in which Pickering explained his view of the origin of these "breaks."

The work on "The Hydrates of Sodium, Potassium and Lithium Hydroxides" (R.S. 88) was carried out on similar lines, but was of much greater interest in that it dealt with more familiar and more important compounds. The purpose and the results of this investigation are summarised in the following paragraphs :—

> "One of the chief reasons which induced many chemists to look with distrust on the conclusions I drew from my work on sulphuric acid was the large number of the hydrates represented as existing in solution. Possibly no exception would have been taken if these hydrates had not exceeded 4 or 5, but the existence of some 18 or 20 was regarded as highly improbable, although as a matter of fact no data existed on which an estimate of the probable number present in such a case could be based. The ground of this objection, however, will be removed if it is found that in other cases a similarly large number of hydrates not only exist, but can be extracted from the solution in a solid, crystalline condition."
>
> "Sodium hydroxide has been found to be thus prolific in crystalline hydrates. In the case of sulphuric acid, between the limits of 1 and $7H_2O$ (inclusive) to each $H_2SO_4$, indications of five hydrates in solution (two of them isolable) were obtained, whereas between these same limits, in the case of sodium hydroxide, no less than eight have been actually isolated, and it is very probable that two others which have not been isolated also exist within these limits" (*J.C.S.*, vol. 63, p. 890 (1893)).

Pickering's equilibrium-diagram for sodium hydroxide and water (fig. 6) is remarkable, both for the care taken in compiling it, and for the exceptional number of freezing-point curves which it contains. It is indeed almost a classic of exact research of the type which is usually classified under the general heading of "The Phase Rule." Specially noteworthy, in the text of the paper, is the care taken in recording the physical behaviour of the different crystalline products which were separated one after another from the solution.

"After a little practice we can tell with certainty when the change occurs, the grittiness, flocculence, opacity, or size of the crystals being the main features in which one hydrate differs from another. These terms, of course, have but a relative meaning, as crystals which appear flocculent when separated during the rapid cooling of a small mass of liquid might be hard and gritty if formed slowly in larger masses:

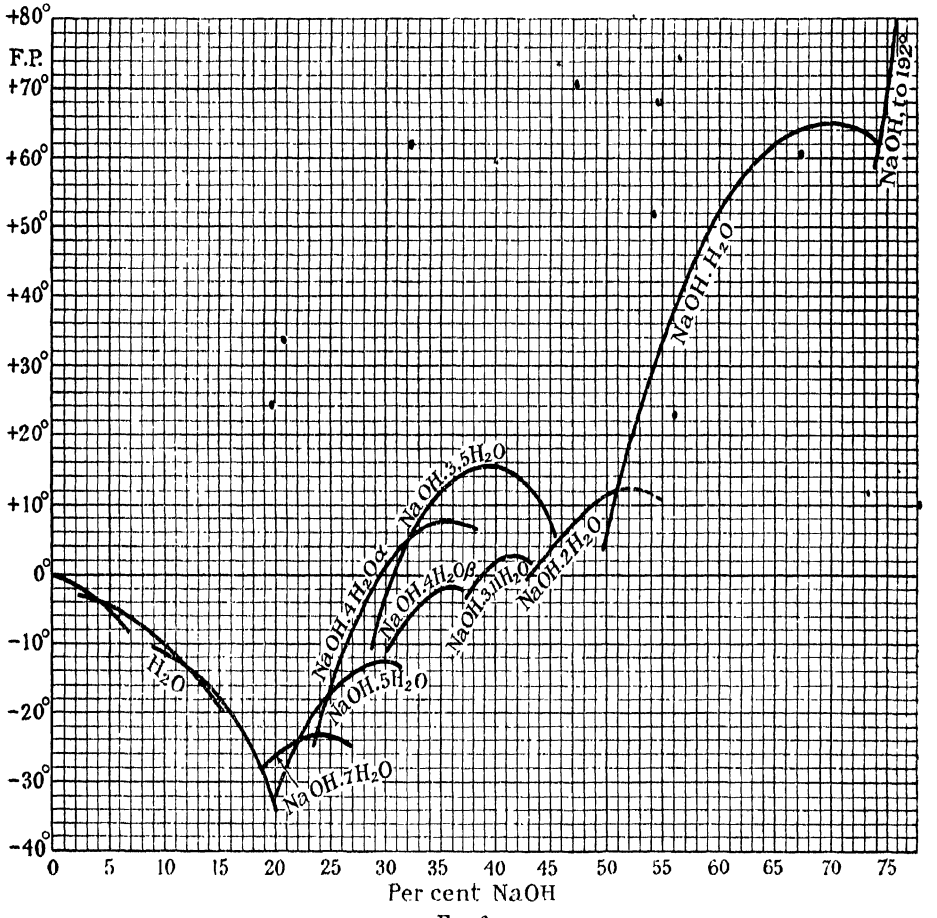


Fig. 6.

nevertheless, they describe with sufficient accuracy the very palpable changes which occur in determinations such as the present" (p. 892).

In a subsequent paper on "The Densities of Solutions of Soda and Potash" (R.S. 96) a series of eight "breaks" was detected in aqueous solutions of sodium hydroxide. "Of these, it will be seen, six certainly agree with six of the hydrates which have been isolated in the crystalline condition; and,

although the remaining two occur in the region of weak solutions where no hydrates were actually isolated, still the freezing-points in this region show two well-marked breaks (and these were the only two shown here), and both of these agree well with those in the density-figure. Such a thorough agreement between the breaks and the hydrates isolated must, I think, settle definitely that these breaks are really due to the hydrates present in solution" (*Phil. Mag.*, vol. 37, p. 365 (April, 1894)).

The isolation of all these hydrates was indeed a remarkable triumph for the "hydrate" theory of solutions, and would probably have been accepted as a decisive vindication of that theory, and of Pickering's method of analysis, but for the fact that Pickering was equally confident of the real existence of a bewildering array of more complex hydrates, *e.g.*, of hydrates containing 1 molecule of sulphuric acid combined with 5·5, 9, 13, 24, 58, 130, 510, 1,500 and 8,000 molecules of water. The idea that a single molecule of sulphuric acid could form a definite chemical compound with many hundreds of molecules of water was indeed too fantastic to be readily accepted, and the attempt to identify every fresh change of curvature with a new hydrate had the effect of bringing the hydrate theory of solution into disrepute, where a more cautious application of its doctrines could scarcely have failed to carry conviction even to its most determined opponents.

(*f*) *The Theory of Solutions Discussed.*—The year 1890 was also memorable for a full-dress Discussion on the Theory of Solution at the Leeds meeting of the British Association. The general position of "the two rival theories," as Pickering calls them, was summed up in the early paragraphs of the Report (Paper No. 48) which he submitted to that meeting, as follows:—

> "The supporters of the hydrate theory claim that the curved figures representing the properties of solutions of various strengths show sudden changes of curvature at certain points, which are the same whatever be the property examined, which correspond to the composition of definite hydrates, and which, therefore, can only be explained by the presence of these hydrates in the solutions; while the supporters of the physical theory, now identified with the supporters of the osmotic pressure theory, claim to have shown that, with weak solutions at any rate, the dissolved substance obeys all the laws which are applicable to gases, and that, therefore, its molecules must be uninfluenced by, and uncombined with, those of the solvent" (p. 311).
>
> "In one respect the supporters of the hydrate theory start now under

a distinct advantage, namely, that their most active opponents do not altogether deny the existence of hydrates in solution, although it is only in the case of strong solutions that they will admit their presence" (p. 311).

Pickering therefore directed his arguments, not merely to a general defence of his method of analysing the experimental curves, but more specifically to proving that discontinuities could be detected also in the region of dilute solutions. Indeed, he asserts that "the indications of sudden changes are nowhere more marked than they are with these very weak solutions." Thus, the rate of fall of the freezing-point of dilute aqueous solutions of sulphuric acid from 0 to 0·07 per cent. was said to be a quarter as great again as it is from 0·07 to 1·0 per cent. (p. 313).

Pickering's discussion of the freezing-points of salt solutions was based on Raoult's supposition that the molecular depression of the freezing-point was constant not only for different solutes, but also for different solvents. This supposition had, however, already been abandoned in favour of van't Hoff's relation, $\delta = 0{\cdot}02\,T^2/L$, according to which the molecular depression $\delta$ depends on the freezing-point T and latent heat of fusion L of the solvent. This part of the attack on the theory of electrolytic dissociation was therefore ineffective; but Pickering nevertheless laid bare the weakest feature of the theory when he said that "the theory of dissociation into ions . . . seems to be quite irreconcilable with our ideas of the relative stability of various bodies and with the principle of the conservation of energy. . . How can we regard it as probable that compounds of such stability and compounds formed with such a development of heat as sulphuric or hydrochloric acid should be thus entirely dissociated by water; still less that these, and all the more stable compounds that we know, should be thus demolished, while all the less stable ones—such as hydrocyanic, sulphurous, boric acids, etc.—remain intact? How can we admit that the more stable a body is, the more prone it is to be dissociated? And if such a dissociation has occurred, it must have been without any absorption of heat, and, consequently, energy must actually have been created" (pp. 318–319).

This most cogent criticism was supplemented by Prof. Fitzgerald, who inquired as to the source of the energy required for dissociation. The answer given by Prof. Ostwald, who was present at the meeting, was that "the ions H and Cl, existing in the aqueous solutions of hydrogen chloride, are by no means identical with the so-called free elements. To use a word to which chemists are accustomed, the ions H and Cl are *allotropic forms* of these elements similar to yellow and red phosphorus, and contain very different amounts of

energy from those which they contain in their common state of hydrogen and chlorine gases . . . ; we must interrogate facts ; and these teach us that the ions generally contain much less energy than the elements in the common state, and therefore a great amount of energy is not called for in the transformation of, *e.g.*, HCl into the free ions H and Cl" (p. 333). To this point Prof. Fitzgerald replied as follows : "I do not like the idea of an allotropic form of the atom, and think the facts of solution, etc., can all be explained by chemical combination between the salt and its solvent . . . without this assumption. A good deal of weight has been laid on the explanation of the equality of heats of neutralisation of ionised bodies by supposing them to be dissociated. How does it happen that the heats of ionisation or dissociation during solution are many of them so nearly balanced by the allotropism of the ionic state ? We are only explaining the obscure by the more obscure in thus reasoning" (p. 329).

Pickering, in a written reply to the discussion in the columns of the *Chemical News*, referred to these *ad hoc* hypotheses in similar terms, as follows :—

> "They involve either the introduction of electric charges from nowhere, just when and where we please, which can combine with matter to generate just as much heat as may be convenient to the theory, or else they hypothecate a new form of atom which shall be *minus* that free energy which we must admit an ordinary atom possesses, or at any rate *minus* just so much of it as will suit the theory in question" (*Chem. News*, vol. 63, p. 171 (April 10, 1891)).

In the light of later developments the discussion was noteworthy for Lodge's suggestion that "it is not quite apparent why . . . the antithesis of the hydrate theory is supposed to be the dissociation theory. Free *molecules* in solution, rather than free *atoms*, would seem to be the opposite to the formation of definite chemical hydrates" (p. 21). In other directions Lodge's views were in agreement with those of Fitzgerald, whose contribution to the discussion showed a remarkable insight into the vital factors of the controversy, as in the following passage :—

> "There seems to be a very important connection, *which cannot be deduced from known principles*,* between conductivity, the variation of osmotic pressure from its value calculated from molecular weights, and the

* The italics are mine (T. M. L.). Pickering himself was not clear on this point, since he held that "according to the chemical as well as the physical theory there must be a mathematical connection between the freezing-points, conductivities, and all other properties of solutions'" (p. 337). This conclusion is far from obvious, since the chemical

chemical activity of a substance in certain relations. The quality upon which these properties depend is, I think, certainly the same quality in each case, and its existence and importance have been brought to light by the labours of our renowned visitors and their collaborateurs, and the discovery is one of the most valuable contributions to chemical physics that has been made of recent years. The visitors call this quality the 'ratio of dissociation.' Prof. Armstrong would rather call it 'measure of affinity.' I would be inclined to point out that the term 'dissociation' is not happily chosen, and that 'affinity' really explains very little, and that it would be better to call it by a new name whose full meaning will require further investigation, and would call it 'measure of ionisation.'"

He considered that the separate action of the ions in osmotic pressure in conductivity and in double decomposition did not require their complete independence, as tested by the ability to diffuse away fully from one another, which alone would justify the use of the term "dissociation."

"I object to the term dissociation as applied to the ions in an electrolyte. All agree that one cannot escape or diffuse without the other following; it may be due to electrical forces between them, it may be for other causes, but in either case I would refuse to call them dissociated. The possibility of independent diffusion I look upon as a test of dissociation. I would therefore appeal to both sides to adopt some neutral term such as 'ionisation' to express the state of ions in electrolytes" (p. 17).

The present writer was, during a period of many years, in agreement with Prof. Fitzgerald in preferring to describe Arrhenius's ratio $\alpha = \lambda_v/\lambda_\infty$ as the "coefficient of ionisation" of the dissolved salt rather than its "degree of dissociation." Modern physical theory, however, appears to call for a reversal of this policy, since it suggests that the ions exist already in a static condition as electrically charged radicals in the crystals of a salt, and that in dealing with the properties of solutions we are concerned with the separation or dissociation of pre-existing ions rather than with their manufacture, by a process of ionisation, from neutral molecules. According to this theory "ionisation"

theory did not include any precise views as to the mechanism of electrolytic conduction. Indeed, in a later paper (R.S. 102) Pickering himself admitted that "The hydrate theory did not lead, and probably never would have led, to an explanation of that peculiar behaviour of electrolytes which simulates dissociation."— (*Nature*, vol. 55, p. 224 (Jan. 7, 1897)).

of the elements takes place during the conversion of sodium and chlorine into common salt, but the ions thus produced only acquire the power of independent movement when the salt is fused or dissolved in an active solvent. From this point of view, then, it is obviously more correct to think of the "dissociation" of the ions than of the "ionisation" of the salt on dissolution or fusion. As regards the definition of "dissociation," the correct view appears to be that a certain proportion of the ions are at any moment *paired*, so that they move together and are not drawn in opposite directions under the e.m.f. used in electrolysis; others, at any moment, are thrust so far apart (*e.g.*, by association with an "atmosphere" of the solvent) that this e.m.f. drives them in opposite directions through the liquid to the electrodes.

The development of the theory of complete ionisation in the crystals of a salt has been accompanied by the appearance of a similar theory of "complete ionisation" of a dissolved salt in dilute solutions. According to this theory, the reduced activity of the ions at a given concentration as compared with their activity at "infinite" dilution is due to electro-striction, *i.e.*, to the drawing together of the opposite ions (acting as a sort of irregular lattice) and not to conversion into undissociated molecules. This theory cannot, however, be extended to more concentrated solutions, where the formation of definite pairs of oppositely charged ions (as in the vapour) is almost inevitable; it appears likely, therefore, that the properties of strong solutions are determined very largely by the degree of dissociation of these neutral doublets, on much the same lines as those drawn by Arrhenius in 1887.

In connection with this memorable discussion, attention may be directed to Ostwald's categorical statement that "pure liquids do not conduct, because their molecules have no space to resolve themselves into ions" (p. 335), a statement that can only have been made in complete forgetfulness of the excellent conductivity of fused salts; also to van't Hoff's statement that the analogy between gases and dilute solutions was "more intended to popularise than to prove the laws in question." van der Waals had, however, made an investigation of the complete kinetic system, taking into account the "movement of the molecules of the two substances mixed, action on themselves and on each other. . . . the result is a very complicated formula, simplified, however, for dilute solutions into this statement 'that the dissolved molecules act on a semi-permeable membrane with strictly the same force as they would do on an ordinary membrane in the gaseous state.' So from a kinetic point of view the law of Avogadro and the 'osmotic pressure' law stand on the same bases'" (p. 336).

(*g*) *Pickering's Criticism of the Theory of Dissociation into Ions.*—The fundamental difficulties of the theory of dissociation into ions became more serious as greater consideration was given to them, and in the spring of the following year, on March 20, 1891, Pickering read before the Physical Society a critical paper of a very incisive character, on "The Theory of Dissociation into Ions, and its Consequences" (Paper No. 72, *Phil. Mag.*, vol. 32, pp. 20–27 (July, 1891)). Pickering's criticisms were expressed in the following terms:—

"The supporters of the present physical theory of solution hold that the majority of salts, acids, and bases, when dissolved in a large excess of water, are entirely resolved into their component ions. . . ."

"When hydrochloric acid gas, for instance, is dissolved in water, the molecules, which were intact to start with, become resolved into their ions, so that each of these acts as if it were a separate unit. This, I believe, is, according to the theory, the total and only change which occurs: the water remains in the same state in which it was to start with. The resolution of HCl into H and Cl atoms has been held of necessity to involve an *absorption* of heat, an absorption considerably in excess of that which we know occurs when it is resolved into hydrogen and chlorine molecules; and, whether the ions are identical with free atoms or not, we have the positive statement of Arrhenius, the originator of the present dissociation theory, that the resolution of a body such as hydrochloric acid into its ions absorbs heat. If then this, which is the only change, *absorbs* heat, whence comes the 17,300 calories which are, as a matter of fact, *evolved* during dissolution?"

"In the communication to which reference has been made, Arrhenius does not consider the thermal results of dissolution, and a subsequent consideration of these seems to have led some of the supporters of the theory to hold a view diametrically opposed to that just quoted. They now hold, I believe, that the decomposition of molecules into their ions *evolves* heat; that that heat, which they still admit must be absorbed by the decomposition of the molecules into ordinary atoms, is more than counterbalanced by the combination of the atoms with electric charges. This change of front must rather be inferred indirectly from the writings of dissociationists than from any definite retraction which they have published; nor does it appear to have been followed by all the supporters of the theory, for the explanation given by Arrhenius of the constancy of the heat evolved on neutralising acids with bases is that it is in all cases due to the combination of the ions H and OH to form $H_2O$, and this

explanation was quoted as recently as September last by Shaw as being one of the strongest arguments in favour of the theory. It may also be remarked that up to July, 1889, Ostwald seems to have held both views, and to have adopted either just as the exigencies of the case suggested: he explains the normal heat of neutralisation as being due to the heat evolved in the formation of a molecule from its ions ('Outlines of General Chemistry' (1890), p. 368), and the abnormal heat of neutralisation as being due to heat evolved in the formation of ions from a molecule, though not, of course, the same molecule as in the previous case (p. 369)."

"The first point, therefore, on which the dissociationists should give us definite information is, whether the dissociation of a molecule into ions is supposed to evolve or absorb heat."

"Presupposing that the answer will be that heat is evolved (at any rate in cases similar to that of hydrochloric acid), their theory cannot be said to be *primâ facie* inconsistent with the conservation of energy; but other very serious difficulties arise which call for explanation."

"The idea of heat being evolved by the combination of a charge with an atom involves the conception that the charge is originally independent of the atom: indeed the main idea of the theory seems to lie in the distinction between an ion, or charged atom, and an ordinary or uncharged atom. We may ask, therefore, whence come these charges? All the ordinary means by which bodies become charged seem to be absent in the present case. No external energy has been expended, no friction can be supposed to exist except such as might result indirectly from an attraction between the water and the acid; but even if the existence of such an attraction were admitted, it could never cause sufficient friction to overcome the very attraction which is the original cause of it, to say nothing of the still stronger attraction which holds the atoms together: induction cannot apply, as both water and acid are supposed to be uncharged to start with, and even if there were a contact difference of potential between these two substances, it would not result in communicating both the + and − charges to one only of the bodies brought into contact—the acid."

"In the second place, how can we imagine that an electric charge, which we must at present regard as an affection of matter, can combine with matter to produce heat and itself remain in *statu quo*? Such a view is little less than endowing the charges with some of the exclusive properties of matter, and calling this new matter into existence just when and where may be most convenient to the theory."

"In the third place, how can it be maintained that the positive electrification of the hydrogen, and the negative electrification of the chlorine, would dissolve the union between them? According to all our experience of electricity, such electrification would make them cling together all the more firmly. Further, if these so-called + and — charges repel each other, why are they attracted by the — and + charges respectively on electrodes during electrolysis? or why, again, do the similarly charged atoms not attract each other (as dissimilarly charged ones are supposed to repel each other) and form hydrogen and chlorine molecules?"

"That a molecule, when decomposed by some force superior to the attraction of its constituent atoms, gives rise to free atoms which are possessed of a certain amount of free energy, and that this free energy, which we call chemical affinity, may really be of the nature of an electric charge, has received the support of the greatest chemists and physicists whom Science has known; but the present theory seems to have nothing in common with such a view—indeed, it seems to be directly opposed to it. On the old theory the atoms when separated have *more* free energy than when combined, on the new theory they have *less*: on the old, the electric charges are the *consequence* of decomposition by some superior force, and form an integral part of the stuff resulting from the decomposition; on the new, they are the *cause* of this decomposition and are something outside and independent of the matter itself. The old theory attributes chemical affinity and combination to the existence of these charges; the new theory considers the charges to be antagonistic to chemical affinity, and to be the cause of chemical decomposition."

"The view has been suggested, I believe, that the supposed dissociated atoms, though no longer held together by chemical attraction, may be still held together by the electrical attraction of their charges. This seems to be but an attempt to overcome a difficulty by changing a name, and so far from really diminishing the difficulty, it would appear only to increase it; for heat has been evolved, and, therefore, the state of combination is more intimate than it was before dissolution, so that the matter must be held more firmly together by these electrical charges than it was by its chemical affinity: how does this help the statement that they are *less* firmly united now—so much less firmly, according to the theory, that they act as independent units? The difficulties as to the origin of the charges and the antagonism of chemical and electrical attraction are, moreover, not removed by this method of expressing the theory."

"Another view, again, was suggested at the recent meeting of the British Association: that, instead of regarding the ions as atoms with electric charges, they might be regarded as allotropic modifications of the atoms themselves. This appears to me to be but hypothecating a new form of matter to satisfy a theory which is inconsistent with known matter, and, inasmuch as atoms of the same substance cannot differ from each other except by possessing different quantities of energy, it practically amounts to the conjuring away a stock of energy that the theory may not be said to be contradicted by the principle of the conservation of energy. But surely such a process is in reality as much a violation of this principle as writing 2 = 4 would be. The energy equation will not equate, so the excess of energy on the one side is boldly struck off by imagining a new form of energyless atom, just as on the electric-charge theory the same is done by saying that the superabundant energy has been expended in combining with charges which have come from nowhere" (*Phil. Mag.*, vol. 32, pp. 20–24 (1891)).

At the time when they were advanced, and for many years afterwards, these arguments appeared to be absolutely conclusive. Modern physics, however, in this as in other directions, had made very revolutionary changes in our views as to what may be regarded as "possible," and what may still be described as "inconceivable." In particular, it has postulated the existence of a new source of chemical energy in the tendency for the positively charged nucleus of an atom to acquire "round numbers" of negatively charged planetary ions, *e.g.*, to form groups of 2, 8, 18 or 32 electrons. Some atoms are therefore particularly ready to take up, and others to part with, units of negative electricity. Thus, in the particular case of sodium chloride, the view has been adopted that the atoms of sodium and chlorine are most stable when they have been converted into ions by the transfer of a single negative charge from each atom of sodium and to each atom of chlorine. Even the solid crystals are therefore supposed to be merely aggregates of oppositely charged ions. In this scheme it is the molecules, and not the ions, of the salt that are regarded as non-existent, since molecules are merely simulated by grouping together pairs of oppositely charged ions to form electrically neutral doublets (compare p. 49), but without any neutralisation of the opposite charges on the two ions. The function of the solvent, then, is merely to separate the pre-existing ions of the salt, and not to manufacture the ions from the neutral atoms of a neutral molecule; but even this requires a definite expenditure of

energy, and once more we are obliged to fall back on the chemical affinity of the solvent for the component parts of the solute in order to account for a process which, now more than ever, is correctly described as the " electrolytic dissociation " of the ions of the salt.

(*h*) *Association* versus *Dissociation in Solutions.*—Perhaps as a direct result of the visit of Ostwald and van't Hoff to the Leeds meeting of the British Association, Pickering began, after the " Discussion on the Theory of Solution," cited under (*f*) above, to publish a series of papers on this subject in German. These German publications, which include seven papers on the cryoscopic behaviour of dilute solutions, need not now be noticed in detail, since they were largely supplementary to the series of papers published in English during this period, and are not essential for tracing the development of the main arguments used by Pickering. One paper, however (No. 60), which he regarded as important enough to be published in the *Chemical News*, as well as in the Berlin *Berichte*, may be referred to, since it illustrates the futility of regarding ionisation and hydration as incompatible conceptions. The English version of the paper bears the title " Association *versus* Dissociation in Solutions," and describes a direct test to determine whether the admixture of water with sulphuric acid results in an increase or a decrease in the total number of molecules. It was quite clear that according to the " physical " theory of solution, the number of units of the solute was increased by its dissociation into ions, but there could be no diminution in the number of molecules of water, since it was asserted that these did not enter into combination with the naked ions formed from the solute. The " hydrate " theory, on the other hand, postulated a diminution in the total number of units as a result of the formation of more complex hydrates from the simple molecules of acid and water. By making use of acetic acid as a solvent, Pickering had no difficulty in showing that " sulphuric acid and water together produce a smaller depression of the freezing-point of acetic acid than the water alone does, so that on adding sulphuric acid to dilute acetic acid, the freezing-point of the latter is actually raised." In an extreme case the depression of the freezing-point by a mixture of acid and water amounted to only one-third of the calculated value. A similar, but less marked, diminution of the depression of the freezing-point, owing to the formation of alcoholates, was observed when calcium chloride or nitrate and alcohol were dissolved together in water ; but a normal depression was observed when alcohol and water were dissolved together in acetic acid. From these results Pickering concludes " that when two substances possessing a strong affinity for each other are mixed, there are fewer acting units present

than when they are separate, and that, therefore, these two substances do not interact so as to produce dissociation, but combination."

The experiment on the depression of the freezing-point of acetic acid by the addition of sulphuric acid and water was afterwards cited by Pickering (in R.S. 102) as a direct challenge to the upholders of the theory of electrolytic dissociation, when he wrote :

> " The explicit evidence afforded by such experiments surely calls for some comment on the part of those whose theories seem to be negatived by it, and their silence on the subject is so significant that it is surprising that it should not have attracted more attention than it has."
>
> " The strong evidence of the existence of compounds such as hydrates in solution, both concentrated and weak, is inconsistent with that perfect freedom of molecules and atoms postulated by the dissociationists, but the discussion of the evidence cannot be attempted here."
>
> " The hydrate theory did not lead and probably never would have led to an explanation of that peculiar behaviour of electrolytes which simulates dissociation, but . . . the theory is perfectly consistent with the observed facts, and, further, affords an explanation of them which is free from the serious objections attaching to the dissociation theory " (*Nature*, vol. 55, p. 224 (January 7, 1897) ).

It was in reply to this challenge that Whetham advanced the view (see p. 33) that " dissociation of the ions from *each other* does not forbid the assumption that the ions are linked with one or more solvent molecules ; " and although Pickering, in a second letter, criticised this conclusion, it has long since become a part of the orthodox view, both of chemists and physicists, as to the real nature of aqueous salt solutions.

(*i*) *The " Gaseous " Theory of Dilute Solutions.*—The " physical " theory of solutions, as contrasted with Pickering's " hydrate " theory, was generally interpreted as meaning that the molecules in a dilute solution are in a condition of " gaseous freedom," the solvent merely playing the part of " so much space." If this picture were correct, it should be possible to recognise in a dilute solution many of the properties of a gas, in addition to finding in the osmotic pressure of the solution a quantitative analogy with the pressure of a gas. Pickering attempted this verification in two ways, but without success.

(i) In R.S. 79 he made a study of " The Heat of Dissolution of Gases in Liquids," the underlying idea being that the heat of dissolution of a vapour or gas should be negligible, if the molecules remained in a gaseous or pseudo

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gaseous condition in solution, without forming any chemical compounds with the solvent. A series of experimental determinations, in which the heat of formation of a liquid mixture was corrected for the heat of vaporisation of one of the components, showed, however, "that, whatever gaseous substance or solvent we take, a considerable amount of heat is evolved during the dissolution, from 5,000 to 10,000 cal., and, therefore, that there is a disappearance of a considerable amount of potential energy, so that we can but conclude that combination in some form or another, whether chemical or otherwise, must have occurred" (*Phil. Mag.*, vol. 34, p. 37 (July, 1892)).

(ii) In R.S. 91 Pickering described "Some Experiments on the Diffusion of Substances in Solution," in order to test in the case of osmotic pressure the analogue of Graham's Law, according to which "the rate of diffusion of a gas should be *cæteris paribus*, inversely as the square root of its density, or of its molecular weight," so that "at a given temperature and pressure the product of the molecular weight, $m$, by the square of the rate of diffusion, $v$, should be a constant." Pickering found that "the values deduced for $mv^2$ are by no means constant, even in those cases where the substances behave normally as to their osmotic pressure, *i.e.*, where the solutions of equal molecular strength give the same osmotic pressure, this latter being measured by the depression exercised by them on the freezing-point of the water in which they are dissolved." Pickering therefore concluded "either that the above supposition is incorrect or that the conditions obtainable in diffusion-experiments are very far from attaining to ideal perfection" (*Phil Mag.*, vol. 35, p. 127 (February, 1893)).

These experiments, and others like them, have long since dispersed the original crude view that molecules in dilute solutions are in a condition which is really like that which obtains in a gas. This hypothesis, like that which assumed that osmotic pressure was produced by a direct bombardment of the semi-permeable membrane by the pseudo-gaseous molecules of the solute, is, however, not necessary in order to account for the applicability to solutions of the *laws* of gaseous pressure; and, in any case, since osmotic pressure is a measure of the number and not of the nature of the dissolved particles, it would not be affected by the formation of complexes of the solute with molecules of the solvent.

## CHAPTER V.

### On the Problem of Discontinuity.

(*a*) *Discontinuities produced by Changes of Temperature.*—We have seen (in Paper No. 20) how Pickering thought that he had obtained conclusive evidence of the real existence of a series of minute local sinuosities in the curves showing the magnitude of the heats of dissolution and heats of hydration of various salts at different temperatures. These sinuosities, if they existed, must have been accompanied by similar irregular fluctuations in the heat-capacity of the various salts as the temperature changed; and since it was quite incomprehensible how the heat-content of a salt could go up by jerks as the temperature was raised (like the thread of a thermometer with too narrow a bore), much complicated speculation was avoided when these sinuosities were admitted (in Paper No. 30) to be due to experimental errors of rather larger magnitude than had been suspected previously.

There was, however, left over from this research a definite claim that the curves, although really quite smooth and free from sinuosities, except those due to experimental errors, nevertheless exhibited a series of abrupt changes of curvature at various temperatures within the limits covered by the experiments. Thus in his "Discussion of the General Results" at the end of Paper No. 30 (*J.C.S.*, vol. 51, pp. 323-24 (1887)), Pickering writes as follows:—

> "Without insisting on the correctness of all the details mentioned above, there can, I think, be little doubt but that the heat of dissolution of salts does undergo sudden changes as the temperature rises, the rate at which heat is developed being lessened at each successive change. The results are far too concordant in themselves to permit of imagining these changes to be merely the result of experimental error, especially when no source of error can be conceived which could come into play so suddenly at certain temperatures and introduce errors exhibiting such regularity. It may be noted also that neither the character of the changes nor the actual temperatures at which they occur bear any relationship to the heat development in the calorimeter, this varying between the limits of + 12,000 and — 16,000 calories."

In the discussion which followed the reading of the paper, Dr. Wright suggested that the lines representing the heat of dissolution of the salts might

in reality be represented by formulæ such as $1 + \alpha t + \beta t^2$, instead of being combinations of straight lines. On examining this suggestion Pickering found that the average errors were doubled by adopting such a formula, and, moreover, that the positive and negative errors were arranged in groups, instead of occurring indiscriminately as they did when a series of straight lines was used.

This conclusion is probably well founded, since there are many cases in which a new factor begins to make its influence felt only after passing through some more or less well-defined temperature, as in the case of the annealing temperature of a metal. There is therefore nothing anomalous in the occurrence of a similar more or less abrupt change of curvature in the numerical value of a physical property on passing through a given temperature.

It is, however, noteworthy that a " break " should have been recorded in the heat of dissolution of a dozen different salts, as well as in that of their hydrates, in the narrow range between 7° and 15° C., although, as Pickering points out, " It is somewhat remarkable that in no case does any marked change appear at 4°, the temperature of the maximum density of water " (No. 20, p. 278). This coincidence may perhaps provide a clue to the origin of these changes of curvature by associating them with some change in the properties of the *solvent* rather than of the *solute*, since the heat of dissolution of a salt is the difference between the energy-content of the salt and solvent separately and of the solution prepared for them. In this connection it is relevant to notice that the specific heat of water, which Pickering represented as increasing progressively with the temperature, has since been shown to pass through a minimum at about 25° (W. R. and W. E. Bousfield, *Phil. Trans.*, A, vol. 211, pp. 199-251 (1911) ). This minimum is probably due to the presence in ice-cold water of a considerable proportion of relatively complex " ice molecules " (perhaps composed of " trihydrol " $H_6O_3$) which soon decompose on heating into " water molecules " (perhaps composed of " dihydrol " $H_4O_2$), and finally into " steam molecules " (or " monohydrol," $H_2O$) (Bousfield and Lowry, *Trans. Faraday Soc.*, vol. 6, pp. 85-104 (1910)). These ice molecules must have a larger specific volume than the water molecules into which they decompose, since the decomposition is accompanied by a contraction, which at first more than counterbalances the normal " physical " expansion of the liquid, and therefore gives rise to the maximum density at 4°. In the same way, the decomposition of the ice molecules gives rise to an abnormally great absorption of heat in the lower ranges of temperature, so that the specific heat, which generally diminishes progressively as the temperature falls, rises again after passing through a minimum at 25°.

The minimum in the specific heat, like the maximum density, is shifted to lower temperatures in aqueous salt solutions and soon falls below 0° and disappears, so that the relationship between specific heat or density and temperature becomes almost linear in the case of the more concentrated aqueous solutions (Bousfield and Lowry, *Phil. Trans.*, A, vol. 204, pp. 253-322 (1905); W. R. and C. E. Bousfield, *Phil. Trans.*, A, vol. 218, pp. 119-56 (1919)), indicating that the ice molecules have already been eliminated from these solutions by the influence of the dissolved salt. The difference in energy-content between the solvent and solute on the one hand and of the solution on the other therefore includes in the former total a complex function of the energy-content of ice molecules, which is largely absent from that of the solutions, and might easily lead to a change of curvature in the experimental curves for the heats of dissolution of the salt. This factor may, indeed, be identical with the "changes undergone by the water molecules themselves," which Pickering thought of as an explanation of the frequent "depression in the curves" at a temperature of 14° (No. 20, p. 290), but which he rejected on account of the different behaviour of sodium sulphate at this temperature. It is, therefore, plausible to suppose that the complex thermal peculiarities of water, as contrasted with the simpler properties of its solutions, may have been responsible for the changes of curvature which Pickering recorded in the heats of dissolution of salts in the range of temperatures within which ice molecules are being formed or broken up.

It is of interest to notice that in a later paper, No. 55, Pickering made a detailed analysis of the curves which represent "The expansion of water and other liquids," and concluded that changes of curvature could be detected at various temperatures, *e.g.*, in the case of water at −2·5°, 0°, 9–11°, 17–20° and 50–60°. There can be no doubt that the equilibrium between the various constituents of liquid water is altered profoundly by changes of temperature. It is therefore not surprising that the curves which express the influence of temperature on its various physical properties should be too complex to be regarded as simple parabolas, and should require to be divided into a series of sections before they can be expressed by means of simple quadratic, or even cubic equations. Since, however, his analysis of the expansion of water was not confirmed by the detection of discontinuities at the same temperature in other physical properties of the liquid, Pickering did not regard these "breaks" as having more than a provisional significance, *i.e.* as indicating the temperatures at which the occurrence of marked changes in the nature of the liquid might perhaps be demonstrated on further investigation. In particular he points

out that " the weakness of the evidence here in comparison with that in the previous work* lies in the fact that we are here dealing with only one property, instead of with the accumulation of confirmatory evidence from wholly independent sources " (*Phil. Mag.*, vol. 30, p. 412 (November, 1890)).

(*b*) *Berthelot and Mendeléef attribute Discontinuities to the Formation of Hydrates in Solution.*—The study of the influence of temperature on the thermal properties of solutions was responsible in the first instance for giving to Pickering the idea that mathematical continuity was not a necessary feature of the functions which represent the variation of a physical property with some change in the conditions under which it is determined. It was, however, in connection with the influence of changes of concentration on the physical properties of a series of solutions that the property of discontinuity became of the greatest interest, since in this case it was possible to assign a definite meaning to the various breaks, by attributing them to the appearance and disappearance of successive compounds of the two components of the solution with one another.

Pickering appears to give the credit of this idea to Berthelot, since in his great paper (No. 49) " On the Nature of Solutions," he writes as follows :—

> " Berthelot in 1875 (*Ann. Chim. Phys.* [5], vol. 4, p. 446) published his determinations of the heat evolved when solutions of different strengths of the commoner acids and alkalis are diluted with an excess of water, and concluded that there were signs of changes near certain points, indicating in an approximate manner the existence of hydrates in solution. . . . Thomsen afterwards (*Thermochem. Untersuch.*, vol. 3, pp. 1–114) went afresh over the same ground, and also investigated the cases of many salts as well. His conclusions—that the action was regular and that hydrates higher than those known in the solid form did not exist in solution—were in direct opposition to Berthelot's and have been widely accepted amongst chemists " (*J.C.S.*, vol. 57, p. 94 (1890)).

Mendeléef, however, revived both the method and the theory of Berthelot in 1886 (*Ber. Deutsch. Chem. Gesell.*, vol. 19, p. 386 (1886)), when he claimed to have detected a series of discontinuities in the densities of sulphuric acid of different concentrations and thereby to have established the existence in solution of the hydrates $H_2SO_4$, $H_4SO_5$ and $H_6SO_6$, with two others containing approximately $12\frac{1}{2}$ and 100 $H_2O$ (see also *Zeitschr. f. physikal. Chem.*, vol. 1, pp. 273–284 (1887)).

In the case of alcohol (*Trans. C.S.*, vol. 51, p. 778 (1887)) the same method

* " On the Nature of Solutions," Papers Nos. 49 and 50.

was used to establish the existence of the three hydrates $3C_2H_6O,H_2O$, $C_2H_6O,3H_2O$ and $C_2H_6O,12H_2O$. Mendeléef's method of proof consisted in showing that, although the density-concentration curve in aqueous alcohol was apparently continuous, it could be broken up into four distinct sections by plotting the first differential coefficient $ds/dp$ against $p$, instead of merely plotting the density $s$ against the composition $p$. The diagram thus obtained consisted of four straight lines, the intersection of which gave the composition of the three hydrates formulated above.

It is indeed obvious that if these three hydrates were formed *successively* by the addition of water to alcohol, the three solutions of corresponding composition would be chemically pure hydrates, whilst any solution of intermediate composition would be a mixture of one hydrate richer, and one hydrate poorer, in alcohol than the solution in question. If, then, there were no change of volume on mixing two hydrates, the densities of the intermediate solutions could be plotted on a straight line joining the points showing the densities of the two pure hydrates, and could therefore be expressed by a linear formula of the type $s = a + bp$. If, however, on account of changes of volume on mixing the two hydrates, the relation between density and composition were a parabolic one, the first differentials would be linear instead. Mendeléef's diagram therefore indicated not only the existence of three hydrates, but also the fact that the densities of mixtures of any two of them could be expressed by a parabolic formula, *e.g.*, $s = a + bp + cp^2$.

Two years later, in an analysis of the data for the electrical conductivity of aqueous sulphuric acid of different concentrations, Crompton (*J.C.S.*, vol. 53, p. 116 (1888)) obtained a series of straight lines after *two* differentiations, *i.e.*, by plotting $d^2k/dp^2$ against $p$, indicating that the original curve could be resolved into a series of cubic parabolas, $k = a + bp + cp^2 + dp^3$.

It is noteworthy that while Pickering followed Mendeléef in advocating Berthelot's view of the nature of solution, and of the influence of hydrate-formation on the properties of a series of mixtures of varying concentrations, he did not accept Mendeléef's conclusions as to the hydrates present in aqueous alcohol. Thus in a paper (No. 56) in the *Zeitschrift für physikalische Chemie* (vol. 6, pp. 10-15 (1890)) he showed that Mendeléef's first differentials could be plotted on a continuous curve, of a somewhat complex shape, but certainly not made up of a series of straight lines. In accord with his own experiments on sulphuric acid, Pickering attempted to analyse Mendeléef's density-curves by means of a second differentiation, but found that the data were not numerous enough nor accurate enough to give definite results. This was largely because of

the narrowness of the range of densities (1·0 to 0·79) of the solutions, which was four times less than in the case of aqueous solutions of sulphuric acid. Pickering criticised Mendeléef's conclusions, however, mainly on the grounds (i) that the breaks occurred in different positions in the different series of data that were available, and (ii) that they did not even occur at identical concentrations in Mendeléef's own determinations of density at five different temperatures, so that (iii) the composition of the supposed hydrates was quite indeterminate. Thus, since the uncertainty in the position of a given "break" was from ± 3 to ± 5 per cent., the various breaks covered practically the whole range from 10 to 95 per cent.

Mendeléef claimed to have detected a linear form in the first differentials of the densities, not only of aqueous alcohol, but also of solutions of 100 different salts, of sulphuric acid, ammonia, hydrogen chloride and other similar substances, and indeed said that he had not yet found a single exception. Pickering was able to assert, on the basis of his own more extensive measurements, that the first differentials of the densities of sulphuric acid were certainly not linear. Moreover, Mendeléef had asserted that no other solution and no other property had been studied with such exactness as the densities of mixtures of alcohol and water, and that for this reason he had chosen this as a typical example. Pickering's proof that the theory was not established in this case therefore implied a complete breaking up of the whole fabric of Mendeléef's theory.

It is remarkable that Pickering should have been so severe a critic of Mendeléef's work, and should have launched against his experiments on aqueous alcohol arguments so similar to those which were used against his own analogous experiments on sulphuric acid. Pickering's position was, however, quite logical, since he had set up for himself a series of rigid standards, and was more concerned than anyone else to see that these standards were maintained, and that claims made on the basis of erroneous or insufficient evidence should be refuted as quickly and as forcibly as possible. Whilst, however, Pickering refused to accept as genuine Mendeléef's three "breaks" and the three corresponding hydrates of alcohol, he claimed in the case of sulphuric acid to have detected discontinuities at not less than 17 different concentrations corresponding with the 17 different hydrates set out on p. 136; and this number was afterwards increased to 22 by applying the same methods to the more complex curves representing the freezing-points of the solutions.

(c) *Analysis by Differentiation*.—In analysing his own data for aqueous solutions of sulphuric acid, Pickering adopted Mendeléef's method of plotting the first differentials of the variation of a given property with concentration, and also

the device, which Crompton (*J.C.S.*, vol. 53, p. 116 (1888)) had applied to Kohlrausch's data for the electrical conductivity of sulphuric acid, of plotting the second differentials. His curves, therefore, included graphs for $s$, $ds/dp$ and $d^2s/dp^2$, all plotted against the percentage $p$ of sulphuric acid in the solution. This method of differentiation was criticised by Lodge in a letter to *Nature* of July 18, 1889, on the "Use or Abuse of Empirical Formulæ, and of Differentiation, by Chemists," in the following terms:

"Prof. Thorpe's review of the work of Mendeléeff suggests to me a question I have several times previously thought of putting, viz., whether chemists are not permitting themselves to be run away with by a smattering of quasi-mathematics and an over-pressing of empirical formulæ. . . .

"To make my meaning clear, I will state a few facts, and if they are unnecessarily obvious I shall be glad to find them so."

"Take percentage composition ($p$), and specific gravity ($s$); $s$ is a function of $p$, and the question is, whether it is a continuous or a discontinuous function. To obtain an answer to this question, the best determinations of $s$ should be plotted on a large scale in terms of $p$, with the probable limits of inaccuracy laid down, and then the curve should be examined to see whether it possesses, at the points of definite constitution, any kind of discontinuity, whether of slope or curvature. The answer may come out, either that such discontinuity certainly exists, or that it possibly exists, or that, if it exists at all, it must be below a certain specifiable order of magnitude. One of these is the definite kind of statement that can be made, and nothing else."

"In order to assist the eye in forming a judgment, some form of mechanical integrator or differentiator might legitimately be run over the curve, provided due care were taken to avoid the creeping in of errors; but I doubt whether anything could be certainly detected in the derived curves that ought not to be visible in the original curve itself."

"The process adopted by chemists seems a less satisfactory plan. . . . They assume some elementary form of empirical expression for the function, say a quadratic expression with three arbitrary coefficients, and they determine these coefficients to suit three points on the curve, first for one portion and then for another, taking these portions in the stages between one definite constitution and another; they thus obtain a set of quadratic expressions for $s$ in terms of $p$, each with a more or less

different set of coefficients: in other words, they find bits of parabolæ which more or less fit successive portions of the actual curve. They then differentiate each of these, and plot $ds/dp$, and they appear to be struck with the fact that, for each portion, these plottings come out precisely rectilinear; while with the observation that discontinuities exist between successive portions they seem quite pleased."

"They sometimes go on to plot $d^2s/dp^2$, and to deduce fresh support for their facts by means of it."

"Now, were it not that eminent persons appear to lend their names to this kind of process, one would be inclined to stigmatise this performance as juggling with experimental results in order to extract from them, under the garb of chemistry, some very rudimentary and commonplace mathematical truths."

"I would not be understood as casting any doubt on the *results* which may, by ingenious and clear-sighted persons, have been arrived at, even by so questionable a process, . . . partly because the hypothesis of definite constitution for solutions or for alloys seems a very probable one, partly because I have myself plotted the $s$ $p$ curve for dilute ethyl alcohol, and clearly perceive the varieties of slope and curvature detected by Mendeléeff, though the changes are scarcely so sharp and definite at definite points as one might wish them to be in order to support the *a priori* improbable hypothesis of actual discontinuity. But what I want to assert, perhaps unnecessarily, is, that no juggling with feeble empirical expressions, and no appeal to the mysteries of elementary mathematics, can legitimately make experimental results any more really discontinuous than they themselves are able to declare themselves to be when properly plotted" (*Nature*, p. 273 (July 18, 1889)).

This criticism drew from Pickering a reply (Paper No. 46, *Nature*, pp. 343–44 (August 8, 1889) which is too long to be quoted in full at this point, since several of the arguments used are discussed more fully in other parts of the present Memoir; but the following sentences, in which the *purpose* of differentiation is described, are of interest as showing that he regarded it merely as a mechanical aid to the detection of discontinuties already existing in the original curves, and generally capable of detection by other methods.

"[Differentiation] will sometimes bring about the recognition of breaks which might be overlooked in the original curve, for, *though the differential*

*curve can show no breaks which do not exist in the original curve,* it may often, as a consequence of its very nature, show breaks clearly which would be recognised only with difficulty in the original curve" (*Nature,* vol. 40, p. 344 (1889)).

'The mathematical argument on which the method depends is that a curve, if it be continuous, will, on differentiation, give either a straight line or another continuous curve; whereas, if it be not continuous, but be made up of different curves, it will yield a series of straight lines or curves. This, I think, is an incontestable fact" (*J.C.S.*, vol. 57, p. 122, (1890)).

The italics in the first quotation were added by Pickering himself when citing it two years later in a "Note on Some Objections to the Work on Sulphuric Acid Solutions (Paper No. 64, *Chem. News*, vol. 64, pp. 1–2 (1891)).* The second quotation is cited by Pickering from his paper (No. 49) "On the Nature of Solutions," which had already been communicated to the Chemical Society, but was not published until the spring of the following year.

In his "Theoretical Chemistry" (*English translation*, p. 445 (1895)) Nernst gave a description of Pickering's methods in the following terms: "Other properties† of solutions have been investigated, according to Mendeléef's method, for 'breaks' [or transition points] of this same sort; thus, the heat of dilution, the specific heat, the freezing-point, the electrical conductivity, etc., were studied; and, of course, these 'breaks' were found the more easily, accordingly as the observations in question were less exact. The method does possess this advantage, in that the 'crop of hydrates' produced is greater the more poorly the experiments are conducted. In particular, it was 'discovered' by Pickering that the use of the second differentiation gives irregularities more easily and more abundantly than the use of the first differential quotient."

"It does not need to be emphasised that by the use of repeated differentiation one can always obtain more or less irregularity in any curve which is empirically obtained, and which therefore has unavoidable errors of observation; and especially when one wishes it, he must certainly find 'transition points.' But on the basis of such an uncritical valuation of the experimental material, no theory of solutions can be erected." Since Pickering's principal argument for the existence of discontinuities depended on the coincidence of

* This "Note" was a considered reply to a discussion at the Chemical Society on June 4, 1891, and is quoted again below on p. 71.

† Pickering, *Chem. News*, vol. 57, p. 116 (1888), and in numerous other references, to cite which would take too much space.

the concentrations at which they were detected in different properties of the same set of solutions (see below, p. 72), it is clear that this criticism (like so many others) was based on a vague impression of Pickering's method rather than on a careful study of his published papers.

It is, however, noteworthy that in his later work Pickering definitely repudiated the theoretical considerations on which the process of differentiation was originally based. Thus, in describing his experiments on the isolation of the hydrates of sodium hydroxides (R.S. 88, compare p. 29) he writes :—

> "There is one other very important point on which the present experiments throw some light, namely, the number of hydrates co-existing in a solution of a given strength. In some cases as many as four hydrates have actually been obtained from the same solutions (30–32 per cent.), and if the curves representing the various crystallisations had been followed further (and we may prolong them with a bent lath with a fair degree of certainty), it is evident that often five, and perhaps sometimes six, hydrates could have been separated from, and therefore must have existed in, the same solutions. Hence, solutions must be very complicated in their constitution, and this is why Mendeléeff's theory as to the rectilineal character of the rate of change of the densities with change of percentage composition should have proved to be incorrect (see *Trans.*, vol. 51, p. 779 (1887); vol. 57, p. 79 (1890)), since it was founded on the supposition that only two hydrates were present simultaneously in a given solution" (*J.C.S.*, vol. 63, pp. 897–98 (1893)).

In a footnote, he adds :

> "I feel somewhat doubtful whether it would be rectilineal even if two hydrates only were present."

In the same way, in his paper on "The Densities of Solutions of Soda and Potash" (R.S. 96), he writes :—

> "The theoretical considerations which led Mendeléeff to conclude that the first differences must be absolutely rectilineal are, no doubt, mistaken ; they depended on the supposition that never more than two hydrates co-existed in solution, whereas my results with the freezing-points of soda solutions prove that at least four of five hydrates may co-exist" (*Phil. Mag.*, vol. 37, pp. 366–67 (1894)).

It is difficult to avoid the conclusion that at this stage Pickering's own views of the nature of solutions had changed profoundly. Thus, there can be little

doubt that, in his earlier work on solutions, whenever he observed a "break" in the properties of a solution at a composition which could be represented by a plausible chemical formula, he regarded the solution as consisting mainly of this one hydrate, and attributed the "break" to a change in the nature of the second principal component of the solution. If, however, a solution could contain half a dozen hydrates simultaneously, the growth and decay of these hydrates must be a progressive process. The identification of the position of the breaks with the composition of various hydrates must then rest on an empirical rather than on the original theoretical basis.

(*d*) *Analysis by Means of a Bent Lath.*—The method of differentiation which Pickering described (*J.C.S.*, vol. 57, p. 67 (1890)) as "a very dangerous and, at the best, a very imperfect tool," was also a very tedious one to apply. Pickering, therefore, at an early stage developed the method of applying a "bent lath" to the study of the experimental data. The lath was used in order to supply a guide by means of which deviations from a simple and smooth curve could be detected, just as a straight-edge can be used to detect a departure from a linear law. Thus in Paper No. 49 he writes :—

> "The curves representing the present results have been drawn with the help of a long thin steel or wooden lath. Such a lath, when bent under the four points of pressure exerted by one's two hands, does not form a curve of any particular nature, and does not necessarily give a curve which will differentiate eventually into a straight line ; but I find that if the experiments form a figure on to which the bent steel *cannot* be fitted, that figure certainly does *not* consist of a single parabolic curve" (*J.C.S.*, vol. 57, p. 68 (1890) ).

The mathematical theory of the bent lath was set out by Mr. E. H. Hayes, Fellow of New College, Oxford, in a paper on "A Consideration of some of the Objections raised by Mr. Lupton to Mr. Pickering's Methods of reducing Experimental Results" (*Phil. Mag.*, vol. 32, p. 99 (July, 1891) ), as follows :—

> "When a uniform naturally straight lath is acted upon by a system of coplanar forces, the form of the curve assumed by a portion of it throughout which none of the applied forces act is such that the product of the radius of curvature at any point and the distance of the point from some fixed straight line is constant, provided that the radius of curvature is very great compared with the thickness of the lath. It immediately follows that the general differential equation of the curve is

$$\frac{d^2y}{dx^2} = \left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^{3/2} \{lx + my + n\},$$

which contains three arbitrary constants. Since this is a differential equation of the second order, the equation of the curve (which can be expressed in terms of elliptic integrals) contains five constants. It is therefore of a generality equal to that of the conic

$$ax^2 + hxy + by^2 + gx + fy = 1$$

or of the curve

$$y = a + bx + cx^2 + dx^3 + ex^4.$$"

"In the bent lath, therefore, we possess a means of drawing a curve through the experimental points, which is of a more general nature than those usually dealt with by arithmetical methods, and in which there can be no abrupt change of curvature, however slight, still less change of direction. To the former change corresponds an abrupt change of direction in the first differential curve, and a breaking up of the second differential curve into two curves which do not meet; to the latter a breaking up of the first differential curve into two curves which do not meet" (pp. 99–100).

Pickering himself dealt specifically with this method of analysis in a paper (No. 78) on "The Recognition of Changes of Curvature by means of a Flexible Lath" (*Phil. Mag.*, vol. 33, pp. 436–66 (1892)). His principal object was to show, in reply to Lupton, who admitted the validity of mathematical analysis but repudiated the graphical method, that these two processes led to precisely similar results. Four series of experimental data were therefore investigated, both by using a bent lath and by using equations of the type

$$y = a + bx + cx^2 + dx^3.$$

The data used were the freezing-points of solutions of propyl alcohol in water and in acetic acid, of sugar in water, and of ethyl alcohol in benzene. It was shown that "the mathematical examination leads to precisely the same conclusion as does the graphic," the errors being abruptly reduced to a minimum on dividing the curves into a proper number of sections, provided that the breaks were at the proper place. No improvement was effected by further subdivision, and greatly increased errors were produced by displacing the breaks, even when this involved dividing the curve into three sections instead of two. In an Addendum to this paper (pp. 462–66) Pickering puts forward, as "an almost conclusive argument in favour of the real existence of [a] break" in the case of propyl alcohol and water, the fact that "a set of results, which can be represented perfectly by two parabolas showing a break, cannot be

represented by a single parabola, even if this has as many constants in it as the two together had " (p. 462).

The great merit of the bent lath was that it made it possible to test whether an experimental curve can be fitted by an equation of the fourth degree, but without the enormous labour of calculating an equation and table of errors for section after section of the curve. Since, however, even a bent lath conforms to an equation of definite type, it is important to consider what would happen on applying this method of analysis to a regular curve, which can be represented by a simple equation, but of a totally different type from that of the bent lath. Pickering deals with this point at the conclusion of his paper (No. 78) as follows :

> " It must be remembered, of course, that a bent-lath curve is not necessarily suited to every curvilinear figure, any more than is a section of a parabola ; but as far as my experience goes the application of a bent lath to a curvilinear figure differing materially from a bent-lath curve (such as a large portion of a hyperbola) would not lead to wrong conclusions, but simply to no conclusions at all. In such a case we find that the error of the drawing increases regularly with the length of the figure drawn in one section, and that any supposed breaks to which we may have been erroneously led by the examination will be found to be false when the method of plotting is altered so as to obtain a figure of a different character " (*Phil. Mag.*, vol. 33, p. 451 (1892) ).

(*e*) *Smoothing.*—Arrhenius in 1889 (*Phil. Mag.*, vol. 28, p. 36 (1889) ), in criticising Pickering's claim to have discovered a series of discontinuities in his experimental curves for the properties of aqueous solutions of sulphuric acid, suggested that if " Mr. Pickering had ' smoothed ' his curve properly he would evidently have removed these angular points or sudden changes of curvature." To this criticism Pickering replied in Paper No. 54, as follows :—

> " The question hinges on the interpretation of the word ' properly.' Prof. Arrhenius seems to think that the ' proper ' amount of smoothing to be made is such that all sudden changes of curvature should be obliterated ; and this, too, in an investigation the sole object of which is to ascertain whether there are such sudden changes or not. I must beg to differ from him. The ' proper ' amount of smoothing I take to be such as will allow but little more error in the experimental points than the known errors of the determinations, or than that which seems to be the

probable error according to the irregularities of consecutive points in the figure. If with such smoothing we are led to conclusions which are obviously false, or which are at variance with the results obtained from independent sources, then and then only must we admit some further unknown source of error, and increase the smoothness of our drawings" (*Phil. Mag.*, vol. 29, p. 429 (1890)).

The point that the correct limit of smoothing must be determined by the actual magnitude of the casual errors, and not by any theoretical view as to the correct form of the curve, was elaborated in Paper No. 78, in replying to Lupton (*Phil. Mag.*, vol. 31, p. 418 (1891)), who had attempted to smooth out the most doubtful of Pickering's discontinuities (at 58 per cent. $H_2SO_4$) by making use of a single parabolic equation to cover a range of concentrations extending over the point at which the discontinuity had been recorded. Lupton's parabola was, however, an obvious misfit, as was shown by the systematic character of the errors. He had, in fact, mistaken the errors on 25 c.c. for errors per cubic centimetre and had therefore multiplied the probable error by 25. The criterion for determining the "proper" amount of smoothing, and the correct number of the sections into which the curve should be divided, was set out by Pickering as follows:—

"The known magnitude of the experimental error is the chief criterion by which the legitimacy of any particular representation of a series of points can be determined; and no representation should be accepted if it attributes to those points an apparent error, either greatly in excess of, or greatly inferior to, the known experimental error. If, moreover, as occasionally happens, two different drawings show the same value for the apparent errors of the points which they are supposed to represent, we are bound to accept the simplest of the two, unless any independent evidence in favour of the other be forthcoming" (*Phil. Mag.*, vol. 33, p. 437 (1892)).

"Mr. Lupton says that 'the smoothing process applied to my first differential diagram ought, if accurately performed, to get rid of these slight changes in first differences which in the second differences mark changes of curvature, and therefore changes of hydration.' But why 'ought'? Surely only on the strength of a foregone conclusion that there are no changes of curvature or of hydration. I must ask Mr. Lupton, just as I asked Prof. Arrhenius (from whom he seems to have borrowed this argument, see *Phil. Mag.*, vol. 29, p. 429) to explain what he means by 'accurate' or 'proper' smoothing. Why does he not take the whole of

one of my first differential density diagrams, and show how it may be accurately smoothed so as to obliterate all changes of curvature? Surely he cannot think that he has sufficiently illustrated the feasibility of this by taking only a small portion of the most regular part of one of these figures. And even if he does, I scarcely think that any one who glances at the result . . . will consider that he has succeeded in the attempt" (*Phil. Mag.*, vol. 32, pp. 97–98 (July 1891)).

In a subsequent Note (No. 64) he passes from general statements to an exact numerical analysis, as follows:—

"The problem of the correct depiction of results graphically is not a very difficult one; we must adopt the simplest drawing which is consistent with the known experimental error, and discard any drawing which attributes an error to the experiments, either greatly in excess or greatly below that of the observed or probable experimental error. As an instance I may take the diagram which was exhibited at the meeting of the Chemical Society, and which will be found in the July number of the *Phil. Mag.* (vol. 32, p. 94), in my answer to Mr. Lupton's criticism. It consists of eleven experimental points representing the rate of change of the density with change of composition, and the question is whether these results should be represented by 5 (the greatest possible number), 4, 3, 2 or 1 curves. The safe limit to be assigned to the experimental error is 0·000008 (*Chem. Soc. Trans.*, p. 71 (1890)), and depicting these results by

| 5 | 4 | 3 | 2 | 1 curves |
|---|---|---|---|---|
| we get: | | | | |
| 0 | 0·000003 | 0·000008 | 0·000007 | 0·000078 |

as the apparent error of the points. Drawn as 5 or 4 curves, this apparent error would be too far below the experimental error; the 3 curve drawing is legitimate as far as the magnitude of the error is concerned, but, as we can simplify the drawing still further without any increase—indeed with a slight decrease—of the apparent error, we are bound to make this simplification, and to accept the 2 curve drawing in preference to the 3 curve drawing. But no further simplification is possible; for simplifying it one degree further produces a sudden tenfold increase in the apparent error, and makes this ten times greater than the ascertained experimental error. Thus the 2 curve drawing is the simplest, and the only possible representation" (*Chemical News*, vol. 64, p. 2 (1891)).

The same point was raised at a later stage in a controversy which was carried on both in German (Nos. 81 and 82) and in English (Nos. 94 and 95) with H. C. Jones on the freezing-points of dilute solutions, and especially of aqueous solutions of sodium chloride.

> "In the *Berichte* (vol. 25, p. 1314), I published a series of determinations with this salt which I considered indicated the presence of changes of curvature at certain points. Mr. Jones subsequently published (*Ber.*, vol. 26, p. 551) some still more accurate determinations, which he considered entirely disproved the existence of these breaks. I proved, however (*Ber.*, vol. 26, p. 1221), that, so far from this being the case, Mr. Jones' results showed the very same breaks as mine did, but in a still more satisfactory manner. I proved that parabolas deduced mathematically from his values so as to allow the existence of these breaks agreed most perfectly with the known experimental error as determined by two independent methods, whereas, when represented by a single parabola without breaks, the error was 10,000 times too large" (*Phil. Mag.*, vol. 37, p. 163 (January, 1894)).

(*f*) *Identity of Breaks in Different Curves.*—Pickering's object in detecting discontinuities in his experimental curves was chemical rather than physical in character, since the "breaks" were used by him as a means of detecting the existence of hydrates in solution. For this reason the "breaks" were of no significance unless they affected in a greater or lesser degree *all* the properties of the series of solutions, although it was obvious that certain breaks might be suppressed if, for instance, two hydrates happened to give identical values for particular physical properties. This point was vital to all Pickering's work. Thus, as early as 1889, in his reply to Lodge in *Nature* (No. 16), he writes as follows:—

> "In my own work I have never considered any breaks as being more than 'suggested' unless they were shown by at least two different properties of the substance under examination; the majority of the breaks which I insist on are shown by more than two, in some cases by as many as seven different properties" (*Nature*, vol. 40, p. 344 (1889)).

It was, however, most difficult to get casual readers, or even keen critics of his papers, to realise the significance of this point. Thus the critical paper of Lupton (*Phil. Mag.*, vol. 31, p. 418 (1891)) begins with the following amazing sentence:

"In the hurry of modern life experimentalists are apt to omit the test of accuracy afforded by obtaining the same results by several different methods. Thus long rows of figures are frequently given which have in reality no experimental basis to rest upon."

Pickering justly complained that "the main feature of the evidence on which I relied was its cumulative character, and this Mr. Lupton seems to have entirely ignored" (R.S. 70, *Phil. Mag.*, vol. 32, p. 91 (1891)).*

The persistent repetition of this error finally led Pickering, in a reply to Rücker under the title "The Densities of Sulphuric Acid Solutions" (Paper No. 76, *Phil. Mag.*, vol. 33, p. 132-144 (1892)), to make use of a diagrammatic way of expressing the concordance of the breaks determined by different methods.

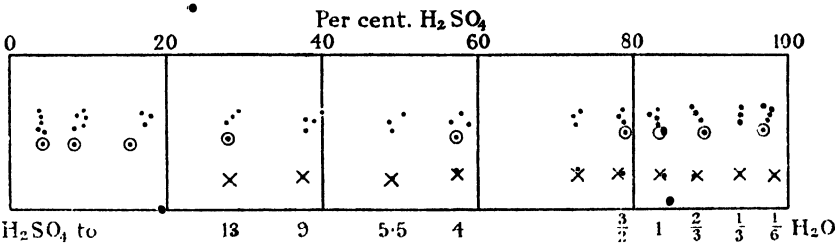



FIG. 7.

This diagram (*ibid.*, p. 134) reproduced herewith as fig. 7, is described by Pickering as follows:—

"The properties originally studied by me were the densities at four different temperatures (from which I calculated the expansion by heat, and, in one case, the contraction on mixing), the heat-capacity from 0 to 10 per cent., and the heat of dissolution. I also utilised Kohlrausch's experiments on the electric conductivity."

"As it may be argued with some plausibility that the similar form of the various density-curves would be likely to lead to the same results when examined by a bent lath, I have contented myself with the following diagram, marking (with dots) the positions of the changes between 2 per cent. and 98 per cent. shown by the densities at 8°, the contractions at 18°, and the three other properties above mentioned. The working curves in these cases are very dissimilar; yet the closeness with which the dots

* Other relevant quotations are to be found in Paper 76, where Pickering refers to "conclusions which depend entirely on the concordance of independent evidence" (*Phil. Mag.*, vol. 33, p. 133 (1892)) and describes "the concordance of independent results" as "the main grounds of my conclusions" (*ibid.*, p. 136).

are grouped around certain percentages is most striking, and the absence of stray dots at other percentages perhaps even more so" (*ibid.*, p. 134).

This paper concludes with a categorical statement of the successive stages by which he had established the real existence of his breaks :

> "From the study of any one, or any few, particular breaks, I concluded—*nothing :* from a study of a whole series of density-results I only concluded that it was advisable to make other series at other temperatures : from the study of the series of four different temperatures my conclusions were merely that I had 'strong presumptive evidence' of the existence of changes, but that confirmatory evidence from the study of independent properties was necessary before such changes could be regarded as established ; and it was only after obtaining such evidence from the study of three or four other properties that I venture to call this evidence proof, and then only with the oft-repeated caution 'that many of these changes were admittedly of a very doubtful nature'" (*ibid.*, p. 143).

This statement, when read in connection with the diagram, is surely conclusive as to the *fact* that discontinuities in the properties of aqueous solutions of sulphuric acid actually occur at certain definite concentrations, and although it does not prove the correctness of Pickering's views as to their *origin*, it certainly explains the warmth with which he repudiated the conclusions of Mendeléef in reference to the hydrates of alcohol, since these were not supported by one-tenth of the evidence which Pickering was able to supply from his own work on sulphuric acid.

(*g*) *Correlation of Discontinuities with Hydrate Formation.*—Pickering considered that it would be important evidence, not only as to the origin of the discontinuities, but also of their real existence, if it were found that they occur at percentages corresponding to simple molecular proportions. The evidence on this point is shown in Table F (p. 136). This table shows a total of 17 breaks, but there were only 7 cases in which the addition of another molecule of water to the formula of the hydrate would alter the composition sufficiently to throw it outside the limits of error within which the discontinuities could be located. Their molecular compositions were as follows :—

$3H_2SO_4, H_2O$
$3H_2SO_4, 2H_2O$
$H_2SO_4, H_2O$
$2H_2SO_4, 3H_2O$
$H_2SO_4, 2H_2O$
$H_2SO_4, 4H_2O$

and $2H_2SO_4, 11H_2O$.

Pickering was able, moreover, to claim that the coincidence of so many of his "breaks" with the composition of simple hydrates was a direct experimental result and could not be attributed to even a subconscious prejudice in favour of locating them at some exact molecular composition. This claim is set out in the following passage (Paper No. 49) :—

> "That this concordance of position of the changes in curvature with the composition of definite hydrates has not been in any way influenced by a knowledge on my part of the latter, I may confidently affirm, for, throughout nearly the whole of the work, I purposely avoided ascertaining the percentage composition of any hydrates, the only exception to this being the case of the monohydrate, and in spite of my knowledge of its composition, and the probability of its causing some marked change, I noticed no change at all corresponding to it either in the case of the experimental curves for the heat of dissolution or expansion" (*J.C.S.*, vol. 57, p. 128 (1890) ).

This point was elaborated more fully in connection with the diagram reproduced in fig. 7, where the calculated compositions of the hydrates are shown by crosses, whilst the experimental breaks from Paper No. 49 are shown by dots and those from Paper No. 50 by circles.

> "It was not until after my examination of the curves was nearing completion that I calculated the corresponding molecular compositions. I then discovered that their percentages corresponded to hydrates of very simple formulæ, whose exact percentages are marked by crosses on the diagram. Now, considering that the various properties were quite independently examined, I ventured to think that the coincidences afforded overwhelming evidence of some real changes in the solutions at the points indicated, and strong evidence that their occurrence had an intimate connection with the existence of a corresponding hydrate. Wishing, however, to make assurance doubly sure, I carried out, *after my first paper was written*, a series of experiments on the freezing-points. The isolation of the tetrahydrate, whose percentage corresponds to one of the most feebly marked of the changes which I had previously discovered, amply justified my view of their connection with hydrates; but the entire agreement of the minor changes, marked ⊙ on the diagram, with those previously found was perhaps even more satisfactory. Of the 13 changes previously found to exist between 2 and 98 per cent., 9 were confirmed, while as regards the others, which were situated in regions of

very low freezing-point, data were either insufficient or entirely lacking" (*Phil. Mag.*, vol. 33, pp. 134–35 (1892)).

(*h*) *Rücker's Analysis.*—Lupton had attempted to smooth over the discontinuity at 58 per cent. $H_2SO_4$ by making use of a single parabolic equation to cover the range from 50 to 68 per cent. Pickering had no difficulty in showing (R.S. 70) that this alternative representation was not good enough to be accepted, since it gave a complete series of systematic errors; in fact, it is doubtful whether it would ever have been put forward, apart from Lupton's own mistake in multiplying the estimated range of errors by 25. Rücker, however (*Phil. Mag.*, vol. 32, p. 304 (1891)), was much more successful, since he was able to devise an equation which fitted the data so well that Pickering himself (in Paper No. 76) writes as follows:—

> "I may as well state at once that I consider Prof. Rücker's equation to agree with the experimental results just as satisfactorily as my own drawings do; and more satisfactorily perhaps than he asserts; for I have recently revised my estimate of the experimental error, and obtain a value for it somewhat larger than I previously did" (*Phil. Mag.*, vol. 33, p. 136 (1892).

Rücker's equation, in fact, gave an average error of 0·000012 for the densities at 17·925° over the range from 47 to 80·5 per cent. $H_2SO_4$, whilst Pickering's estimate gave a mean error of 0·000011 to 0·000012. Pickering, however, adds the following criticism of the type of equation used by Rücker:

> "Prof. Rücker has not confined himself to the use of the parabola or any other simple equation but has used an equation of a complex and highly artificial form, for which, I believe, there is no precedent, and for which, as an expression of physical facts, there would seem to be . . . no probability whatever. Prof. Rücker first finds an equation (a combination of an exponential curve with a straight line) $y = a + bx - cd^x$, which agrees well with two or three experimental points between 47 and 51 per cent., and again with those between 72 and 80·5 per cent., these two portions constituting together but 3/40ths of the total length of the figure. For all solutions weaker than 47, and stronger than 80·5 per cent., there is no semblance of an agreement; and the whole of the middle portion of the curve between 51 and 72 per cent. lies a little below that given by experiment, and cannot therefore be accepted as a representation of the experiments. In order to rectify this defect, and to raise this portion of

his curve, Prof. Rücker ingrafts on to it a 'hump' by means of a fourth term, $m/(n^x + n^{-x})$. Now it is obviously possible in the case of any figure such as that under discussion, where any changes of curvature which exist are by no means very abrupt, but are only 'minor changes,' to mould a curve to the exact form of the experimental figure, if it is lawful to pare it down or plaster it up whenever it may be necessary, and the mere fact of obtaining such an equation to fit can, I maintain, prove nothing beyond the skill of the operator" (*ibid.*, p. 137).

Pickering criticises this result also on the ground that the data cover only *three* of his breaks and that two of these are close to the limits of the range covered by Rücker's equation, which breaks down almost immediately beyond them. He admits, however, that "Prof. Rücker's equation successfully bridges over . . . the uncertain break at 58 per cent." (p. 141). He attributed his "failure to recognise the sensible continuity of the figure," not to the method, but to the fact that he had "invariably used the lath bent into the simplest form," *i.e.*, without an inflexion, whereas he now found that when bent into an inflected form the lath would fit over the supposed change at 58 per cent., although this curve would not yield a straight line on differentiation.

Pickering's admission of the essential continuity of the density curve at 58 per cent. is of special importance in view of the fact that this is the composition of the tetrahydrate, $H_2SO_4$, $4H_2O$, which contains 57·66 per cent. $H_2SO_4$, and *that this is one of the only two hydrates that could be separated from the solutions by freezing.* Pickering's further comments on Rücker's equation are, however, very illuminating:—

> "The hump in Prof. Rücker's equation begins to be appreciable at a certain point, and again becomes inappreciable at another point, and if the quantities constituting it have any physical meaning at all, they must mean that a certain substance is present, or that certain physical conditions exist, to an appreciable extent between these points only, and are altogether inappreciable throughout the whole of the rest of the solutions, whether stronger or weaker. This is precisely what occurs with a hydrate, according to my views. But let us go further and see at what points this temporary disturbance begins and ceases. Without much error we may say, I think, that any deviation would first begin to be practically appreciable when it attained a magnitude of about a half to a quarter that of the mean experimental error, say, one-third; this would be $4 \times 10^{-6}$ in the present case; and

the point at which the fourth term in the equation attains this magnitude is 72 per cent., almost the exact point at which my break occurs, + 72·8 per cent.; and, further still, diminishes to this magnitude, and again becomes inappreciable, at 49·9 per cent., just where another of my breaks occurs—51 per cent. in the present series of experiments, 49·9 per cent. in the mean of all my experiments. I should, however, not place much value on the concordance in this second case, owing to Prof. Rücker's equation extending such a short distance beyond this point. We are forced, I think, therefore, to regard Prof. Rücker's results as affording additional evidence in favour of my principal contention—the practical starting of a fresh order of things at certain definite points. In fact, the only dilemma on to the horns of which Prof. Rücker's results have placed me is, not that which he imagines (*loc. cit.*, p. 313), but that of having to decide whether the graphic or mathematical method is best suited for discovering those points at which practical changes in solutions occur" (p. 139).

"Prof. Rücker would, no doubt, point out that, although the fourth term in his equation is appreciable throughout a certain range only, it is not actually non-existent in other parts, and that, therefore, there is no true mathematical discontinuity. I never, however, ventured to assert that the changes occurred so suddenly as to prove strict mathematical discontinuity; and I fail entirely to see how such discontinuity could ever be proved or disproved by any experiments which were not absolutely free from experimental error, and which were not infinite in number. Indeed, those hydrates, the presence of which in appreciable quantities conditions a particular rate of change of density, etc., between certain points, cannot be regarded as being entirely absent from other solutions—a view which the principles of dissociation and the gradual removal of such hydrates or substances in the solid or gaseous form from such solutions necessitate (see *Chem. Soc. Trans.*, pp. 22, 23 (1889); pp. 138, 340 (1890))—the only statement which we can make on the strength of experiments is that the amount of the substances present is inappreciable, or otherwise, by those experiments. In the same way the suddenness with which a change of curvature occurs can only be determined within limits comparable with those of the experimental error. My 'breaks,' in fact, are similar to those which we get in most cases of a change of condition, where the practical existence of the break is beyond doubt, although its absolute abruptness may always be doubted, and could certainly never be proved in a strictly mathematical sense" (*ibid.*, p. 140).

How nearly an agreement had been reached at this stage is shown by the fact that Rücker's criticism concluded with the following paragraph :—

> " I have before stated that I think that the curves in some parts—if not discontinuous—have peculiar features which suggest special physical causes. Thus between 84 and 94 per cent. they are obviously nearly straight lines. My doubts have always had reference to the minor changes of curvature and to the use of the ruler in detecting them. They are confirmed by the above investigation " (*Phil. Mag.*, [V], vol. 32, p. 313 (1891)).

If, indeed, it is once admitted that a section of a complex experimental curve may be so nearly linear that it cannot be represented with equal accuracy by any other type of geometrical figure, the whole of Pickering's case for the real existence of " breaks " is conceded, since the ends of the linear section at least must represent " the practical starting of a fresh order of things " so far as the form of the curve is concerned. As regards the origin of the " breaks," there is more room for differences of opinion (see Chapter VII) ; but the real point of contention was whether the properties of a solution were continuous functions of the properties of their components, or whether the simple properties of a mixture were distorted by the incessant intrusion of " hydrates " or of other compounds of solvent and solute. In this respect Rücker's verdict is clearly in favour of Pickering's contention and against those " dissociationists " who contended that there was no evidence for the existence of hydrates in solution, even when a hydrate could be crystallised out from the solution by freezing it (see, for instance, *Phil. Mag.* [V], vol. 32, p. 360 (1891)).

(*i*) *Other Work on Hydrates.*—The two papers (Nos. 76 and 78) from which so many of the preceding quotations have been taken may be regarded as the climax of this period of controversy, although Pickering had still to meet the criticisms of Walker, of H. C. Jones, and of Meyerhoffer, in addition to those of Arrhenius, Lunge, Lupton and Rücker. His later work on hydrates was, however, devoted mainly to accumulating additional evidence from the study of other cases, and included the isolation of a series of hydrates of the amines (No. 86), of two new hydrates of nitric acid (No. 87), of two hydrates of hydrogen chloride, $HCl . 2H_2O$ and $HCl . 3H_2O$ (No. 80), three hydrates of hydrogen bromide, $HBr . 2H_2O$, $HBr . 3H_2O$ and $HBr . 4H_2O$ (No. 92), and three hydrates of hydrogen iodide, $HI . 2H_2O$, $HI . 3H_2O$, and $HI . 4H_2O$ (No. 83), and finally a series of hydrates of the alkalis (No. 88). No new principle was, however,

involved, and this period closes with a correspondence between Pickering and Whetham (R.S. 102), which contains at least the outlines of a treaty of reconciliation between the two warring theories. In or about the year 1897 Pickering took up new work in horticulture, and never returned to the experimental study of the old problem of hydrates in solution.

## CHAPTER VI.

### General Review of Pickering's Work on Hydrates in Solution.

It will be appropriate at this stage, after having summarised Pickering's experimental work and the controversies that followed the publication of his papers on the nature of solutions, to express an opinion on the various points that were raised and debated, as they appear after an interval of more than thirty years.

(*a*) *Real Existence of Discontinuities and of Hydrates in Solution.*—In the first place, the writer of this Memoir is compelled to admit the validity of the evidence which led Pickering to assert that the properties of solutions of sulphuric acid vary in a more or less discontinuous manner with changes of concentration. In particular, it can scarcely be doubted that the "breaks" which he observed in different properties are not distributed casually on the different curves, but occur at definite concentrations. On this point the diagram, which is reproduced as fig. 7 on p. 73 appears to be quite conclusive.

Again, there is no difficulty in admitting that the hydrates which Pickering was able to crystallise out from his solutions by freezing have a real existence in the solution as well as in the solid crystals. Moreover, the fact that some of these hydrates were first detected by Pickering in solution before they were known to exist in the solid state is a strong argument in favour of the view that in certain cases at least the discontinuities correspond with the composition of definite hydrates, and are due to their presence in the solution.

On the other hand, whilst admitting freely the existence in solution, not only of the hydrates which can be crystallised out by freezing, but possibly also of some others which cannot be separated in this way, the writer, in common with other physical chemists, would limit the number of stable hydrates to a much smaller total than the number of breaks which Pickering detected. In particular, he would consider it necessary to seek for some other explanation of all discontinuities which correspond with hydrates of great complexity, including not only hydrates containing a large excess of water or of sulphuric acid, but also complex hydrates of intermediate composition, such as $6H_2SO_4$, $7H_2O$ and $7H_2SO_4$, $6H_2O$. Such an explanation may be sought in a view, which was suggested by the writer of the present Memoir,

in an article on "The Present Position of the Hydrate Theory of Solutions," published in *Science Progress* of October, 1908. This was to the effect that, since a hydrate influences the properties of a series of solutions over a range of concentrations, it may produce more than one discontinuity in this range. The number of hydrates that must be postulated in order to account for the experimental results established by Pickering is then considerably less than the number of discontinuities which he detected, and may perhaps be not very much greater than the number of hydrates that can be separated by freezing the solutions.

(*b*) *Sulphuric Acid as a Hydrate.*—Mendeléef, and those who followed him most closely in developing the "hydrate theory" of solution, regarded the process of solution as essentially chemical in character. Water dissolved a salt because it combined with it, and this combination was supposed to involve practically the whole of the water as well as the whole of the salt. It is not clear whether any limit was fixed to the amount of water that could be held by each molecule of the salt; but it is at least certain that Mendeléef regarded as a definite hydrate a solution of the composition $H_2SO_4$, $150H_2O$, and that Pickering included in his list of hydrates compounds containing 131, 508, 1600 and 5182 $H_2O$.

These extreme views as to the complexity of the hydrates existing in aqueous solutions have never been generally accepted. The prevailing feeling appears to be that such compounds, even if present in the solution, would be so unstable that they could only persist in minute proportions, and would therefore be incapable of producing any abrupt change in the properties of the liquid. On the other hand, when dealing with hydrates of exceptional stability, it is possible to prove that all the conditions which Mendeléef and Pickering postulated are literally fulfilled in the behaviour and properties of the solutions. This is notably true of sulphuric acid, which can be regarded as a monohydrate of sulphur trioxide, $SO_3 . H_2O$. It is only a little less obviously true in the case of the pyrosulphuric acid, $H_2S_2O_7$, which may be written as $2SO_3 . H_2O$; and, even in the case of the dihydrate* $SO_3 . 2H_2O$, it is possible to demonstrate the real existence of the compound from the more obvious properties of the liquid as well as from its behaviour on freezing.

The type of discontinuity which appears in these cases is illustrated in fig. 8,† where the conductivity, density and capillarity of sulphuric acid at different

* The various hydrates are here regarded as derived from sulphur trioxide, and not from sulphuric acid, as in the other parts of this Memoir.

† Lowry, *Science Progress*, p. 140 (July, 1908).

concentrations have been plotted over a range, from 60 to 100 per cent. $SO_3$, which includes—

*the half-hydrate, $SO_3$, $\frac{1}{2}H_2O$
the mono-hydrate, $SO_3$, $H_2O$
the di-hydrate, $SO_3$, $2H_2O$.

In the case of each of these hydrates, discontinuities of the type postulated by Mendeléef and by Pickering are visible to the naked eye without requiring any assistance either from differentiation or from the use of a bent lath.

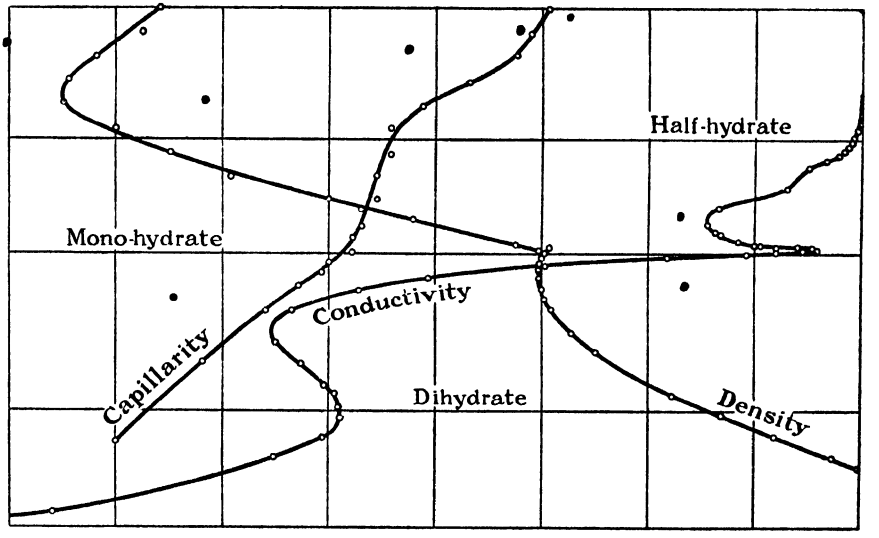



FIG. 8.

(i) *Conductivity.*—The conductivity curves, plotted from the data of Kohlrausch (*Wied. Ann.*, vol. 17, p. 69 (1882)), are those in which the presence of the three hydrates is most clearly indicated. As is well known, both water and sulphur trioxide are excellent insulators when pure; but a mixture of one part of sulphur trioxide with four parts of water is one of the best electrolytic conductors, the specific conductivity rising at this concentration to 0·7388 reciprocal ohm per centimetre cube at 18° C. This composition agrees fairly closely with that of a hydrate of the formula $SO_3$, $18H_2O$; but since mixtures are generally better electrolytes than pure substances, there is no justification for postulating the existence of a hydrate of this composition. On the other hand, when the ratio of the two components is reversed, it is found that a

* The various hydrates are here regarded as derived from sulphur trioxide, and not from sulphuric acid, as in the other parts of this Memoir.

mixture of four parts of sulphur trioxide to one part of water has very little conductivity. The conductivity-curve indeed shows a minimum, which is as sharp as a knife-edge, at a composition corresponding closely with that of the " monohydrate " $SO_3$, $H_2O$. Thus at 81·44 per cent. $SO_3$ the conductivity falls to 0·0080 ohm cm.$^{-1}$, a minimum which is barely 1 per cent. of the maximum recorded above.

The extreme sharpness of this minimum is shown by the fact that the conductivity is increased by 100 per cent. when the solution is mixed with 0·17 per cent. $H_2O$ or 0·23 per cent. $SO_3$. The analytical composition given by Kohlrausch for the minimum is $SO_3 : H_2O = 0·9975 : 1$ ; but it is obvious that no analytical method could provide more than a rough check on the real position of the minimum. We should, indeed, expect that a physico-chemical method of standardisation, depending on adjusting the liquid to a minimum conductivity, would be a far more exact method than any direct process of gravimetric or volumetric analysis. In other words, all the arguments used by Pickering in defending, against the criticisms of Lunge, his process of standardising sulphuric acid by adjustment to maximum freezing-point (p. 11), might be repeated with equal effect in the case of the minimum conductivity.

The " half-hydrate," $2SO_3$, $H_2O$, has an even lower conductivity, 0·0008 ohm cm.$^{-1}$, than the " monohydrate," $SO_3$, $H_2O$ ; but as mixtures of this acid with an excess of sulphur trioxide are also insulators, the minimum is less striking, since the curve merely drops to the axis of zero conductivity and remains there until it reaches the end of the diagram.

On the other hand, the minimum corresponding with the composition of the " dihydrate," $SO_3$, $2H_2O$, at 69 per cent. $SO_3$, shows a diminution of conductivity which is much less pronounced than in the case of the " monohydrate." The actual value of the conductivity at this minimum, 0·0980 ohm cm.$^{-1}$ at 18°, is 12 times as great as in the case of the monohydrate, and 120 times as great as in the case of the " half-hydrate." Moreover, since the addition of $2\frac{1}{2}$ per cent. of $SO_3$ or of $H_2O$ increases the conductivity by only 3 per cent., the minimum is 300 times less sharp than in the case of the " monohydrate." Nevertheless, just as a maximum in a freezing-point curve is in general a clear indication of the crystallisation of a pure compound from the melt, so a minimum conductivity is characteristic of a pure compound ; and the real existence of the " dihydrate " $SO_3$, $2H_2O$ in solution can be inferred with certainty from the course of the conductivity-curve, in spite of the fact that there is no obvious discontinuity at this point of the curve.

(ii) *Density.*—It is a remarkable fact that the density, like the conductivity,

passes through a sharply defined *minimum* at the composition of the "monohydrate." This minimum has been rendered visible in the diagram by plotting the densities on a very open scale. According to Knietsch (*Ber.*, vol. 33, p. 4102 (1901)) the minimum occurs at 81·14 per cent. $SO_3$, whereas the theoretical composition for the monohydrate is 81·63 per cent. $SO_3$; but it is again reasonable to suppose that the true composition of the liquid of minimum density and of the hydrate are probably identical. The density-curve, however, appears to pass smoothly through the compositions both of the half-hydrate and of the dihydrate. Neither of these compounds, therefore, is capable of producing the same gross type of discontinuity as sulphuric acid, although Pickering, by using more refined methods, was able to detect a "break" at the composition of the hydrate $SO_3$, $2H_2O$ in the density curves for four different temperatures. The fact that only one of the three hydrates produces a visible discontinuity in the density-curve may be explained by supposing that the aggregate $SO_3$, $H_2O$ is exceptionally bulky in solution, like the ice molecules in cold water, and that the density of the other hydrates corresponds more closely with their percentage composition.

In addition to the minimum at 100 per cent. $H_2SO_4$, the diagram shows the existence of two maxima, one on each side of the minimum. One of these maxima, which had been studied by Pickering in Paper No. 49, is referred to again in a note (Paper No. 74) on "The Contraction on mixing Sulphuric Acid and Water" (*Chem. News*, vol. 65, pp. 14–15 (1892)). In this note he showed that at temperatures ranging from 8° to 38°, the maximum contraction *per unit weight* occurred at concentrations changing progressively from 67·0 to 70·1 per cent. $H_2SO_4$. The corresponding concentrations for the maximum contraction *per unit volume* were relatively steady at 75·8 to 76·3 per cent. $H_2SO_4$. In the former case there was an obvious shifting of the maximum with rising temperature, which contrasted in a striking manner with the fixity of the concentration of the "breaks," *e.g.*, at 84·4 to 84·5 per cent. $H_2SO_4$ in the four density-curves. Moreover, neither of these maxima occurred at a point corresponding with the composition of the hydrate, $H_2SO_4$, $2H_2O$ = 73·14 per cent. $H_2SO_4$, or with any of the compositions at which breaks had been detected by studying other properties of the solutions.

This result was opposed to the conclusions of Lunge and of Mendeléef, who thought that the maximum coincided with the composition of the dihydrate; but it was in agreement with Pickering's own view that "a maximum point by no means necessarily coincides with a change of curvature," and with his earlier statement, when replying to the criticisms of Arrhenius in Paper No. 33,

where he writes: "It is obvious that the highest and lowest point in a curvilinear figure may occur in the middle of the most regular portion of it, and such points have nothing to do with the changes of curvature here dealt with" (*Phil. Mag.*, vol. 29, p. 433, footnote (1890)). One may, indeed, suppose that the maxima in the density-curves are due to a contraction on mixing two or more pure compounds, and that (like the maxima in the conductivity-curves) they are therefore characteristic of mixtures rather than of homogeneous compounds.

(iii) *Capillarity.*—The capillarity-curve does not show either a maximum or a minimum; but it exhibits well-defined changes of direction at the compositions of the monohydrate and half-hydrate. The curve, although perhaps theoretically continuous, could obviously be represented more accurately by a series of three straight lines than by a single continuous curve. The composition of the dihydrate, however, is not marked at all on this curve.

(c) *Influence of Dissociation.*—The reversibility of the process of "ionisation" was a fundamental postulate of Arrhenius's theory; and although recent years have seen the development of a new theory of complete ionisation, it still remains true that the "electrolytic dissociation" of an ionised salt must be thought of as a reversible process. In the case of Mendeléef's hydrate theory, however, the existence of a reverse action was not an essential feature, but rather a disturbing factor, the existence of which was somewhat grudgingly admitted. Indeed, the introduction into the "hydrate theory" of the idea of reversibility had the effect of destroying the theoretical justification of Mendeléef's "breaks"—a result that was of exceptional importance since the real existence of the breaks themselves was contested. This may perhaps be made clear as follows:—If we assume that the hydrates are all stable, and that dissociation is negligible in each case, we might expect to find each section of the concentration-property diagram exhibiting the properties of a binary mixture of two hydrates, one forming the upper and the other the lower limit of concentration of the section. Each section of the curve would then be straight or gently curved, but with very sharp changes of direction at the junctions, since the curve on one side of the junction would exhibit the properties of mixtures of a hydrate Y with a hydrate X, whilst on the other side it would show the properties of mixtures of Y with a totally different hydrate Z. But if it is admitted that the intermediate hydrate Y dissociates on fusion into the higher and lower hydrates X and Z, it is obvious that the discontinuity must disappear, since all the solutions in this range become ternary mixtures of X, Y and Z, in continuously varying proportions.

Dissociation, therefore, is fatal to the appearance of abrupt "breaks" in the

properties of a series of solutions. Nevertheless, it must be recognised that very rapid alterations of direction and of curvature may occur when hydrates of great stability are formed. This appears to have been the view entertained by Pickering, who admitted that the hydrates of sulphuric acid might dissociate in solution of their own accord at atmospheric temperatures, just as they do in a far more obvious manner at the boiling-point, when all but the very strongest solutions yield a distillate of pure water. Indeed, at the close of his big paper "On the Nature of Solutions," Pickering sets out as one of a series of outstanding problems the following question :

> "How can the fact that the changes occur so sharply at the exact composition of certain hydrates be reconciled with the extent to which we must, I think, necessarily imagine that these hydrates are dissociated, even when the water and salt is present in the exact proportions required for their formation ? "

To this question he replies as follows :—

> "These and other questions I leave for the discussion of abler mathematicians than myself ; my present work has no pretentions beyond being an experimental investigation " (*J.C.S.*, vol. 57, p. 138 (1890) ).

Whilst, however, Pickering paid formal homage to the ideas underlying the law of mass-action, there are many indications that he did not appreciate either the value or the significance of this law.* Thus, in a letter to *Nature* (No. 46), from which two passages have already been quoted, he outbids his opponent by frankly advising chemists not to make use of mathematical formulæ at all, since " the introduction of mathematical formulæ into chemistry almost invariably involves the exclusion of common sense " ; and he closes the letter with a contemptuous reference to the law of mass-action as " what may be termed the $x$ and $y$ theory of chemical action, studied on paper by Guldberg and Waage," a theory which " has led unfortunate chemists into a labyrinth of cumbrous mathematical expressions for erroneous facts, where the common sense of Berthollet would have given them a simple explanation of all the true facts of the case (*Nature*, vol. 40, pp. 344 (1889) ).

In view of the character of these references to the law of mass-action, it is perhaps not surprising that in practice Pickering treated the effects of

* See, for instance, the last paragraph of Paper No. 64 (quoted on p. 142), where Pickering appears to regard it as universally true that an excess of water must necessarily " diminish the relative proportion " of a given hydrate in a solution.

dissociation as of very slight significance. Thus the points obtained by differentiating the experimental numbers were represented by sharply intersecting curves, and their essential continuity was regarded as a matter of remote and theoretical, rather than of immediate and practical, importance. It is, indeed, remarkable that the admission that the hydrates of sulphuric acid were all liable to dissociate was accompanied, not by a restriction in the number of stable hydrates which Mendeléef had postulated, but by an increase in the total number from 4 to 22. It is, therefore, of even more importance than before to inquire how this greatly increased number of "breaks" can be interpreted, whilst admitting that the number of hydrates of marked stability must be strictly limited.

(*d*) *Dissociation of Hydrates on Fusion.*—It is well known that if two metals X and Y form a compound XY, this compound can often be detected by the occurrence of a maximum at the composition XY in the freezing-point curve for the series of binary alloys. If XY were a very stable compound, this maximum would be extremely sharp, since the freezing-point of XY would be depressed abruptly, and to an equivalent extent, by an excess of X or of Y. If, however, the compound XY dissociates on fusion, the maximum becomes rounded to a degree which corresponds with the extent to which the compound is decomposed. Thus a slight dissociation would merely round off the tip of the central peak of the W-shaped diagram, since the dissociation would be repressed almost completely by a slight excess of X or Y. If, however, the dissociation were great, the peak would be replaced by a smoothly rounded plateau or hump; and, if the dissociation were sufficiently great, the freezing-point curve of the compound might be submerged completely beneath the two arms of the V-diagram showing the freezing-points of the two components. In that case the existence of the compound could only be inferred from a study of the properties of the liquid, by methods analogous to those used by Pickering to detect the presence of hydrates which could not be separated from the liquid by freezing.

The absence of complete discontinuity resulting from partial dissociation of a hydrate can be illustrated perfectly by means of Pickering's freezing-point diagram for sulphuric acid and its solutions (Paper No. 50, *J.C.S.*, vol. 57, p. 338 (1890)), which is reproduced here as fig. 1 (p. 38). As this diagram indicates, the existence of the three compounds $H_2SO_4$, $H_2SO_4$, $H_2O$, and $H_2SO_4$, $4H_2O$ can be established by freezing them out from the solutions. Thus from 0 to 37 per cent. $H_2SO_4$ pure ice separates; but from 37 to 68 per cent. the tetrahydrate $H_2SO_4$, $4H_2O$ crystallises out, and from 75 to 92 per cent. the

monohydrate, $H_2SO_4$, $H_2O$. Beyond 93 per cent. anhydrous sulphuric acid is obtained. Subsequent work has shown that the dihydrate, $H_2SO_4$, $2H_2O$, can also be crystallised out in a narrow range of concentrations from 68 to 75 per cent. $H_2SO_4$.

As Pickering pointed out, the freezing-point of sulphuric acid itself is depressed quite abruptly by the small changes of concentration which result from the addition to the acid of a small excess either of $SO_3$ or of $H_2O$. The monohydrate $H_2SO_4$, $H_2O$, however, instead of giving a peak like a knife-edge, produces only a smoothly rounded hump on the curve, the discontinuity at the maximum having been destroyed completely by the partial dissociation of the hydrate when fused. The tetrahydrate, $H_2SO_4$, $4H_2O$, on the other hand, is shown in Pickering's diagram as giving rise to a sharp maximum like sulphuric acid itself. This hydrate, however, melts at a very low temperature, and all the evidence suggests that it is of even smaller stability than the monohydrate, a view that is confirmed by the fact that this section of the freezing-point curve is much broader in its outline than the sections which represent the crystallisation of the monohydrate or of sulphuric acid itself. It will therefore be generally admitted (on the basis of much evidence of a similar character which has been obtained subsequently) that Pickering was probably in error in representing the peak as being formed by the sharp intersection of two freezing-point curves, and that it should have been shown as even more smoothly rounded than the peak for $H_2SO_4$, $H_2O$.

(*e*) *Dissociation of Hydrates at Higher Temperatures.*—The relative extent to which different hydrates (or different intermetallic compounds) dissociate *at the melting point* is indicated, although not quantitatively, by the rounding of the maximum on the freezing-point curve; but this dissociation may be expected to increase when the temperature is raised. Thus in the case of sulphuric acid, it is well known that all solutions containing less than 98·3 per cent. $H_2SO_4$ yield pure water on distillation, that solutions containing more than 98·3 per cent. $H_2SO_4$ yield sulphur trioxide, and finally that a solution containing 98·3 per cent. $H_2SO_4$ distils without change of composition at 338° C. as a mixture of $SO_3$ and $H_2O$ in proportions corresponding with the composition of this maximum-boiling mixture. On distillation, therefore, all the hydrates, *including sulphuric acid itself*, are dissociated into water and sulphur trioxide.

Evidence is, however, also available of the progressive dissociation of these hydrates at much lower temperatures. Thus Kohlrausch records the fact that whilst the conductivity of sulphuric acid falls to a *minimum* at 100 per

cent. $H_2SO_4$, the temperature-coefficient of conductivity rises to a *maximum* value of 4 per cent. per degree at the same concentration. The obvious effect is to flatten out the minimum in the conductivity-curve when the temperature is raised, but to make it even sharper than before on cooling the solution to the freezing-point. It is, therefore, an obvious inference that the conductivity of pure undissociated sulphuric acid would probably be zero, that the trace of conductivity recorded above is due to incipient dissociation, and that the exceptionally rapid increase of conductivity as the temperature rises is caused by a progressive increase in the degree of dissociation of the acid.

(*f*) *Influence of Dissociation on Properties.*—If there were no dissociation at all in a series of hydrates, it is clear that the concentration of each hydrate would rise to 100 per cent. in a solution of identical composition, and fall to 0 per cent. at the composition of the next hydrate of the series. The diagram showing the percentage of each hydrate in liquids of different composition would therefore consist of a series of triangles, the base of each triangle terminating just below the apices of the two adjacent triangles. The general character of the diagram is shown in fig. 9 (*a*), where it has been assumed for the sake

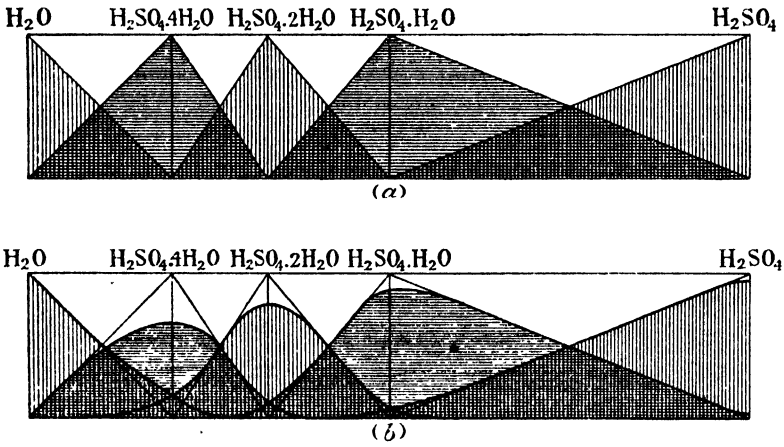



FIG. 9.

of illustration that sulphuric acid forms stable hydrates with 1, 2 and 4 molecules of water, that these do not dissociate at all, and that no other hydrates exist in the solutions.

If, however, a given hydrate were dissociated, say to the extent of 10 per cent., into the two neighbouring hydrates, the apex of the triangle would be rounded off, so as to diminish its height by 10 per cent., whilst there would be a corresponding rounded extension of the base of the two adjacent triangles,

which would each be raised to 5 per cent. on a scale of molecular compositions, instead of falling to 0 per cent. at their point of intersection. The actual concentration of a given hydrate in a series of solutions of this kind would therefore be represented by a curve made up of two straight sides, joined by a "fillet" at the maximum and by two more "fillets" to the axis of zero concentration, as in fig. 9 (*b*).

The detailed consideration of a scheme of this kind will be found in a later section of this Memoir, but it is already clear that, since the diagram represents the chemical constitution of the liquid, and not merely one of its physical properties, any modification of the diagram as a result of the dissociation of the hydrates would affect *all* the physical properties simultaneously, and would therefore satisfy the principal criterion which must be applied to any explanation of Pickering's discontinuities, namely, that they must always occur at the same concentrations, whatever may be the nature of the property investigated.

(*g*) *Analysis of Exponential and Hyperbolic Curves.*—In considering the possibility that the number of discontinuities may exceed the number of hydrates in a given series of solutions, it is instructive to consider what would happen on applying the method of differentiation, or the process of analysis by a bent lath, to a curve (or section of a curve) which was obstinately non-parabolic in form. An excellent example of this type is afforded by the curves with which the writer of this Memoir is most familiar, namely, those which express the influence of the wave-length $\lambda$ on the rotatory power $\alpha$ of an optically active medium. In this case, Drude's formula

$$\alpha = \Sigma \frac{a}{\lambda^2 - b},$$

deduced from theory, is evidently of the correct mathematical form to represent the physical facts. A single term of this formula, *i.e.*, a mere two-constant equation, fits perfectly the data for certain simple compounds such as octyl alcohol (Lowry and Richards, *J.C.S.*, vol. 125, p. 1593 (1924)). The dispersion-curves ($\alpha$ against $\lambda^2$) of these compounds are thereby proved to be true rectangular hyperbolas. Ethyl tartrate, however, gives anomalous curves, exhibiting an inflexion, maximum and reversal of sign. One can imagine a worker with a bent lath, or a mathematician with a table of logarithms attacking these curves in order to determine the minimum number of parabolas that could be used to express them, and perhaps concluding that *four* sections gave an error of suitable magnitude, each section being represented by an equation containing three or four constants, thus requiring perhaps a dozen constants (and three breaks) to express the curve. When, however, the

correct type of formula is used, it is found that an equation containing two terms of opposite sign, and including only four arbitrary constants, represents the data perfectly from end to end without a single break (Lowry and Cutter, *J.C.S.*, vol. 121, p. 532 (1922) ).

Even more relevant, though less familiar to the writer, is the case of the exponential type of curve which expresses the law of probabilities, or the distribution of optical densities in a medium exhibiting a selective absorption of light. This curve (fig. 10, *a*) contains a maximum M, two points of inflexion I and J, and two sections K and L approaching asymptotically to the horizontal axis. As Pickering pointed out in a passage (*Phil. Mag.*, vol. 33, p. 451 (1892)) which has already been quoted on p. 69, no amount of differentiation could convert a continuous curve of this or any other kind into a discontinuous series of straight lines if the course of the curve were known with perfect accuracy; but since the "sides" I and J of such a curve can in practice be drawn better by using a straight-edge than by making use of "French curves," it is clear that the margin of inaccuracy in the experimental values need not be very wide in order to make it possible to draw the first differentials in the form of five distinct sections, two of which, I′ and J′ (fig. 10*b*), would be

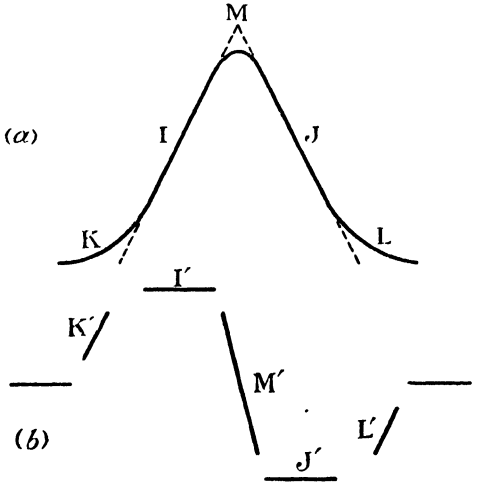



FIG. 10.

shown as horizontal straight lines (corresponding with the nearly linear character of the two portions of the original curve on either side of the two points of inflexion), whilst the other three sections might be drawn either as straight lines or as curves. The mere refusal of the curve to adopt a parabolic form would then lead inevitably to the appearance of discontinuities, unless

the experimental points were so close together, and so exactly located, as to enable the essential continuity of the curve to be recognised even after differentiation.

(*h*) *Significance of Rücker's Exponential Terms.*—It will be recalled that Rücker succeeded in smoothing out one of the least-marked of Pickering's discontinuities by superposing on his original curve, $s = a + bx + cd^x$ (which itself contained an exponential term), a smaller exponential term of the type $m/(n^x + n^{-x})$. The addition of this subsidiary term had the effect of grafting on a hump, which raised the calculated value for the density of the acid by

0·000055 at 61·01 per cent.,
0·000010 at 52·91 and 69·10 per cent.,
0·000002 at 46·94 and 74·98 per cent.,

and by inappreciable amounts of higher and lower concentrations. After making this addition, the values calculated from the equation agreed with the observations over a range which covered the supposed breaks at 51, 58, 72·8 and 78 per cent.

Pickering commenting on this equation in Paper No. 76, in a passage (*Phil. Mag.*, vol. 33, p. 139 (1892)) which has already been quoted on p. 77, suggests that the beginning and the ending of the "hump" represent "the practical starting of a fresh order of things" at these particular points. So far as I am aware, it was always assumed by Pickering and by other workers who accepted his "hydrate theory" of solutions, that this "fresh order of things" must be one resulting from the formation of a hydrate corresponding in composition with the concentration at which the break occurs. Pickering's contention certainly contains, however, at least the rudiments of an alternative explanation of the breaks. Thus we may suppose that a hydrate of considerable stability nevertheless dissociates slightly on fusion. If the dissociation is only slight, however, it will be easily repressed by a small excess of either component, and in practice will be limited to a very narrow range of concentrations. The effect of dissociation will then be twofold.

(i) In the first place, it will destroy absolutely the discontinuity at the precise composition of the hydrate, since at the point of maximum dissociation the rate of change of the degree of dissociation will be at a minimum. The theoretical position of this discontinuity may, however, still be inferred from the adjacent sections of the curve, where the effects of dissociation are no longer appreciable; in other words, the original position of the apex of a triangle can be located, even after the apex itself has been replaced by a

rounded "fillet," by producing the straight remnants of the two adjacent sides until they intersect.

(ii) In the second place, the two points at which dissociation ceases to be appreciable will themselves become new points of discontinuity, lying more or less symmetrically on either side of the theoretical composition of the hydrate.

This conclusion resembles closely the suggestion which I made in 1908 (*Science Progress*, p. 144, July, 1908) that the formation of the tetrahydrate $H_2SO_4$, $4H_2O$ "*may be responsible, not only for the break at* 59 *per cent.* $H_2SO_4$, *corresponding with the composition of the hydrate, but also for the adjacent breaks at* 50 *per cent. and* 72 *per cent.* $H_2SO_4$." At that time it was thought that the two discontinuities on either side of the maximum might represent the points at which a given hydrate began to appear in and to disappear from the solution. The considerations set out above now indicate that these two discontinuities probably represent *the limits of dissociation* of the hydrate in presence of an excess of one or other of its constituents, and that its range of existence in the solution would be indicated by two more distant "breaks." The two alternative views, that the discontinuities are due to the appearance and disappearance of hydrates, or to the beginning and ending of their dissociation, are not so different as might appear at first sight, since it can be seen that in fig. 10 (*b*) the limits of dissociation of the dihydrate $H_2SO_4$, $2H_2O$ are identical with the points at which the monohydrate and tetrahydrate begin to appear in the solution.

It is probably not a mere coincidence that the small exponential term, which Rücker added to his equation in order to graft a "hump" on to his original smooth curve, is identical in type with the equation that would be required in order to represent one of the debased triangles of fig. 10 (*b*). Thus, if we identify the maximum value of the "hump" in Rücker's equation with the composition of a hydrate, and its limits with the points at which the dissociation of the hydrate (and, therefore, also the concentration of two of the adjacent hydrates) becomes inappreciable, we are probably quite near to a complete mathematical solution of Pickering's problem. Since, however, even the number of hydrates present in the solutions is not known, and the extent to which they dissociate is entirely unknown, all the constants of the equations would have to be determined empirically. We may therefore plead Mr. Lupton's excuse that "the hurry of modern life," in the present day, as 25 years ago, precludes the undertaking of so monumental a task as the deduction of a complete mathematical expression for the various curves in which Pickering detected his discontinuities.

(*j*) *Detailed Analysis of Pickering's Discontinuities.*—Pickering's freezing-point curve for aqueous solutions of sulphuric acid is much more highly specialised than those which represent the other physical properties, since it is obviously composed of four distinct sections, and these yielded a further "crop" of discontinuities on analysis. The total of 22 discontinuities which Pickering detected in this series of solutions may therefore be discussed most conveniently under the titles of the four compounds which successively appear as the solid phase when the solutions are cooled, as set out on p. 138 in an extract from Paper No. 50 (*J.C.S.*, vol. 57, p. 331-69 (1890) ).

(i) *Sulphuric Acid.*—A most obvious kink occurred at 100 per cent. $H_2SO_4$, but Pickering claimed also to have detected at 100·63 per cent. $H_2SO_4$* "a sudden change of curvature of almost as marked a character as any other in the whole series." "The angle made by the two sections of this branch is re-entrant and the change of curvature is therefore unquestionable" (p. 350). Discontinuities were also detected at 99·5 and 98·6 per cent., and it was claimed that these results indicated the presence of the compounds

$$36H_2SO_4, SO_3$$
$$36H_2SO_4, H_2O$$
$$12H_2SO_4, H_2O.$$

Pickering himself says, however, in reference to the evidence for the existence of this group of hydrates, that "these indications must be accepted with great caution" (p. 353). The first of these hydrates is indeed purely speculative, since 100·6 per cent. $H_2SO_4$ corresponds to only 30 instead of 36 molecules of $H_2SO_4$ to 1 molecule of $SO_3$, which requires 100·5 per cent. $H_2SO_4$ as the apparent strength of the solution. In any case, if the existence of a discontinuity at a composition so near to that of sulphuric acid itself is attributed to the formation of a new hydrate, we must suppose not only that this heavy complex (of molecular weight about 3600) exists in the solution, but also that it is the predominant constituent of all samples of sulphuric acid which contain a small excess of sulphur trioxide. On the other hand, this predominant hydrate must disappear almost completely on dilution with a minute trace of water, since otherwise it could scarcely be expected to make the properties of the solutions change with any degree of abruptness at the composition indicated. It is, indeed, much easier for a modern reader to believe that the

* This is a conventional method of expressing the strength of an acid containing an excess of sulphur trioxide as compared with that required to produce sulphuric acid.

discontinuities in question depended on errors of observation,* or on some secondary change in the properties of the solution, rather than on a complete rearrangement of the molecular structure of the acid.

The supposed discontinuities at 99·5 and 98·6 per cent. are even more doubtful, since Pickering admits (p. 349) that "down to about 97 per cent. the experimental points can be represented by a gentle curve differing but little, though appreciably, from a straight line"; but this "would represent seven consecutive determinations as being all too low to the extent of as much as 0°·4." Since the irregularity here is an abrupt drop of all the points over a range of 1 per cent., giving a line which forms a step with the main curve at each end, the only explanation of the breaks which is consistent with any known theory either of hydration or of ionisation is the existence of untraced sources of error, such as those which led to the development of minute sinuosities in the curves representing the heats of dissolution of salts.

(ii) *Monohydrate.*—The monohydrate, $H_2SO_4$, $H_2O$, produces a smoothly rounded maximum at 84·5 per cent. $H_2SO_4$ and + 8·53° C. The study of this compound is of special interest as illustrating the effects of Pickering's method of analysis when actually applied to a dissociating hydrate. In particular, it affords full experimental confirmation of the conclusion arrived at above, that the discontinuity at the composition of the hydrate disappears completely, but may be replaced by a pair of discontinuities at the limits of dissociation, together with a more distant pair of discontinuities at the limits of existence of the hydrate.

In the present instance Pickering had no difficulty in detecting changes of curvature in the freezing-point curve on either side of the maximum, but it was with some difficulty that the maximum itself could be persuaded to appear as a discontinuity.

> "The maximum here is rounded off in a way which affords a striking contrast to the maximum at $H_2SO_4$" (*J.C.S.*, vol. 57, p. 339 (1890)).
>
> "In some of the possible ways of drawing this portion of the figure we get indications of a change of curvature at the apex, 84·6 per cent.; in others we do not. That the monohydrate exists is unquestionable; that it exists in solution is also, I maintain, a necessary consequence of our being able to obtain it from a solution, and it appears curious, at first sight,

* The break at 100·63 per cent. did not depend on differentiation, but could be seen as an obvious kink in the freezing-point curve for the concentrations from 100 to 101 per cent. $H_2SO_4$.

that its existence should be marked by a change of curvature of such an uncertain nature" (*ibid.*, p. 348).

Clearer evidence of a change at 84·6 per cent. was obtained on differentiation, "the differential from 86 to 82 per cent. consisting of two straight lines meeting at this point; but the change is by no means well marked, and is in striking contrast with the change at 82 per cent." (*ibid.*, p. 348).

From these remarks it is clear that the sharp discontinuity at 84·6 per cent. had been destroyed by dissociation, but that its original position could still be inferred from a study of the adjacent parts of the freezing-point curve, which were obviously made use of in the process of differentiation. Its place was taken, however, by two pairs of discontinuities on either side of the maximum, one pair being about 2 per cent. and the other about 5 per cent. above and below the maximum at 84·5 per cent. From this point of view, it is very interesting to notice that the "sharp changes of curvature" at 82 and 86 per cent. were not recorded in any of the seven properties studied previously, but were detected first in the freezing-point curves. There is therefore good reason to suspect that they represent the working limits of the correction for dissociation of the monohydrate, $H_2SO_4$, $H_2O$, rather than the rising into predominance of the very complex hypothetical hydrates represented by the formulæ

$$6H_2SO_4, 7H_2O \text{ and } 7H_2SO_4, 6H_2O^*.$$

Similar remarks may be made in reference to the other two symmetrically placed discontinuities at 90 and 79 per cent. respectively. These "are of a very marked character, and require no aid from differentiation to render them evident. They are both marked by the existence of re-entrant angles" (p. 349). Changes at two points of similar composition, namely,

88·7 instead of 89·8 per cent.,
78·4 instead of 79·0 per cent.,

had already been detected by other methods (see Table F), and had been attributed to hydrates of the formulæ

$3H_2SO_4, 2H_2O$ (theory 89·1 per cent.)
$2H_2SO_4, 3H_2O$ (theory 78·4 per cent.)·

but, since these hydrates also have never been isolated in the solid state, it is just as plausible to think that they may be due to a final stage in the

* Pickering, making use of a rough "rule of six," writes these as $6(H_2SO_4, H_2O) + H_2SO_4$, and $6(H_2SO_4, H_2O) + H_2O$ (p. 353), and so brings them into relation with the compounds containing $36H_2SO_4$, which have already been referred to above (p. 95).

dissociation of the monohydrate, the predominance of which in the whole range from 74 to 92 per cent. $H_2SO_4$ is proved by the behaviour of the liquids in depositing crystals of this compound on cooling.

(iii) *Tetrahydrate.*—The tetrahydrate, $H_2SO_4$, $4H_2O$, contains 57·66 per cent. $H_2SO_4$, and melts at — 25°, giving rise to a well-marked maximum in the freezing-point curve. The same compound also crystallises out from all solutions containing from 37 to 68 per cent. $H_2SO_4$; but the freezing-points were so low that accurate measurements were no longer possible, and no attempt was made to detect discontinuities in the freezing-point curve on either side of the maximum.

We have already seen, from Pickering's discussions with Lupton and with Rücker, that the discontinuity in the *density-curves* at the actual composition of the tetrahydrate was "of a very doubtful character" (*J.C.S.*, vol. 57, p. 76 (1890)), in spite of the fact that this was one of the only two hydrates which Pickering was able to isolate by freezing. Thus, he writes in Paper No. 70 as follows:—

> "It is by some strange accident that Mr. Lupton was led to attack the only one break in the density-curves which I mentioned as being 'of a very doubtful character'; and it is by a still stranger accident that the only hydrate on which his investigation 'seems to throw very grave suspicion' is the very one which actually *does* exist, which has been isolated in the crystalline condition, and to the isolation of which I was led by a reliance on the very method which Mr. Lupton considers to be fallacious and worthless" (*Phil. Mag.*, vol. 32, pp. 93–94 (1891)).

Pickering claimed, however, to have observed an "undoubted change in the curvature" at the maximum in the *freezing-point curve*, just as in the case of sulphuric acid itself (p. 353). His drawing, therefore, shows a sharp chisel-edge at the summit of the broad hump of the tetrahydrate section of the curve. Since, however, there are only two experimental readings (at 55·1 and 56·9 per cent.) in the range of 10 per cent. (from 50 to 60 per cent.) which includes the maximum, this method of representation is entirely arbitrary; and it is almost certainly incorrect, since the tetrahydrate is even less stable than the monohydrate, and may therefore be expected to give rise to an even flatter maximum. We can, indeed, represent the facts equally well by assigning to the maximum at 57·5 per cent. $H_2SO_4$ the smoothly rounded contour which modern theory demands, and which the doubtful character of the "break" in the density-curve would lead us to expect.

We may therefore conclude (in strict agreement with the views set out above as to the influence of dissociation on the behaviour of a hydrate) that the tetrahydrate is incapable of producing any strong discontinuity in the properties of solutions of its own composition, although its presence must be admitted, and its influence recognised, over the whole range of concentrations within which it can be crystallised out from the solutions by cooling. In the case of the tetrahydrate, the freezing-points were not measured with sufficient accuracy to permit of the detection of discontinuities in other parts of its range of stability; but, by studying the properties of the solutions at atmospheric temperatures, Pickering had already detected two additional discontinuities at 49·92 per cent. and 73·04 per cent. $H_2SO_4$. Of these discontinuities, the former, at 50 per cent. $H_2SO_4$, occurs at a point corresponding with the composition of a hydrate $H_2SO_4$, $5\frac{1}{2}H_2O$, which has not been isolated, and which we should scarcely expect to find in the solution. On the other hand, the discontinuity at 73·04 per cent. $H_2SO_4$ corresponds closely with the composition of a dihydrate $H_2SO_4$, $2H_2O$, which has since been isolated by freezing (Biron, *Journ. Russ*, vol. 31, p. 517 (1899); Giran, *C. R.*, vol. 157, p. 221 (1913)), its low melting-point, — 37° C., and the very narrow range of concentrations, from 68 to 75 per cent. $H_2SO_4$, within which it is stable, having hindered its detection in earlier experiments. There is, therefore, a sound experimental reason for attributing the discontinuity at 73 per cent. $H_2SO_4$ to the presence of a dihydrate in solution. But, since the dihydrate melts at a lower temperature than the monohydrate, $H_2SO_4$, $H_2O$, or the tetrahydrate, $H_2SO_4$, $4H_2O$, and is evidently even less stable than the weaker of these two compounds, it is not very likely that it could have produced a definite discontinuity in the properties of the solutions when examined at a temperature 60° above its highest melting-point. On the other hand, it is noteworthy that Rücker and Pickering both associated the well-marked discontinuities at 73 per cent. and 50 per cent. $H_2O$ with the "very doubtful" discontinuity at 58 per cent. These three compositions correspond, in fact, with the upper and lower limits and the maximum of Rücker's "hump"; and it was Pickering himself who added that, if this hump had any physical significance at all, it must mark the limits within which "a certain substance is present or . . . certain physical conditions exist to an appreciable extent" in the solutions. It is, therefore, at least equally reasonable to attribute both discontinuities, at 73 per cent. and at 50 per cent., to the dissociation of the tetrahydrate, instead of to the exclusive influence of the very unstable dihydrate and of an unknown hydrate with $5\frac{1}{2}H_2O$.

(iv) *Solutions depositing Ice.*—In Pickering's experiments (Paper No. 50) all

the solutions containing less than 37 per cent. $H_2SO_4$ deposited ice on freezing. Nevertheless, he was able to record eight more discontinuities in the range from 40 to 0 per cent. $H_2SO_4$, as follows :

| | | | |
|---|---|---|---|
| 38·58 | per cent. | ($H_2SO_4$, | $9H_2O$ = 37·701 per cent.) |
| 29·5 or 29·59 | per cent. | ($H_2SO_4$, | $13H_2O$ = 29·526 per cent.) |
| 17·2 or 18·92 | per cent. | ($H_2SO_4$, | $24H_2O$ = 18·492 per cent.) |
| 8·7 and 8·7 | per cent. | ($H_2SO_4$, | $58H_2O$ = 8·585 per cent.) |
| 4·0 or 3·99 | per cent. | ($H_2SO_4$, | $130H_2O$ = 4·021 per cent.) |
| 1·0 or 1·06 | per cent. | ($H_2SO_4$, | $510H_2O$ = 1·057 per cent.) |
| 0·35 or 0·34 | per cent. | ($H_2SO_4$, | $1500H_2O$ = 0·362 per cent.) |
| 0·07 or 0·105 | per cent. | ($H_2SO_4$, | $8000H_2O$ = 0·068 per cent.) |

In this list, the earlier percentages are those at which discontinuities were detected in the freezing-point curves of Paper No. 50 ; the later ones are those derived from a study of " other properties " in Paper No. 49.

The first three discontinuities may actually be due to the formation and dissociation of some one relatively stable hydrate, which cannot be isolated by freezing. This possibility can be justified in Pickering's own words as follows : —

> " The question which naturally suggests itself at first is, why, if there are yet other compounds, as my former work implies, do they also not crystallise out, each forming an independent curve with a rising and falling branch ? The answer is obvious. Different substances, as is well known, differ widely in the ease with which they pass from the liquid to the solid condition ; a solution of a composition corresponding to a definite hydrate, say, $H_2SO_4$, $9H_2O$, will contain not only this hydrate, but a certain proportion of its products of decomposition, and, at a given temperature, it may be supersaturated with the $9H_2O$ hydrate, and with higher and lower ones ; one of these latter, although present in much smaller proportions than the $9H_2O$ hydrate, will separate out in preference to it, if it assumes the solid condition more easily. In fact, the crystallisation of a particular hydrate must be determined by the ease with which it assumes the solid condition, the relative proportions in which it is present, its solubility in the other substances present, and the temperature of its normal freezing-point " (*J.C.S.*, vol. 57, pp. 350–51 (1890) ).

This view cannot, however, be extended to the discontinuities recorded in the more dilute solutions, containing less than 10 per cent. $H_2SO_4$, and

therefore corresponding with the composition of hydrates containing $50H_2O$ or more. Aggregates such as

$$H_2SO_4,\ 510H_2O,$$
$$H_2SO_4,\ 1500H_2O,$$
$$H_2SO_4,\ 5000H_2O,$$

with molecular weights up to nearly 100,000, would surely be colloidal in character; and although the formation of complex aggregates in presence of a large excess of one component is by no means impossible, it is most unlikely that a hydrate containing some 500 molecules of water would predominate so strongly over its neighbours with 499 or 501 molecules as to give rise to any perceptible discontinuity. These discontinuities, at least, must therefore be attributed to some other cause than the abrupt appearance and disappearance of new hydrates.

This general argument can be reinforced by a study of the thermo-chemical data. Thus the formation of sulphuric acid from its anhydride liberates 19,400 calories, but only 6400 calories are liberated in converting sulphuric acid into its monohydrate, $H_2SO_4$, $H_2O$. The additional heat liberated in the formation of the dihydrate, $H_2SO_4$, $2H_2O$, and the tetrahydrate, $H_2SO_4$, $4H_2O$, is only 3040 and 2700 calories for the additional $H_2O$ and $2H_2O$ respectively. In the case of the most complex hydrate with $8000H_2O$, the heat of formation amounts only to 3 or 4 calories per molecule of water. It is, therefore, inconceivable on thermochemical as well as on general grounds that such a compound could have any marked degree of stability, and it is hardly to be wondered at that the formulation of such a complex should be regarded almost as a *reductio ad absurdum* of the hydrate theory of solutions.

In seeking for an alternative explanation of the discontinuities in dilute solutions, it is instructive to notice that whilst the middle sections of the curves could usually be reduced to a linear form by one or two differentiations, even the second differentiation failed to reduce their end portions to a linear form. I feel sure, therefore, that the discontinuities which Pickering claimed to have detected, both in very weak and in very strong solution (and which present such great theoretical difficulties when their origin is considered), were not mathematical discontinuities, but were merely the result of attempting to reduce to the form of parabolas experimental curves which obeyed some different law, but which could not be investigated satisfactorily on account of the extreme magnitude of the ratio of the two constituents. Alternatively this conclusion can be expressed by saying that a continuous process, such as the last stages of electrolytic dissociation, might very well turn the course of

the curve in such a way as to produce a " break " in the analysis of the curve into parabolas, without the intervention of a new hydrate or other novel type of molecule in the solution.

In reviewing the whole series of hydrates, an additional argument may be used. Thus the simpler compounds $H_2SO_4$, $H_2SO_4,H_2O$, $H_2SO_4,2H_2O$ and $H_2SO_4,4H_2O$, which have been isolated by freezing the solutions, exhibit a small progressive increase of molecular weight from 98 to 116, 134 and 160. The more complex hydrates postulated by Pickering range in molecular weight up to 144,242. If we were to admit that these complex hydrates are interposed between the simpler ones in the manner suggested by Pickering, and in such a way as to become successively the dominant components of the solution, the addition of water to sulphuric acid would result in alternations of molecular weight from 98 to several thousands. The relative smoothness of the freezing-point curves shows that these violent alternations do not exist. We may, therefore, conclude once more that the more complex hydrates, which are still unknown in the solid state, do not exist to any marked extent in solution; and that the discontinuities recorded in the various properties of the solutions must be attributed to the influence of a relatively small number of simple and stable hydrates, instead of to a series of hydrates equal in number to the series of discontinuities and occurring at identical compositions.

(*k*) *General Conclusions.*—The general results arrived at in the preceding discussion may be set out in five propositions, as follows :—

(1) *If a hydrate does not dissociate it will produce a well-marked point of discontinuity at its theoretical composition.*

(2) *In the case of a dissociating hydrate there will be no discontinuity at the actual composition of the hydrate.*

(3) *The curves on either side would, however, probably intersect at this composition if extrapolated.* A discontinuity would then be revealed most clearly by avoiding the points nearest to the actual composition of the hydrate.

(4) *If the dissociation is not too great, discontinuities may be detected by Pickering's method at the points where the dissociation of a given hydrate ceases to be appreciable.* Between these points two curves, which would intersect if produced, are joined by a continuous loop, like the " fillet " in an engineering drawing; the discontinuities represent the two ends of this loop.

(5) *In the case of a dissociating hydrate two pairs of discontinuities might be*

*detected on each side of the theoretical composition.* The exponential figure, which represents the concentration of a dissociating hydrate in solutions of different strengths, must contain two points of inflexion, and, therefore, two linear sections; the ends of these two lines would probably be shown up as a series of four discontinuities by the use of a bent lath if the hump were sufficiently pronounced.

These five propositions lead to the curious conclusion that the composition of a dissociating hydrate is only indicated by "a very uncertain break," but may give rise to much more obvious breaks on either side of the theoretical composition. These more obvious breaks cannot, however, be identified with new hydrates, as Pickering supposed, but are merely secondary effects of the dissociation of the hydrate which gives the "uncertain break" at an intermediate composition. This conclusion, although directly opposed to Pickering's own interpretation, agrees very closely with his unconscious diagnosis. In Paper No. 76, for instance, the "uncertain break" at the composition of the *tetrahydrate* (58 per cent.) is discussed in conjunction with the collateral breaks at 73 and 51 per cent., which Pickering admits (as a matter of mathematics, but not of physics or chemistry) to be a secondary effect of the hump at 58 per cent. In Paper No. 50 there was a similar bracketing of the "uncertain" change of curvature at the theoretical composition (84·5 per cent.) of the *monohydrate* by "palpable" "sudden changes" at 82 and 86 per cent., which we may now regard as secondary effects of the dissociation of the monohydrate, instead of primary effects of two new hydrates containing 6 : 7 or 7 : 6 $H_2SO_4 : H_2O$. It will also be recalled that Pickering himself modified his (insufficient) experimental data in order to assign symmetrical formulæ to hydrates represented by breaks at 99·5 and 100·6 per cent. $H_2SO_4$, so that these two breaks can perhaps be regarded as related in some way to the dissociation of *sulphuric acid* itself, although the evidence is more scanty than in the two preceding cases.

If these arguments are admitted, it will be seen that the number of hydrates ought to be much fewer than the number of "discontinuities." In particular, the three hydrates which Pickering was able to separate out by freezing can be used to account for 11 of the 22 breaks which he claimed to have detected. Of the other 11, (i) three are placed between sulphuric acid and its monohydrate (at 98·6, 97·0 and 93·9 per cent.); (ii) three more (38·6, 29·6, 18·9 per cent.) are placed in the region of moderate dilution, near to and on either side of the maximum of electrical conductivity at 30 per cent. $H_2SO_4$; (iii) five more

occur at dilutions from 29 to 8000 $H_2O$. It is a matter of pure speculation whether it is necessary to assume the existence of a hydrate with less than one molecular proportion of water, and of another with more than four, in order to explain the discontinuities cited under (i) and (ii) above. My own opinion would not be opposed to such an assumption; but as regards the breaks in dilute solutions cited under (iii) above, no similar explanation can be given. I should therefore prefer to suppose that (when the vapour pressure of the solution is nearly constant) the hydration and electrolytic dissociation of the acid proceed according to a regular law, but not according to one which readily conforms to the laws of flexure of a bent lath, which is, after all, a mechanical and not a chemical property of matter.

It will be observed that the explanations given above are all in harmony with the view that the discontinuities detected by Pickering are real, and conform to the test which was the key to all his arguments in that the discontinuities *occur at similar concentrations* when derived from the study of different properties.

## CHAPTER VII.

### Colloid Chemistry.

Pickering's horticultural interests led him to make a close study of some problems which can be grouped conveniently under the general heading of "Colloid Chemistry." These studies formed the subject of three papers. No. 108 on "Emulsions," No. 125 on "The Detergent Action of Soap," and No. 127 on "Flocculation."

(a) The work on emulsions can be summarised best by quotations from the paper (*J.C.S.*, vol. 91, pp. 2001–21 (1907)).

> "When any liquid insoluble in water is mixed with the latter and broken up into minute globules, as when it is forced through a syringe, the globules remain more or less permanently emulsified whenever the water contains soap or some other emulsifying agent in solution. The whole of the liquid, however, is not an emulsion, properly so called, but a mixture of the emulsion with excess of soap solution; on standing, the true emulsion separates, and, if the substance emulsified is lighter than water, rises to the surface. This is precisely analogous to the separation of cream from milk" (p. 2001–02).
>
> "For each temperature, and for each proportion of paraffin oil, the quantity of emulsifier which must be present ranges between certain definite limits; thus, to emulsify 75 volumes of oil with 25 volumes of water, the latter must contain from about 0·7 to 1·8 per cent. of potash soap" (p. 2002).
>
> "Emulsification appears to occur suddenly: when soap is used, and the solution is not very strong, it is possible to judge immediately by the working of the syringe whether it has occurred or not; but when it has not occurred, no continuance of the pumping, without altering other conditions, will produce emulsification" (p. 2002).
>
> "The increase of viscosity on emulsification is easily explained by the great increase in the extent of the oil-water surface on the oil being reduced to minute globules. An ordinary emulsion, although containing 70 to 80 per cent. of mobile paraffin oil, is as viscid as thick cream, and its viscidity increases with the proportion of oil present, even when that oil is a very light one, such as a benzine. With very high percentages of oil, the emulsion becomes practically solid, resembling a blanc-mange. Emulsions

containing as much as 99 per cent. of ordinary lighting oil have been made, the remaining 1 per cent. being a 1 per cent. solution of soap. Such strong emulsions, however, cannot be obtained directly; they must be made by taking a weaker emulsion, and gradually increasing the paraffin in it, churning it after each addition. Even these strongest emulsions are true emulsions of the oil; that is, it is the oil which is in globules, and the water, although so small in amount, which is the menstruum. There are no signs of the existence of an emulsion of water in oil. As a consequence of this, an emulsion (even a 99 per cent. one) will mix perfectly with water to form a weaker emulsion, but it will not mix with more paraffin, unless, of course, that paraffin is emulsified with it by further churning" (pp. 2002–03).

"Apparently, a precipitate consisting of an insoluble substance which is wetted more easily by water than by oil, if in a sufficiently fine state of division, will equally act as an emulsifier. . . . Emulsions made with an insoluble emulsifier are in every respect similar to those made with soap, etc., except that they never seem to de-emulsify spontaneously" (pp. 2020–21). "Besides the ease of manufacture, and the absence of spontaneous de-emulsifications, these emulsions possess the advantage of not being decomposed by the addition of caustic soda, as are emulsions with soap, and caustic soda is required when the emulsion is used as a winter wash for trees" (p. 2021.)

"Solids which are not sufficiently fine-grained to emulsify will, in many cases, when present in considerable proportions, form quasi-emulsions. In these, the particles of oil are merely entangled with the particles of solid, and may be separated from them by such simple means as dilution with water. Lime is an instance of a substance which forms a quasi-emulsion which can be used for spraying purposes. Other substances, including many recently formed precipitates, and, probably, all crystalline solids, seem to be incapable of forming even quasi-emulsions" (p. 2021).

(*b*) Pickering's views on the detergent action of soap are summarised as follows:—

"The detergent action of soap is due, in part, to its power of emulsifying oil, the oil globules of which become enclosed in a pellicle which prevents them rendering contiguous substances oily; in part to the lowness of surface tension between oil and soap solution; and perhaps in part to the union of dirt with the acid soap produced by hydrolysis. A more important

factor is that oils, even paraffin oils, dissolve in soap to form soluble compounds, which contain in some cases nearly equal weights of oil and soap. . . . The compound formed is not decomposed by excess of water, but dilution of the soap previous to its treatment with oil results in much less oil combining with it, because a larger proportion of the latter becomes emulsified."

"The combination of soap with oil is accompanied by a series of physical changes explicable by the nature of the products formed—a soluble, limpid compound, on the one hand, and an emulsion, which is almost solid, on the other. The proportions of oil and soap which will unite with each other depend on the chemical, and not merely physical, nature of the reagents, and an appreciable heat-disturbance, either negative or positive, accompanies the reaction. Naphthalene does not behave towards soap as paraffin does, but dissolves in it to a limited extent, some of the crystalline substance separating on cooling or dilution. The presence of naphthalene decreases the amount of paraffin dissolved by soap" (*J.C.S.*, vol. 111, p. 101 (1917)).

(*c*) The experiments on flocculation arose out of the observation that when clay soils are frozen, a change occurs in the ultimate particles, which, when agitated with water, are found to sink more rapidly than before. This is due to the shrinking of the individual particles, and their agglomeration into clots. It is the reverse of the change occurring in flocculation by acids, where there is an increase in the size of the individual particles. The basic copper sulphates, copper hydroxide, ferric hydroxide and alumina all behave in the same way as clay. Quantitative experiments showed that the volume of sediment deposited by a suspension of clay, after freezing for two hours at −18°, was only about 19 per cent. of the volume deposited from a similar sample which was not frozen.

The experiments on flocculation by freezing were followed by others on the flocculation of kaolin by acids, alkalis and salts. The concentrations, in equivalents per litre, at which flocculation was complete were approximately as follows:—

| | |
|---|---|
| 0·0003 N to 0·001 N ..... | $\frac{1}{2}H_2SO_4$, HCl, $HNO_3$. |
| About 0·01 N ..... | $H_2CO_3$, $\frac{1}{2}K_2SO_4$, KCl, $KNO_3$. |
| 0·1 N to N ..... | NaOH, KOH, $\frac{1}{2}K_2CO_3$. |

Analysis showed that, in the case of hydrochloric and sulphuric acid, practically the whole of the flocculant was removed from the liquid up to the point at

which flocculation became complete, after which there was no more removal. Alkalis also produce flocculation, just as do acids and salts, but not till the proportions present are a hundred to a thousand times greater. Evidence was obtained that sodium hydroxide is absorbed by the sediment, but on account of the greater strength of the solutions concerned, it was not possible to prove that the combination with the sediment is quantitative.

## CHAPTER VIII.

### VALENCY.

Pickering's first theoretical paper on "Atomic Valency" (R.S. 17), dealing mainly with the question of "residual affinity," was read before the Chemical Society on December 3, 1885; an abstract was published in the *Proceedings* and the complete paper was issued as a pamphlet. A second theoretical paper on "Valency" was communicated to the Chemical Society in 1917; this paper also was not published in full, but a brief abstract of it is given at the end of Paper No. 124. Valency problems are also discussed in a paper (R.S. 21) "On Water of Crystallisation," and in a long series of experimental papers on metallo-compounds (Nos. 105 to 124), leading up to a final paper, No. 126, on "Problems Bearing on Residual Affinity," in which a large number of theoretical questions were discussed.

(*a*) *A Theory of Residual Affinity.*—Pickering's theory of residual affinity is curiously like a revival in more modern terms of the teaching of Berzelius. The fundamental postulate is "that the number which represents the valency of any elementary atom, although it may very nearly approach to a whole number, is not exactly a whole number . . . . In other words, that an atom of A may be so nearly capable of saturating two atoms of B that it may form a stable compound with these two atoms, but that the compound thus formed will still retain some residual valency or combining power, either of A or of B, as the case may be, capable of exerting itself on some other molecule exhibiting a similar residual valency, and thus combining with it to form a molecular or, as we may term it, a 'residuary' compound" (p. 5).

Purely for the purpose of illustration, numerical values were assigned to the valencies of certain atoms, *e.g.*, H = 1, O = 1·98, $K_2$ = 2·159, Mg = 1·99 $SO_4$ = 2·135. On this basis water was slightly positive, 2 — 1·98 = 0·02, potassium sulphate was also slightly positive, 2·159 — 2·135 = 0·024, whilst magnesium sulphate was slightly negative 1·99 — 2·135 = — 0·145. Potassium sulphate with its "positive valency" was unable to combine with water which had a similar positive valency; but it readily formed a double salt with magnesium sulphate, and since this double salt was still negative, 0·024 — 0·145 = — 0·121, it resembled magnesium sulphate and differed from potassium sulphate in being able to combine with water. Its combining power for

water was, however, less than that of magnesium sulphate, since the negative character of the latter was diminished to an almost equal extent by a molecule of water and by one of potassium sulphate. Sodium sulphate, with its large power of combining with water, was an obvious exception to the general rule, but Pickering suggested that it was also widely different from potassium sulphate in its ability to form double salts.

In defence of this theory Pickering referred to the atomic weights, which exhibit definite deviations from the whole-number rule, and suggested that similar deviations from integral valencies were equally plausible. If he had been able, as in the case of atomic weights, to *measure* these deviations, Pickering's application of the old theory of "dualism" to the modern problem of "molecular compounds" might have been of permanent value; but, since it did not rest on any quantitative experimental basis, the theory remained barren, and no permanent gain resulted from the attempt to go "back to Berzelius." Such a fate is perhaps inevitable in the case of any quantitative theory, in which the desired numerical constants are not capable either of being measured directly or of being calculated by an indirect method from other data.

(*b*) *Water of Crystallisation.*—The term "water of constitution" or of "halhydration" was originally applied by Graham (*Trans. R. S. Edin.*, vol. 13, p. 297 (1836); *Chem. Soc. Mem.*, vol. 1, pp. 82, 106 (1843); *Phil. Mag.* [iii], vols. 6, 10, 11) to one of the molecules of water in the sulphates of magnesium and its homologues. The gist of the theory is that the so-called constitutional water is not *water* at all, but hydrogen and oxygen forming part of the nucleus itself. Thus Epsom salts may be regarded as a hexahydrate of the salt $SO(O_2Mg)(OH)_2$, instead of as a heptahydrate of the anhydrous sulphate. This theory was extended by Frankland and Japp to include not only the *monohydrate*, but also the *dihydrate* of sulphuric acid, since they formulated these two hydrates as $SO(OH)_4$ and $S(OH)_6$. This formulation represents the water molecules as having been resolved into their constituent atoms, in just the same way as when formaldehyde or chloral combines with water to form a glycol, thus:—

$$CH_2:O + H_2O = CH_2(OH)_2$$

$$CCl_3.CH:O + H_2O = CCl_3.OH(OH)_2.$$

Against this view Pickering cited the thermochemical data for the addition of successive molecules of water to three typical compounds as follows:—

| | $SO_3$ | $MgSO_4$ | $SrBr_2$ |
|---|---|---|---|
| $+1\ H_2O$ | 21,320 | 6980 | 6150 |
| 2 | 6379 | 2250 | 3800 |
| 3 | 3039 | 3600 | 3100 |
| 4 | 1719 | 3210 | 3100 |
| 5 | 1183 | 2230 | 3160 |
| 6 | 750 | 2110 | 4000 |
| 7 | 550 | 3700 | |

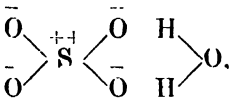
In the case of magnesium sulphate he offers the criticism that the heats of hydration were obtained by dissolving partially dehydrated salts, and were therefore the heats of hydration of mixtures (*e.g.*, of $MgSO_4$, $H_2O$ and $MgSO_4$, $7H_2O$), and not of definite compounds ; but he makes a sound point in noting that even in the case of strontium bromide, where no atomic compound can be formulated, the heat of monohydration exceeds the heat liberated on adding subsequent molecules of water, in precisely the same way as in the case of magnesium sulphate. In this respect his arguments anticipate in a curious way the familiar argument by which Werner sought to show the identity in general character of the compound $SO_3$, $H_2O$, where an atomic formula was possible, and $AuCl_3$, HCl, where it was not possible. Pickering was, however, prepared to go still even farther than Werner, and to argue that sulphuric acid itself might be a mere hydrate $SO_3$, $H_2O$, and not an atomic compound. This conclusion, however, was incompatible with his own argument that the neutral monohydrate $MgSO_4$, $H_2O$ could not be $SO(O_2Mg)(OH)_2$, since the two hydroxyl groups of the latter compound should have given some signs of acidity just as in $SO_2(ONa)(OH)$. Pickering's main conclusion was that

> " The theory that the sulphates contain either one or two molecules of ' constitutional ' water finds no confirmation whatever in general considerations as to their formation, properties, composition and analogies with other salts " (p. 430).

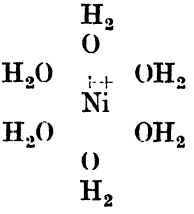
We cannot assert with confidence that we have progressed much farther in the intervening forty years. We believe now that the crystals of potassium and magnesium sulphates contain the ions $\overset{+}{K}$, $\overset{++}{Mg}$ and $\overset{--}{SO_4}$ ; and Werner has taught us to attach special significance to the numbers four and six on account of the high order of symmetry to which they give rise. It is therefore easy to imagine *six* molecules of water arranged symmetrically around the ion of the bivalent metal of a hydrated salt of the type of magnesium sulphate ;

but it is not yet clear how the seventh molecule of water is placed in a crystal of Epsom salts. In reply to Pickering's statement that "we have no grounds for supposing that the various water molecules in a hydrated salt are not all combined in the same manner, and do not all occupy exactly the same position with the regard to the salt nucleus; that, in short, a hydrated salt is not* a symmetrical substance," we can only assert that the same high order of symmetry can never be reached with seven identical units as with six units, and that for this reason the *seven* molecules of water of crystallisation are probably arranged in a dual pattern in which six molecules are arranged in identical positions, whilst the one molecule left over from this symmetrical arrangement must be differently placed.

It may be noted further that, according to modern views, the splitting of a molecule of water into its two radicals or ions is a more facile process than was formerly supposed. It is, therefore, no longer quite so important to distinguish between the addition of whole molecules of water to the molecule or ions of a salt, and the addition of the constituent atoms or ions of water, since these may be grouped into a pattern in which the division into molecules is purely arbitrary, just as in the case of ice. The most important distinction is perhaps that suggested by Ciamician in 1890, that in the case of an *anion* the attached water is held by the hydrogen and in the case of a *kation* by the oxygen (*Zeitschr. physikal. Chem.*, vol. 6, pp. 403 06 (1890)). This would enable us to write a hydrated sulphate ion as



where four tetrahedrally arranged oxygens can be joined by six molecules of water, of which only one is shown, whilst a hydrated nickel ion would be written as



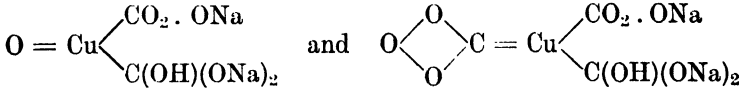
with six oxygen atoms arranged at the corners of an octahedron around the centrally placed metallic ion. The latter arrangement has been verified by

* Notice the double negative: Pickering's argument is that a hydrated salt *is* a symmetrical substance.

X-ray analysis in the analogous case of $NiCl_2.6NH_3$, but our knowledge of the structure of the hydrated anions is less advanced than that of the ammoniated kations.

(*c*) *Metallo-Compounds.*—Pickering was led to the study of metallo-compounds on account of their use as fungicides and insecticides, but followed up his initial observations by others which had no direct technical applications. During a period of about ten years, from 1907 to 1916, he remained a diligent worker in this field. In the course of this work he prepared a large number of new compounds, including especially the copper-derivatives of organic acids. In these compounds the copper was often held in a form which was quite different from that of the inorganic salts ; and in some cases it could be proved that the copper was a constituent of the anion, instead of forming the kation of the salt. This phenomenon was observed, not only in alkaline cupricarbonates (Paper No. 110), where the kation was provided by the alkali metal, but also in the case of salts containing no second metal, *e.g.*, in the malate and citrate, where electrolysis revealed the presence of "a deep blue anion travelling in one direction, and a pale blue cation in the opposite direction" (Paper No. 118, *J.C.S.*, vol. 101, p. 1631 (1912) ). In general it appeared that this electronegative copper was characterised by an intense colour, about 19 times deeper than in the salts (Paper No. 118, *J.C.S.*, vol. 101, p. 1632 (1912) ), and that solutions containing it generally yielded a scale or glass instead of crystals on evaporation (Paper No. 123, *J.C.S.*, vol. 107, p. 957 (1915) ). Pickering found that "alcoholic groups are necessary for the formation of such compounds" (Paper No. 116, *J.C.S.*, vol. 101, p. 174 (1912) ), since in 19 cases where no such group was present the addition of alkali to the copper salt precipitated a basic salt, whereas in 13 other cases where alcoholic hydroxyl groups were present, a soluble cupri-salt of the alkali was formed, with or without the formation of some basic salt.

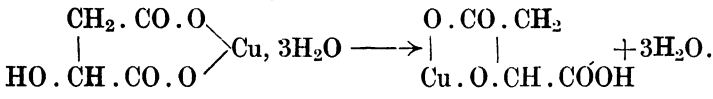
Analysis showed that in these cupri-salts there had been an addition of CuO to the parent acid, instead of a mere displacement of $H_2$ by Cu (Paper No. 117, *J.C.S.*, vol. 101, p. 1624 (1912) ). Pickering supposed at first that these compounds contained a quadrivalent atom of copper linked directly to two or even to four carbon atoms, in aggregates such as




(Paper 110, *J.C.S.*, vol. 95, p. 1426 (1909) ) ; but he soon put forward "another view, which is, perhaps, less open to objection"—namely, "that the hydrogen

atoms of alcoholic hydroxyls become displaced by — CuOH groups " (Paper 113, *J.C.S.*, vol. 99, p. 179 (1911) ).

Pickering's investigations did not lead to any complete or final elucidation of the structure of the bewildering array of compounds which he brought into being. In the case of the malates, however, the phenomenon with which he was dealing has been cleared up completely by the recent work of Wark (*J.C.S.*, vol. 123, pp. 1826–40 (1923) ; vol. 125, pp. 2004–09 (1924) ), who has shown that the dehydration of neutral cupric malate is accompanied by the formation of an isomeric cuprimalic acid from which a series of salts can be prepared. This change can be represented by the scheme



Pickering discovered a large number of cases (over forty in all) which can probably be explained on similar lines (see Abstracts on pp. 152–156).

In the last experimental paper of this series, Pickering sums up his theoretical conclusions as follows :—

> " When first formed the metallo-compound appears to contain the elements of water in addition to the formula MR, but in many cases it can be dehydrated without losing its distinctive properties, and in this condition it is strictly isomeric with the normal salt, from which it differs markedly in physical properties, and in constitution ; for electrolysis shows it to contain the metal in the anion. Over forty pairs of such compounds have been obtained, in which thirteen different metals and five acids figure, whilst the colour phenomena of copper salts leave no doubt that similar compounds exist in the case of all organic acids."
>
> " Whatever explanation is given of the existence of the metallo-form of copper salts must apply equally to those of the other metals now examined. That iron, manganese, cobalt, nickel, and perhaps lead, should act as tetrads is not surprising, but it may be thought otherwise in the case of the other metals. It is clear, however, that restricted views on the subject of valency are no longer possible. So-called saturated compounds combine with each other, and, therefore, must possess some affinity, and also valency ; for valency, or definite points of attachment, is essential for combination in definite proportion. Such affinity and valency must belong to the atoms composing the molecule, for we cannot devise any system for attributing affinity and valency to a molecule

if its constituent atoms possess neither. Now, the residual affinity of an atom, when combined with another, may be insufficient to bind to itself a third atom, but quite sufficient to satisfy the residual affinity of such an atom when it is already in a state of combination ; hence residual affinity and higher valencies will come into play in the formation of complexes, although the lower valencies alone operate in the formation of simple compounds. Platinum in the compound $PtCl_6K_2$ has been shown to be united with all six atoms of chlorine, though in simpler compounds its maximum valency is 4. A similar fact has been established as regards cobalt and chromium, whilst the usually bivalent copper is quadrivalent in $CuCl_4K_2$. It is only in the case of carbon and hydrogen, amongst the more familiar elements, that there appears to be no residual affinity and no higher valency values ; and to this must be attributed the building up of compounds of these two elements in a manner which is impossible in any other case" (Paper No. 124, *J.C.S.*. vol. 109, pp. 249–50 (1916) ).

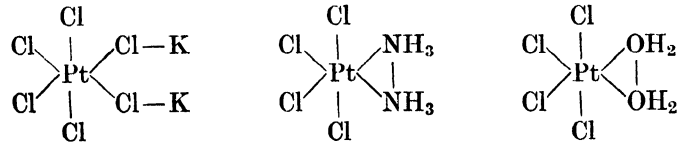
Pickering's views on the valency-problems arising out of the study of the metallo-compounds are set out at greater length in a paper on "Valency," of which a copy is retained in the archives of the Chemical Society. This paper was not accepted for publication, but the "Conclusions" quoted above were probably prepared as a condensed abstract of the views there enunciated, since the first paragraph is extracted almost word for word from the theoretical paper. This theoretical paper was concerned primarily with a defence of the view, which Wark's experiments appear to render unnecessary in the case of the cuprimalates, that the cupri-compounds contain quadrivalent copper. This view was justified by reference to Werner's "New Ideas on Inorganic Chemistry," but the paper also contains a well-founded criticism of the more vulnerable points of Werner's exposition.

"The distinction between principal and auxiliary valencies in this theory is not clear. Principal valencies are defined (p. 57) as those which permit saturation capacities to be measured in terms of hydrogen atoms (that is, the ordinarily accepted valencies as in Cl—, $H_3C$—, etc.), and auxiliary valencies those which bring about the stable union of such radicals as are capable of existing as independent molecules, as $-OH_2$, $-NH_3$, etc., but whether these two forms of valencies are supposed to be fundamentally different, or whether the number of auxiliary valencies exhibited by an atom or radical is definite or not, is uncertain. In some cases the auxiliary valencies are distinguished from the principal ones by

using dotted lines to represent them in the structural formulæ, but in other cases, even with the same compound, this is not so : sometimes the number of auxiliary valencies appears to be definite (' Boron, in trimethyl boron, has one unsaturated auxiliary valency ' (p. 45) ), whereas in other cases, such as those of $C_2O_4$, $CO_3$, etc., the auxiliary valencies, as mentioned above, must be variable ; further, we learn on p. 64 that no precise distinction can be drawn between the principal and auxiliary valencies. The manner in which the atoms in the outer sphere are supposed to be connected with the other atoms is also not clear ; they are uniformly represented in the formula as being united to the atoms in the inner sphere, and not to the central atom, but it is stated that ' the atoms in the second sphere still remain bound to the central atom, the only difference being that they no longer occupy a position in direct contact with that atom ' " (p. 43).

" Without minimising the high value of the co-ordination of the great mass of facts presented by Werner, the theory itself consists of little more than assigning a valency of six (or sometimes four) to certain elements, and altering that of the other elements to any value which may fit this arrangement. That high valency values must be assigned to many metals, etc., seems to be imperative, though it is only by unduly straining at an idea of uniformity, and by unnecessarily ignoring accepted valency values, that the values of 6 or 4 can be maintained in all cases (*e.g.*, thallium, vanadium, boron, etc.),* but if such higher valencies must be assigned to some elements where they have not been generally accepted, why refuse to assign higher values also to other elements where they have already been accepted ? It is only necessary to have pentavalent nitrogen, tetravalent oxygen, and trivalent halogens to bring Werner's formulæ into accordance with the valency theory, without in any way altering the significance of these formulæ as expressions of the reactions of the compounds ; and, moreover, such apparent anomalies as hexavalent thallium, vanadium, etc., will disappear."

As illustration he writes :




* " The force of analogy is, doubtless, over-rated throughout by Werner : he dwells often on the analogy between the reactions $SO_3 + H_2O$ and $AuCl_3 + HCl$ or $AuCl_3 + H_2O$ ; but there are no chemical reactions between which some analogies, and also some differences, may not be traced, and a reliance on the analogies only is a dangerous proceeding."

the platinum being regarded as hexavalent, chlorine as tervalent, nitrogen as quinquivalent and oxygen as quadrivalent. These valencies were all supposed to be of the ordinary type, and were represented by the symbols of ordinary bonds, the use of principal and subsidiary valencies being therefore unnecessary.

Apart from this critical section, the principal interest of the paper is found in a table which was used to demonstrate that a " reduction in energy of combination occurs when an atom increases in valency, . . . though the actual extent of the reduction cannot be determined." In this table the ratio A : B of the heats of combination (per atom of oxygen or of a halogen) in the lower and higher compound is given for 18 pairs of oxides and for 12 pairs of halides. Pickering showed that " With the exception of the gold halides, which will be referred to below, there are only two cases where the value of B is not less than that of A, and in these the excess is quite insignificant in view of the uncertainties attaching to the values."

One feature common to both of Pickering's papers on " Valency " is the refusal to accept the idea of a general attraction between molecules, apart from a localised attraction between their atoms. Thus in the first paper we read :—

> " At first sight there may appear to be no reason why molecules should not attract each other chemically, just as atoms do, and effect a " molecular " combination comparable with ' atomic ' combinations ; on closer inspection, however, such a view must become improbable, if not untenable. We know of no form of attraction in nature exerted by a mass of matter which is not in reality the resultant of the attractions of the constituent particles of that mass ; but it is irrational to imagine that the very different atoms constituting a salt such as $MgSO_4$ should all have exactly the *same* attraction for a water molecule, we must assume that they exhibit *different* attractive forces, and this at once destroys the idea of the attraction of a molecule *qua* molecule" (Pamphlet, p. 4).

Similarly in the second paper we read :—

> " It is inconceivable that a molecule can possess any chemical affinity other than that possessed by its constituent atoms, and, if it combines with any other atom, it can do so only through the residual affinity possessed by one or other of these constituent atoms."

Pickering's conclusion is in close accord with modern views, since each nucleus and each planetary electron must have a specific share in the mutual

attraction which leads to union between two molecules. There is much evidence which suggests that the localised attractions of the atoms (*e.g.*, the simultaneous attraction of one hydrogen for two oxygens) are responsible for the formation of many molecular compounds even in organic chemistry. The case which appears most likely to form an exception to Pickering's view is the formation of a compound from two complex ions, *e.g.*, quinine sulphate, since this may be held to depend on the mutual attraction of the opposite charges of the two ions ; but, in view of the fact that an electron cannot be subdivided, the attraction between the ions can still be formulated in accord with Pickering's views, since the surplus electron and the surplus positive charge must certainly be localised in the molecule, and can probably be assigned to individual atoms in each ion.

## CHAPTER IX.

### Annotated Bibliography.

R.S. 1. *Action of Sulphuric Acid on Copper.* *J.C.S.*, vol. 33, pp. 112–139 (March, 1878) (28 pages). Also *Moniteur Scientifique*, vol. 21, pp. 588–608 (1879).

Pickering's earliest chemical paper dealt with a problem in pure inorganic chemistry. The formation of a black residue by the action of sulphuric acid on copper had long been known, and a series of analyses had been made by Maumené in 1846 (*Ann. Chim. Phys.* [iii], vol. 18, p. 311 (1846) ). Pickering found that "this residue invariably consisted of copper and sulphur only, and never contained oxygen, as stated by Berzelius (*Traité de Chimie*, vol. 4, p. 324) and Maumené" (p. 113). He regarded the primary formation of an insoluble product as due to the production of *cuprous sulphide*, according to the equation

$$5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O; \qquad \text{(i)}$$

*cupric sulphide* and *sulphur* were then formed as secondary products from this cuprous sulphide as follows :—

$$Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O, \qquad \text{(ii)}$$

$$CuS + 2H_2SO_4 = S + CuSO_4 + SO_2 + 2H_2O. \qquad \text{(iii)}$$

From the fact that in all cases in which free sulphur was present with cupric sulphide, the sulphide, after extraction with carbon disulphide, contained the theoretical proportion of copper, he concluded that the sulphur thus found *was entirely soluble in carbon disulphide.* Analysis of the gases proved that "no gas insoluble in water, such as oxygen or hydrogen, was given off from the liquid during the action" (p. 114), and it was also "proved beyond doubt that in no case was any hydrogen sulphide liberated" (p. 114).

The most interesting result of the research was the discovery that by working at low temperatures (once at 80°, once below this, and once at 130°) it was sometimes possible to secure a ratio of "copper as sulphide" to "copper as sulphate" which was practically 2 : 3, as required by the equation (i) above, whereas in the rapid action at a high temperature (270°) only copper sulphate was formed. It was also proved that whereas in presence of an excess of copper, the insoluble residue consisted entirely of cuprous sulphide, this residue was

changed completely into cupric sulphide and sulphur by the further action of the sulphuric acid after the copper had all been dissolved.

Paper 1 (*a*). *Ammonium Nitrate. Chem. News*, vol. 38, p. 267 (December 6, 1878). (See p. 4.)

R.S. 2. *Action of Hydrochloric Acid on Manganese Dioxide.* (*J.C.S.*, vol. 35, pp. 654–673 (September, 1879) (20 pp.).

In a paper "On Manganese Tetrachloride," published in the *Journal of the Chemical Society* in September, 1878 (*J.C.S.*, vol. 33, p. 409 (1878) ), W. W. Fisher claimed (i) that this compound was produced by the action of cold concentrated hydrochloric acid on the oxides $MnO_2$, $Mn_2O_3$ or $Mn_3O_4$, and (ii) that, on the addition of water, manganese dioxide was always precipitated in the ratio of one atom of manganese to every two atoms of active chlorine in the liquid, in accordance with the equations

$$MnCl_4 + 2H_2O = MnO_2 + 4HCl, \quad \text{(i)}$$

$$MnCl_4 + 2KI = MnCl_2 + 2KCl + I_2. \quad \text{(ii)}$$

Pickering pointed out that these experimental results were equally in harmony with equations in which the higher chloride was represented as $Mn_2Cl_6$ instead of $MnCl_4$, since this merely involved adding a molecular proportion of $MnCl_2$ to each side of the equation.

Pickering showed, however, that the facts were not correctly represented by the simple equation (i), since the precipitate always contained from one-eighth to one-quarter of the manganese in the form of MnO, assuming the "available oxygen" in the precipitate to be in the form of $MnO_2$. The ratio of manganese precipitated to available chlorine in the solution was therefore about 1 : 1·64 instead of 1 : 2. The amount of manganese dioxide which could be reprecipitated was also found to vary from 47 per cent. at — 20° and 46 per cent. at 0° to only 9 per cent. at 61°. Since not more than 50 per cent. of the manganese dioxide could be precipitated, Pickering concluded that the higher chloride must be $Mn_2Cl_6$ and not $MnCl_4$; but his attempts to prepare a double salt of this compound were unsuccessful, since the crystals which separated after adding ammonium chloride had the composition $MnCl_2$, $2NH_4Cl$, $H_2O$, and a similar decomposition of the higher chloride occurred when sodium or potassium chloride was used. Later workers have succeeded in isolating from the solution double salts of the type $MnCl_3$, 2KCl, containing tervalent manganese; but manganic chloride, $MnCl_4$, and the manganichloride, $K_2MnCl_6$, in which the manganese is quadrivalent, have been prepared by other methods.

R.S. 3.—*Reaction between Sodium Thiosulphate and Iodine.* *J.C.S.*, vol. 37, pp. 128–140 (March, 1880) (13 pp.).

In the course of the work described in his second paper, Pickering found it possible to estimate the higher oxides of manganese by adding them to a solution containing a large excess of potassium iodide and a little hydrochloric acid, and titrating the resulting solution directly. The same method could be used for potassium dichromate, but it was not applicable to manganese ores, since ferric oxide would give rise to ferric chloride and hence to a liberation of iodine. When applicable, however, the modified process gave higher figures and was more accurate than the original method of Bunsen.

R.S. 4.—*On the Basic Sulphates of Iron.* *J.C.S.*, vol. 37, pp. 807–828 (December, 1880) (22 pp.).

In this paper, Pickering gives a list of 15 basic ferric sulphates which had been stated to exist according to various authorities on the subject. His experiments proved the definiteness of the sulphate $2Fe_2O_3$, $SO_3$, and tended to disprove the existence of any other. The best authenticated of these was the body $Fe_2O_3$, $2SO_3$, but even in this case the strongest piece of evidence which could be adduced in favour of its existence was based on "a single analysis of a solitary specimen of mineral."

R.S. 5.—*The Detection of Starch and Dextrin.* *Chem. News*, vol. 42, pp. 311–312 (December 23, 1880) (2 pp.).

R.S. 6.—*On the Sulphides of Copper.* *J.C.S.*, vol. 39, pp. 401–408 (August, 1881) (8 pp.).

This paper is a study of the progressive decomposition of cupric sulphide by three different agents, namely, (i) in a current of hydrogen with formation of hydrogen sulphide, (ii) in a current of carbon dioxide with formation of sulphur dioxide, (iii) by heating alone when free sulphur was liberated. Pickering found that the sulphide parts with its sulphur in two separate and equal portions and at totally different temperatures. Thus, in a current of hydrogen, half the sulphur was removed as hydrogen sulphide at temperatures below 265°, the initial action taking place at about 200°; the remainder was removed at about 600°. In a current of carbon dioxide half the sulphur was removed as sulphur dioxide at about 130° to 150°; a further evolution of sulphur dioxide began at about 230° and a complete conversion to metallic copper was effected at temperatures of 300° to 350°. When heated alone, half the sulphur only was liberated at a temperature of about 300°.

From these results, all of which indicate an initial conversion of cupric sulphide to cuprous sulphide (followed in two cases by a conversion to metallic copper), Pickering drew the conclusion that the sulphide must contain two atoms of sulphur, and should be represented as $Cu_2S_2$ and not CuS. This conclusion could scarcely be maintained to-day, since equations such as

$$2CuS + H_2 = Cu_2S + H_2S$$

would certainly be admitted as valid; indeed, an action of this kind could not be regarded as evidence of the presence of two atoms of copper in the molecule of the monosulphide, unless it were postulated that two molecules of the same kind could not interact with a third molecule of a different kind.

R.S. 7. *Notes on the Oxides of Manganese. Chem. News*, vol. 43, pp. 189–190, 201–202, 213–214, 225–227 (April 29, May 6, 13, 20, 1881).

R.S. 8. *On the Constancy of Thiosulphate Solutions. Chem. News*, vol. 44, pp. 277–279 (December 9, 1881.)

R.S. 9. *On the Sulphates of Aluminium. Chem. News*, vol. 45, pp. 121–123, 133–135, 146–147 (March 24, 31, April 6, 1882).

Paper 9 (*a*). *Testing for Barium or Sulphuric Acid. Chem. News*, vol. 46, p. 223 (November 17, 1882).

The limit of sensitiveness is about 1 part of barium per million.

R.S. 10. *On the Constitution of Molecular Compounds. The Molecular Weight of Basic Ferric Sulphate. J.C.S.*, vol. 43, pp. 182–185 (April, 1883) (4 pp.).

In this paper Pickering attempted to determine the molecular weight of basic ferric sulphate by preparing a series of definite hydrates. He concluded that arrests in the loss or gain of weight took place when the basic sulphate was exposed to dry or moist air at various temperatures and that these corresponded to 14 hydrates of the general formula $Fe_2(SO_4)_3, 5Fe_2O_3, nH_2O$. He concluded, therefore that the anhydrous basic salt had a molecular weight of 1200 and must be represented by the formula $Fe_2(SO_4)_3, 5Fe_2O_3$, and not by the simpler formula $2Fe_2O_3,SO_3$, which requires a molecular weight of only 400.

It is doubtful whether these partially hydrated or dehydrated powders would now be regarded as definite hydrates; but in any case the argument assumes again that two molecules of salt cannot react, with gain or loss of water, to form a hydrate, although reactions of this type are sufficiently familiar, *e.g.*, in organic chemistry, where the formation of acetic anhydride from acetic acid would not

now be admitted as a conclusive argument in favour of the bimolecular character of acetic acid.

R.S. 11. *Note on a Basic Ammonio-Copper Sulphate.* *J.C.S.*, vol. 43, pp. 336–338 (July, 1883) (3 pp.).

The compound $CuSO_4$, $3CuO$, $2NH_3$, $5H_2O$, was prepared by moderate dilution with water of a solution from which the tetrammine $CuSO_4$, $4NH_3$, in a not very pure form, was deposited on standing. On heating at 100° it gave the basic salt $CuSO_4$, $3CuO$, $3H_2O$ by loss of two molecules of ammonia and two molecules of water.

Paper 11 (*a*). *Supersaturation.* *Chem. News*, vol. 47, p. 85 (February 23, 1883).

R.S. 12. *On the Basic Sulphates of Copper.* *Chem. News*, vol. 47, pp. 181–184 (April 20, 1883) (4 pp.).

Paper 12 (*a*). *Aluminium Sulphate.* *Chem. News*, vol. 48, p. 275 (December 14, 1883).

Paper 12 (*b*). *The Heat of Hydration of Salts.* *Chem. News*, vol. 49, p. 216 (May 16, 1884).

Attention is directed to the importance when calculating the heat of hydration of a salt of starting with solid ice instead of with liquid water, since otherwise the latent heat of fusion is added to the chemical heat of hydration.

R.S. 13. *Modifications of Sodium Sulphate.* *J.C.S.*, vol. 45, pp. 686–690 (December, 1884) (5 pp.).

In investigating certain discrepancies in the published data for the heat of dissolution of various sulphates, Pickering discovered that the molecular heat of dissolution (+ 420 $H_2O$ at 20·4°) of sodium sulphate which had been dried at temperatures of 150° or below, was only 57 cal., whilst specimens dried at a red heat liberated 760 cal., a value that was increased to about 860 cal. when the salt was actually melted. He concluded, therefore, that the salt existed in a stable α-form, which by heating is converted, by an endothermic action (absorbing about 703 cal.), into the β-form. The fused salt was found to revert slowly to the normal form, the heat of dissolution falling in three months to 438 cal. only. Berthelot obtained for the fused salt a value as high as 1664 cal., falling to 1244 cal. in two months. Pickering appears to accept the curious view that "much weight cannot be attached to the absolute results obtained with fused salts, since they often retain a considerable amount of heat of

fusion" (p. 689). This view is not easy to translate into language which is in harmony with modern ideas. These could only lead to the conclusion that there may be a transition temperature for anhydrous sodium sulphate at some temperature between 150° to 200°, and that some additional endothermic action results from complete fusion, *e.g.*, a state of strain which is released by keeping; but the data for analysing the phenomenon from the standpoint of phase equilibrium, etc., were not unnaturally omitted in a paper written forty years ago. The phenomenon appears, however, to be specific, since in a subsequent paper R.S. 15) the heat of dissolution (+ $420H_2O$) of potassium sulphate at 22·8° is shown to be practically constant at — 6200 cal., the figure selected as most trustworthy being —6256 cal. In the same way the values for $Li_2SO_4$ at 22·75° were practically constant at about 6500 cal. before and after fusion. Pickering therefore concludes that "here, as in the case of potassium sulphate, we find no evidence of there being more than one modification of the salt" (p. 99).

Paper 13 (*a*). *Estimation of Oil in Cattle Cake. Chem. News*, vol. 51, p. 181 (April 17, 1885).

A rapid method of extraction with ether is described.

Paper 13 (*b*). *Crystalline Basic Cupric Sulphates. Chem. News*, vol. 52, p. 2 (July 3, 1885).

R.S. 14. *On the Molecular Weights of Liquids and Solids. Evidence deducible from the Study of Salts. Chem. News*, vol. 52, pp. 239–240, 251–253 (November 13 and 20, 1885).

R.S. 15. *Notes on the Heats of Dissolution of the Sulphates of Potassium and Lithium. J.C.S.*, vol. 47, pp. 98–99 (January, 1885) (2 pp.).

See under R.S. 13 above.

R.S. 16. *Calorimetric Determinations of Magnesium Sulphate. J.C.S.*, vol. 47, pp. 100–104 (January, 1885) (5 pp.).

In this paper the molecular heat of dissolution (+ $420H_2O$ at 22·2°) is given as 12,131 cal. for the monohydrate $MgSO_4$, $H_2O$ (dried at 150° to 160° and 20,765 cal. for anhydrous magnesium sulphate. Attention is directed to the different manner in which the anhydrous and monohydrated salts dissolve in water. The former cakes, but dissolves quickly when pounded up in water, whereas the latter does not cake, but takes about ten minutes to dissolve, rendering the water milky meanwhile. On account of this difference of behaviour, Pickering concludes "that the monohydrate cannot be formed as the first product of the hydration of the anhydrous sulphate" (p. 104).

R.S. 17. *Atomic Valency. Proc. C.S.*, vol. 1, pp. 122–125 (1885) (4 pp.). Published as a pamphlet, Harrison and Sons, 1886 (16 pp.). (See p. 109.)

R.S. 18. *On the Nature of Solution. Chem. News*, vol. 54, pp. 215–217 (1886). Reprinted as a pamphlet (8 pp.). (See p. 29.)

R.S. 19. *Modifications of Double Sulphates.* Part I. *J.C.S.*, vol. 49, pp. 1–12 (January, 1886) (12 pp.) *Specific Heat Determinations.* Part II. *J.C.S.*, vol. 49, pp. 12–16 (January, 1886) (5 pp.).

Copper potassium sulphate $K_2Cu(SO_4)_2, 6H_2O$ yields three anhydrous forms on drying at 100°, 150° to 290° and 300° to 400° C. The heats of dissolution at 18·25° were α-form 9709 cal., β-form 6200 cal., γ-form 8407 cal. The heats of formation from anhydrous simple salts were α-form −571 cal., β-form 2649 cal., γ-form 731 cal.

In Part II the specific heats were found to be as follows :

$$K_2SO_4,\ 0\cdot190\,;\ CuSO_4,\ 0\cdot135,$$

$$\alpha\text{-}K_2Cu(SO_4)_2,\ 0\cdot1682\,;\ \beta\text{-}K_2Cu(SO_4)_2,\ 0\cdot154\,;\ \gamma\text{-}K_2Cu(SO_4)_2,\ 0\cdot176.$$

Pickering concludes that "the three modifications of potassium copper sulphate . . . are as clearly distinguished by their different specific heats as they are by their different heats of dissolution" (p. 14).

Similar phenomena were observed in the case of potassium magnesium sulphate, for which the molecular heats of dissolution were as follows :—

| | |
|---|---|
| α-form (prepared at 110° to 155°) .. | 12037 cal., |
| β-form (fused) .. .. .. | 7431 ,, |
| Heat of transformation .. .. | 4606 ,, |

The heats of formation from the anhydrous simple salts were

| | |
|---|---|
| α-form .. .. .. .. | 2485 cal. |
| β-form .. .. .. .. | 7091 ,, |

Berthelot recorded a diminution in the heat of dissolution of the fused salt from 8039 to 5588 cal. after keeping for three weeks and powdering, but Pickering was unable to confirm this.

Paper 19 (*a*). **On Multiple Sulphates*, by Emily Aston and Spencer Umfreville Pickering. *J.C.S.*, vol. 49, pp. 123–130 (March, 1886) (8 pp.).

Vohl (*Ann.*, vol. 94, p. 57 (1855)) had described 42 multiple sulphates of the type

$$K_2SO_4,\ CuSO_4,\ 6H_2O + K_2SO_4,\ MgSO_4,\ 6H_2O$$

* Indexed under Aston (Miss), Emily Alicia, and Pickering, Spencer Percival Umfreville, in R.S. Catalogue.

containing 2, 3 or even 4 double-salts of the Schönite type in the molecule. Pickering found, however, that the composition of the crystals varied with the composition of the solutions from which they were deposited. Solutions containing copper and magnesium sulphates gave either crystals with the form of copper sulphate with $5H_2O$, or crystals having the form of magnesium sulphate and containing $7H_2O$. In the case, therefore, of "copper and magnesium sulphates, either, when in excess, will induce the other to crystallise out in a form, and with a proportion of water, foreign to its nature" (p. 129). This phenomenon is now described as *isodimorphism*.

R.S. 20. *The Influence of Temperature on the Heat of Chemical Combination.* *J.C.S.*, vol. 49, pp. 260–311 (May, 1886) (52 pp. with 7 plates).

Quotations from this paper have already been given (p. 7).

The data determined were the heats of dissolution in 400 to 420 $H_2O$ (3/40 gram.-mol. in 600 c.c.) of anhydrous, hydrated, and double salts, *e.g.*,

$$Na_2SO_4 \text{ and } Na_2SO_4,\ 10H_2O$$
$$MgSO_4 \text{ and } MgSO_4,\ 7H_2O$$
$$K_2SO_4,\ K_2Mg(SO_4)_2 \text{ and } K_2Mg(SO_4)_2,\ 6H_2O.$$

The last series of measurements was also repeated with copper instead of magnesium. From these data it was possible to calculate—

(1) The heat of hydration of the hydrated salts, since this was merely the difference of the two heats of dissolution ;

(2) The heats of formation of the double salts from the simple salts.

In calculating the heats of hydration, however, Pickering preferred to work out the values for a solid salt combining with solid ice to form a solid hydrate. He therefore subtracted from his heats of hydration a hypothetical molecular latent heat of ice, calculated from the formula :

$$l_m = 1423{\cdot}33 + (c - c')\mathrm{T} \text{ cal.},$$

where the specific heat $c$ of water was taken as

$$c = 17{\cdot}96 + 0{\cdot}00072\mathrm{T} + 0{\cdot}0000162\mathrm{T}^2$$

and the specific heat $c'$ of (super-heated) ice as

$$c' = 9{\cdot}052 + 0{\cdot}0185\mathrm{T}.$$

On plotting out his results, Pickering obtained a series of sinuous curves.

R.S. 21. *On Water of Crystallisation.* *J.C.S.*, vol. 49, pp. 411–432 (June, 1886) (22 pp.).

In this paper Pickering discusses the nature of water of crystallisation, and the relationship which it bears to the salt with which it is associated (see pp. 110 to 111).

R.S. 22. *Note on the Calibration and Standardising of Mercury Thermometers.* *Phil. Mag.*, vol. 21, pp. 180–185 (March, 1886) (6 pp.).

R.S. 23. *Experimental Error in Calorimetric Work.* *Phil. Mag.*, vol. 21, pp. 324–330 (April, 1886) (7 pp.). (See p. 15.)

R.S. 24. *On Delicate Calorimetric Thermometers.* *Phil. Mag.*, vol. 21, pp. 330–342 (April, 1886) (13 pp.). (See p. 15 and compare R.S. 32 and 33 below).

Paper 24 (*a*). **Hydration of Salts*, by Miss E. M. Farrer and S. U. Pickering. *Chem. News*, vol. 53, p. 279 (June 11, 1886).

Paper 24 (*b*). †*The Composition of Hydrated Salts*, by Spencer U. Pickering and P. G. Sanford. *Chem. News*, vol. 54, pp. 277–278 (December 3, 1886), pp. 22–23, and 46 (January 14 and 28, 1887).

A controversy with Maumené, who held that chemical composition was based on a system of *equal weights* instead of the generally accepted equivalents.

Paper 24 (*c*). *The Nature of Solution.* *Chem. News*, vol. 55, pp. 152–153 (April 1, 1887).

Paper 24 (*d*). *On a Fundamental Law of Thermochemistry.* *Chem. News*, vol. 55, pp. 227–228 (May 20, 1887).

R.S. 25. *On Solution.* *Chem. News*, vol. 56, pp. 181–182 (October 28, 1887) (2 pp.).

R.S. 26. *On the Thermal Phenomena of Neutralisation, and their Bearing on the Nature of Solution.* *Chem. News*, vol. 56, pp. 191–192 (November 4, 1887) (2 pp.).

Four notes, 24 (*d*), 25, 26 and 35, were devoted to correcting errors arising "from misunderstanding the thermal phenomena of neutralisation."

* Indexed under Farrer (Miss), E. M., and Pickering, Spencer Umfreville, in R.S. Catalogue.

† The first paper and letters are indexed under Pickering and Sandford, P. Gerald, in R.S. Catalogue; the final letter was signed by Pickering only.

R.S. 27. *On the Constitution of Basic Salts. Chem. News*, vol. 56, pp. 211–212 (November 18, 1887) (2 pp.).

R.S. 28. *Decomposition of Sodium Carbonate by Fusion. J.C.S.*, vol. 51, pp. 72–74 (January, 1887) (3 pp.).

Abnormally large heats of dissolution, first recorded by Berthelot (*Ann. Chim. Phys.*, vol. 29, p. 311), led to the recognition of the fact that fusion causes a partial conversion of sodium carbonate into the hydroxide. The maximum excess of 200 calories after fusion would correspond with the conversion of 1·4 per cent. of the carbonate into hydroxide; but this figure is probably too low owing to absorption of moisture, and Pickering concludes that "the amount of decomposition occurring on simple fusion is probably about 3 per cent." (p. 74).

In the case of samples which had been fused and kept in contact with carbon dioxide, abnormally *low* heats of dissolution were observed, the results obtained being more than 400 cal. below, instead of above, the normal salt, as a result of the conversion of the hydroxide into *bi*carbonate.

R.S. 29. *The Heat of Hydration of Salts. Cadmium Chloride. J.C.S.*, vol. 51, pp. 75–77 (January, 1887) (3 pp.).

In a discussion on the nature of solution (R.S. 18), Nicol (*Chem. News*, vol. 54, p. 191) laid considerable weight on the supposed fact that the heat of hydration of cadmium chloride was a negative quantity. Pickering now records for the heats of dissolution the following values: —

| | |
|---|---|
| $CdCl_2$ dried at 200° C. | + 3300 cal. |
| „ „ | + 3211 cal. |
| $CdCl_2, H_2O$ | + 625 cal. |
| $CdCl_2, 2H_2O$ | — 2284 cal. |

These figures, which contain an allowance for the latent heat of fusion of the (solid) water in the hydrated salts, give the following values for the heats of formation of the hydrates from the anhydrous salt and *solid* water at the same temperature: —

$CdCl_2, HO$ + 1092 cal.

$CdCl_2, 2H_2O$ + 2421 cal.

These figures, instead of being *negative* are *positive* and larger than the values for sodium carbonate or sulphate. Thomsen appears to have analysed a specimen of the dihydrate, and then to have used for his calorimetric work a specimen (probably prepared at a higher temperature) which was really the

monohydrate, since it gave a corresponding value for the heat of dissolution; hence the error in Nicol's statement.

R.S. 30. *The Influence of Temperature on the Heat of Dissolution of Salts.* *J.C.S.*, vol. 51, pp. 290–356 (April, 1887) (67 pp., with 8 plates).

This paper has already been cited (p. 57). In view of criticisms offered by Tilden (*Proc. C.S.*, p. 198 (May 20, 1886)) Pickering now withdraws his claim to have discovered a series of local sinuosities in the heats of dissolution of salts, as set out in paper R.S. 20. "The peculiarities which I noticed in the lines representing the heat of dissolution consisted of indentations occurring at various points, converting these lines into a series of curves: as to the existence of such indentations I now consider that I was quite wrong; they do not exist, but that changes more or less sudden do occur in these lines, and in the nature of the molecular aggregates of a salt in solution, the present work will, I trust, place beyond a doubt" (p. 291).

The temperatures at which this new series of changes occurred were set out in the following table (p. 324):—

| Salt. | 1st change. | 2nd change. | Interval. |
|---|---|---|---|
| | ° | ° | ° |
| Potassium sulphate | 14·0 | Higher than 27 | >13·0 |
| ,, nitrate | 12·0 | ,, ,, 25 | >13·0 |
| Sodium chloride | 10·0 | 24 (?) | 14·0 (?) |
| Potassium ,, | 9·5 | 24 (?) | 14·5 (?) |
| Strontium nitrate | 9·0 | 21 | 12·0 |
| ,, chloride | 8·0 | 13 (?) | 5·0 (?) |
| Rochelle salt | 8·0 | 20 | 12·0 |
| Sodium acetate | 7·5 | 21 (? 19·5°) | 13·5 (? 12·5°) |
| ,, carbonate | 7·0 | 18 | 11·0 |

In one other point this paper contains a reversal of opinion. In the earlier paper, R.S. 20, the changes in the heat-capacity of the solution were explained by the formation of higher hydrates as the temperature rises. The present results, however, were explained "in a diametrically opposite manner" by supposing that at these *higher* temperatures some alteration had occurred which absorbed heat (p. 327).

Paper 30 (*a*). [*Heat of Dissolution of Racemic and Tartaric Acids.*] *J.C.S.*, vol. 51, pp. 367–368 (1887).

Contributed to a paper by W. H. Perkin "On Tartaric and Racemic Acids, and the Magnetic Rotation of their Ethereal Salts."

R.S. 31. *On the Thermal Phenomena of Neutralisation, and their Bearing on the Nature of Solution and the Theory of Residual Affinity.* *J.C.S.*, vol. 51, pp. 593–601 (July, 1887) (9 pp.).

A controversial paper in reply to Nicol (see pp. 21 to 25).

R.S. 32. *On Delicate Thermometers.* *Phil. Mag.*, vol. 23, pp. 401–405 (May, 1887) (5 pp.). (See p. 17.)

R.S. 33. *On the Effect of Pressure on Thermometer-bulbs and on some Sources of Error in Thermometers.* *Phil. Mag.*, vol. 23, pp. 406–411 (May, 1887). (6 pp.). (See p. 18.)

R.S. 34. *Note on the foregoing Communication.* [The Determination of the Constitution of Carbon Compounds from Thermochemical Data. By Henry E. Armstrong.] *Phil. Mag.*, pp. 109–112 (February, 1887) (4 pp.).

R.S. 35. *On the Constancy in the Heat produced by the Reaction of Certain Salts on each other.* *Chem. News*, vol. 57, pp. 75–76 (February 24, 1888) (2 pp.).

Compare R.S. 26 and 27.

R.S. 36. *The Heat of Dissolution of Substances in Different Liquids, and its bearing on the Explanation of the Heat of Neutralisation, and on the Theory of Residual Affinity.* *J.C.S.*, vol. 53, pp. 865–878 (December, 1888) (14 pp.).

This paper is a continuation of the controversy with Nicol (see pp. 21 to 25).

R.S. 37. *The Nature of Solutions as elucidated by the Heat evolved on their Dilution.* Part 1. *Calcium Chloride.* *Proc. C.S.*, vol. 4, pp. 35–37 (1888) (3 pp.).

Paper 37 (*a*). *On Solution.* *Chem. News*, vol. 57, p. 220 (June 1, 1888).

A reply to Durham (compare R.S. 25).

R.S. 38. *On Thermochemical Constants.* *Phil. Mag.*, pp. 53–62 (July, 1888) (10 pp.).

Thomsen in his thermochemical studies has been struck by the fact that identical numbers or multiples of identical numbers sometimes recurred, *e.g.*,

*Heat of Formation of aqueous Iodic Acid.*

$I_2, O_6, H_2, aq = 111590 = 3 \times 37197.$

*Heat of Formation of aqueous Periodic Acid.*

$I, O_6, H_5, aq = 184400 = 5 \times 36880.$

In two papers in the *Berichte* (vol. 5, p. 170, and vol. 6, p. 239) he claimed to have detected the existence of a "constant of affinity" of about 18,000 cal., multiples of which were detected in 31 reactions. Pickering showed that this "constant" was of an entirely fictitious nature depending on "the chances of coincidences occurring in a certain number of numbers." This was shown by selecting a different arbitrary number, namely, 15,000 cal., when it was possible to prepare a list of 110 reactions giving this number or a multiple of it.

R.S. 39. *The Nature of Solutions. Chem. News*, vol. 60, pp. 68 (Aug. 9, 1889).

R.S. 40. *The Principles of Thermochemistry. J.C.S.*, vol. 55, pp. 14–33 (January, 1889) (20 pp.).

This paper is full of statements which could not now be maintained, since they are based upon the view, put forward by Thomsen in 1853 (*Pogg. Ann.*, vol. 92, p. 34, and *Ber.*, vol. 6, p. 425), but long since abandoned, that "every simple or complex action of a purely chemical character is associated with a production of heat." Pickering's own principle is expressed by saying that "Inasmuch as combination is the result of the saturation of affinity, and the saturation of this affinity must always liberate a corresponding amount of heat, it is evident that *every act of combination must cause an evolution of heat, and that in any reaction where heat is absorbed this absorption must be due to some accompanying decomposition*" (p. 16). In order to illustrate his meaning, Pickering suggests that "if potassium be brought into the presence of excess of hydrochloric and hydrobromic acids in aqueous solution, . . . my proposition states, the potassium will be converted entirely into chloride or bromide according as the gross heat of formation of one or other of these salts is the greater" (p. 17); in other words, he appears to deny the existence of all reversible actions, on the ground that if one action is exothermic, the converse action must be endothermic, and therefore impossible.

The most difficult cases to explain on the basis of his principle were—"(1) The endothermic results on dissolving solids in liquids. (2) The endothermic results on diluting strong solutions. (3) The endothermic results attending double decomposition between substances in solution." Some of these endothermic actions had been set aside by Berthelot as merely "physical" changes. Pickering regarded this device as often unsatisfactory, but found a reserve of heat by supposing that the solute in a dilute solution was not merely *fused* but *vaporised*, so that the latent heat of vaporisation, as well as the latent heat of fusion, must be supplied in effecting the dissolution of a salt.

Modern physical chemistry, as is now generally known, gets over this difficulty by drawing a sharp distinction between (i) the *free energy*, which must diminish, as in an electric cell, which can only act in the direction of the e.m.f. in the circuit, and (ii) the *total energy*, the changes in which, in accordance with thermodynamic principles, may be either greater or less than the changes in the free energy, according as the temperature coefficient of the free energy is positive or negative. Endothermic actions are therefore possible in all cases in which the temperature-coefficient of the free energy is negative and large, whilst the change of free energy itself is positive but small.

Pickering's doubts as to the location of the absolute zero at — 273° may be regarded as dissipated by later work, together with his theoretical questionings of the principles of thermochemistry.

Paper 40 (*a*). *Solubility of Brass. Chem. News*, vol. 59, p. 119 (March 8, 1889).

A reply to Blount on a point raised in the preceding paper.

R.S. 41. *Note on the Heat of Neutralisation of Sulphuric Acid. J.C.S.*, vol. 55, pp. 323–326 (June, 1889) (4 pp.).

In a previous paper (No. 31) Pickering had accounted for the existence of abnormally high heats of neutralisation (*e.g.*, in the cases of sulphuric, hydrofluoric, hypophosphorous and selenic acid) by means of "a possible, though conjectural explanation, based on peculiarities in the amount of the residual affinity possessed by the acids (*Trans.*, p. 598 (1887) ). The object of the present note is to give a simpler and more satisfactory explanation of such exceptions. The heat of neutralisation of these acids is *not* abnormally high" (see p. 23).

R.S. 42. *The Expansion of Water and other Liquids. Proc. C.S.*, vol. 5, pp. 89–90 (1889).

R.S. 43. *The Nature of Solutions as elucidated by a Study of their Freezing Temperatures. Proc. C.S.*, vol. 5, pp. 106–109 (1889).

R.S. 44. *Isolation of a Tetrahydrate of Sulphuric Acid existing in Solution. Proc. C.S.*, vol. 5, pp. 128–130 (1889).

R.S. 45. *The Law of the Freezing Points of Solutions. Proc. C.S.*, vol. 5, pp. 149–154 (1889); *Proc. C.S.*, vol. 6, pp. 9–10 (1890).

R.S. 42–45 are preliminary notices of work which was subsequently published in full (compare R.S. 49, 50, 55, etc.).

R.S. 46. *Use or Abuse of Empirical Formulæ and of Differentiation by Chemists.* *Nature*, vol. 40, pp. 343–344 (August 8, 1889).

A reply to Lodge (see p. 64).

R.S. 47. *On some Effects of Lightning.* *Nature*, vol. 40, pp. 415–416, and 620–621 (August 29 and October 24, 1889).

R.S. 48. *The Present Position of the Hydrate Theory of Solution* (with Discussion). *British Association Report*, pp. 311–328 (1890); *Chem. News*, vol. 62, pp. 185, 194; vol. 63, pp. 147, 157, 169; *Zeit. f. physikal. Chem.*, vol. 7, pp. 378–426.

This was a full-dress debate in which Gladstone, Walker, Ramsay, Armstrong, Fitzgerald and Lodge took part, as well as Ostwald and van't Hoff, whilst Arrhenius sent a written contribution to the discussion.

Pickering claimed not only to have established the hydrate theory by a "proof as nearly absolute as it is possible to conceive," but to have done this "without in any way rejecting the facts on which the advocates of the osmotic pressure theory rely—approximate constancy, approximate regularity, and approximate similarity between dissolved and gaseous matter." In doing this he felt that he had "done far better work than the mere establishment of the hydrate theory, by pointing out a possible *modus vivendi* for both theories almost in their entirety, and by helping to break down that wall of separation between physicists and chemists which is fast crumbling into dust." This *modus vivendi*, however, it should be noticed, admitted van't Hoff's theory of osmotic pressure, but left no room for the theory of ions, which was regarded as definitely erroneous.

Other points dealt with in this report, and in the discussion which followed, are considered on pp. 45 to 49.

R.S. 49. *The Nature of Solutions, as elucidated by a study of the Density, Electric Conductivity, Heat Capacity, Heat of Dissolution, and Expansion by Heat of Sulphuric Acid Solutions.* *J.C.S.*, vol. 57, pp. 63–184 (March, 1890) (122 pp. with three plates).

This monumental paper covers over 120 pages, with 16 figures in the text and 3 plates at the end. The experimental data include determinations of the densities at four different temperatures of aqueous solutions of sulphuric acid at intervals of 1 or 2 per cent. over the whole range of concentrations from 0 to 100 per cent., and of the heats of dissolution of 75 different solutions from 5 to 100 per cent., making a total of six or seven hundred determinations. These

data were all analysed according to the method described under (*b*) below, together with the coefficients of expansion and heat capacities, the contractions on mixing deduced from the densities, the heat capacities determined from the heats of mixing of certain solutions, and Kohlrausch's conductivity data.

(*a*) *Densities.*—Of the experimental data, the most valuable are a series of densities of solutions prepared by diluting pure anhydrous sulphuric acid. "In plotting out the freezing-points of a series of acids containing somewhat more water and more anhydride than $H_2SO_4$ itself, we get a figure consisting of two nearly straight lines rising up so as to meet at a very sharply marked angle, and the point at which they meet must correspond, for reasons which I need not enter into at present, to the definite compound $H_2SO_4$ itself; the point of intersection of these lines may be ascertained to within $\pm$ 0·01 per cent. or less. In this way I have determined by means more reliable than any analysis, the strength of a large quantity of acid" (p. 72). This method, which gave in two determinations

99·928 per cent.,
99·932 per cent.,

appeared to be correct to $\pm$ 1 part in 50,000. All the other acids were prepared by dilution of this stock acid by one of the following three methods:—

A. By exposure to moist air for a month, with subsequent addition of water.
B. By addition of ice.
C. By the very cautious addition of water.

Their *relative* concentrations, which depended only on weighing, were thought to be accurate "to about one unit in the fourth decimal place of the percentage, provided no loss of anhydride occurred in making them;" and as the concentration of the stock acid was based upon a very sensitive physico-chemical process instead of upon the ordinary methods of volumetric or gravimetric analysis, the *absolute* concentrations were perhaps only 10 times less accurate. Some 360 densities were determined at 7·978°, 17·925°, 28·064° and 38·203° $\pm$ 0·002, at concentrations ranging from 0·049 to 99·857 per cent., and from these Pickering compiled (i) a table of densities for 54 exact (and generally integral) percentages at 8° and 18° and for 46 percentages at 28° and 38°, and (ii) a second very full table for 65 percentages at every 2° from 0° to 40°, using for 0° the values collected by Mendeléef.

This series of density-determinations, which is still the best on record, was used by Marshall (*J.S.C.I.*, vol. 18, p. 4 (1899)) as the basis of an easy and accurate method of preparing a standard acid for volumation analysis. The

actual standardisation was done by determining the density of the acid at 18°, after diluting to about 84 per cent. $H_2SO_4$, by the addition of one-fifth of its volume of water to the pure concentrated commercial acid. This concentration was selected because it was found that the effects of an error in the determination of density (or of temperature) were here at a minimum.* The work of standardisation was also simplified by compiling a table *of relative densities in air, instead of absolute densities in vacuo*, so that a mere comparison of the apparent weights of acid and of water contained in a pyknometer at 18° suffices to give the concentration of the acid. Dilution of a known weight (or the whole) of the acid in the pyknometer to a known volume with water then gives a standard acid of accurately known strength.

(*b*) *Differentiation.*—The experimental data in the paper were examined with a view to finding out "whether the curves representing these results exhibited any sudden changes . . . or not" (p. 65); and the main conclusion was that the "facts elucidated by this work afford absolute proof that the properties of solutions do not vary regularly with their composition" (p. 137), but, on the contrary, show "the existence of more or less sudden changes of curvature at certain points" (p. 132).

The process used to detect (or to render more obvious) the discontinuous character of the curve was to differentiate the experimental results, *i.e.*, in addition to plotting the values $s$ of a given property against the concentration $c$, Pickering plotted $ds/dc$ against $c$, or even the second differential $d^2s/dc$, against $c$.

Pickering himself warned his readers that "many of the individual changes in curvature . . . are admittedly of a very doubtful nature, especially when considered by themselves. Their existence can only be established by the concordant indications of independent properties" (p. 69). This coincidence showed that the discontinuities ultimately revealed by differentiation were "not the chance outcome of the taste of the draughtsman" depending on the particular function of the property used, or the method of plotting selected, but were definite characteristics of the solutions themselves. The identity of the discontinuities revealed by different properties of the same solutions is shown in the following Table F (p. 136):—

* The density passes through a maximum at about 97·5 per cent. and through a point of inflexion at about 80 per cent. $H_2SO_4$ (Pickering, p. 74).

## Table F.—Position (in Percentage Values) of the Changes of Curvature shown by the Various Properties of Solutions of Sulphuric Acid examined.

| Densities. | | | | Expansion by heat. | Electric conductivity. | Heat capacity. | Heat of dissolution. | Mean. | Molecular composition shown. | Composition of definite hydrates. |
|---|---|---|---|---|---|---|---|---|---|---|
| At 38°·203. | At 28°·064. | At 17°·925. | At 7°·978. | | | | | | | |
| N.D. | N.D. | N.D. | N.D. | (a) N.D. | (99·5) | N.D. | 99·35 | 99·47‡ | 35·4 $H_2SO_4$ $H_2O$ | 36 $H_2SO_4$ $H_2O$ = 99·493 |
| | | | | | | | | | | (35 ,, ,, = 99·478) |
| ,, | ,, | 97·2 | 97·7 | 97·31 | (96·8) | ,, | 97·3 | 97·38 | 6·82 ,, ,, | 6 ,, ,, = 97·444 |
| | | | | | | | | | | (7 ,, ,, = 97·030) |
| 93·5 | 94·0 | 93·6 | 94·0 | 93·84 | 94·0 | ,, | 93·83 | 93·89 | 2·82 ,, ,, | 3 ,, ,, = 94·233 |
| | | | (88·0) | 88·65 | — | ,, | 88·95 | 88·70 | 1·44 ,, ,, | 3 ,, 2 ,, = 89·095 |
| 84·4 | 84·5 | 84·5 | 84·5 | 83·37 | 84·0 | ,, | 84·0 | 84·24 | $H_2SO_4$ 1·02 $H_2O$ | 1 ,, 1 ,, = 84·488 |
| 78·2 | 77·5 | 78·0 | 79·0 | 78·57 | — | ,, | 79·0 | 78·43 | ,, 1·49 ,, | 2 ,, 3 ,, = 78·407 |
| 72·8 | 73·3 | 72·8 | 73·3 | 72·74 | [73]* | ,, | 73·0 | 73·04 | ,, 2·01 ,, | 1 ,, 2 ,, = 73·142 |
| | | | | (61·88)† | [63]* | | | (61·88)† | | — |
| 59·0 | 57·0 | 58·0 | (58·0) | 56·69 | — | ,, | 59·15 | 58·14 | ,, 3·92 ,, | (1 ,, 4 ,, = 57·656 |
| 49·0 | 50·0 | 51·0 | 51·0 | 49·05 | — | ,, | 49·25 | 49·92 | ,, 5·46 ,, | 1 ,, 5·5 ,, = 49·756 |
| | | | | | | | | | | 1 ,, 5 ,, = 52·137) |
| | | | (40·0) | 39·15 | (37·5) | ,, | 37·75 | 38·58 | ,, 8·70 ,, | 1 ,, 9 ,, = 37·701 |
| 32·0 | 29·0 | 29·5 | 30·0 | 28·81 | N.D. | ,, | 28·25 | 29·59 | ,, 12·94 ,, | 1 ,, 13 ,, = 29·526 |
| N.D. | N.D. | 18·5 | 18·5 | 19·49 | ,, | ,, | 19·15 | 18·92 | ,, 23·44 ,, | 1 ,, 24 ,, = 18·492 |
| ,, | ,, | 8·8 | 10·5 | 10·49 | 9·5 | 9·85 | 9·0 | 9·69 | ,, 50·8 ,, | 1 ,, 58 ,, = 8·585§ |
| | | | | | | | | | | (1 ,, 50 ,, = 9·821) |
| ,, | ,, | 4·0 | 4·3 | 4·00 | 3·5 | 4·1 | 4·07 | 3·99 | ,, 131 ,, | 1 ,, 130 ,, = 4·021 |
| ,, | ,, | 1·05 | 1·05 | — | N.D. | 1·0 | 1·13 | 1·06 | ,, 508 ,, | 1 ,, 510 ,, = 1·057 |
| | | | | | | | | | | (1 ,, 500 ,, = 1·080) |
| ,, | ,, | 0·25 | 0·35 | (0·35) | ,, | N.D. | 0·40 | 0·34 | ,,1600 ,, | 1 ,, 1500 ,, = 0·362 |
| | | | | | | | | | | (1 ,, 1600 ,, = 0·339) |
| ,, | ,, | N.D. | N.D. | N.D. | ,, | ,, | 0·105 | 0·105 | ,,5182 ,, | 1 ,, 5000 ,, = 0·109 |
| | | | | | | | | | | 1 ,, 5200 ,, = 0·104 |

(a) The values in this column are 7/10000ths lower than those in Table E (p. 118), where the later determinations of the strength of the acid were taken.

* 73 or 63 per cent., but very uncertain. † This change is too doubtful to be counted.

‡ The values for the means are 7/10000ths higher than they should be according to the numbers in the first eight columns, the alteration having been made in accordance with the later determinations of the strength of the acid.

§ The position of this change is defined so much more clearly by the experimental curve of the heat of dissolution (8·7 per cent.) than by any other curve that I have taken the composition indicated by this to be the more probable one.

R.S. 50. *The Nature of Solutions, as elucidated by the Freezing-Points of Sulphuric Acid Solutions. J.C.S.*, vol. 57, pp. 331–369 (May, 1890) (39 pp.).

This communication was "an account of determinations of the freezing-points of solutions of sulphuric acid, made with a view to obtain still further evidence of the existence of hydrates in solution than had been obtained by a study of their densities, heat of dissolution, etc." (p. 331).

(*a*) *Crystallisation of Hydrates.*—The freezing-point curve is made up of four sections representing the crystallisation of

(i) $H_2SO_4$, (ii) $H_2SO_4, H_2O$, (iii) $H_2SO_4, 4H_2O$, and (iv) $H_2O$.

The isolation of the new tetrahydrates of sulphuric acid on July 31, 1889, was one of Pickering's most dramatic triumphs, since he had proclaimed to a somewhat sceptical world the existence of a long series of hydrates in solution, and now was able to exhibit to his critics one of the series of unknown compounds, whose existence had been questioned, in the form of a crystalline compound melting at $-25°$.

Pickering discusses four possible views as to the mechanism by which the crystals of the tetrahydrate might be formed, and justly concludes that "the only tenable proposition" is that "the molecules of the hydrate *are formed in the liquid*,* and exist there till the temperature is lowered to its freezing-point." He adds that "when a liquid freezes and melts at a definite temperature, when the temperature remains constant till the whole of the liquid is frozen, when any alteration in its composition lowers its freezing-point, we have the most certain evidence yet adduced for regarding that liquid to be a definite, though possibly somewhat dissociated, compound. If we deny this argument when applied to the hydrate in question, we must deny it in all cases, and conclude that neither the monohydrate, nor sulphuric acid itself, nor, indeed, any other liquid, is a definite substance" (pp. 340–41).

(*b*) *Discontinuities.*—In addition to describing the crystalline hydrates of sulphuric acid, Pickering made a minute analysis of the data with the aid of the process of differentiation. The object of this analysis was not to detect the existence of new solid phases, which would merely increase the number of sections into which the freezing-point curve was obviously divided, but to detect hydrates *in solution* by means of their secondary influence on the course of the freezing-point curve for a constant solid phase. The results of this analysis are shown in Table A :—

* The italics are mine.—T. M. L.

Table A.—Position (in Percentage Values) of the Changes of Curvature.

| | Freezing points. | Other properties. | Composition of the definite hydrates. |
|---|---|---|---|
| 1. | 100·6 | N.D. | 36 $H_2SO_4$, $SO_3$ = 100·499 |
| 2. | 100·0 | N.D. | $H_2SO_4$, = 100·000 |
| 3. | 99·5 | 99·17 | 36 $H_2SO_4$, $H_2O$ = 99·493 |
| 4. | 98·6 | - - | 12 ,, = 98·492 |
| 5. | 97·0 | 97·38 | 6 ,, ,, = 97·444 |
| 6. | N.D. | 93·89 | 3 ,, ,, = 94·233 |
| 7. | 89·8 | 88·70 | 3 ,, 2 ,, = 89·095 |
| 8. | 86·0 | N.D. | 7 ,, 6 ,, = 86·403 |
| 9. | 84·5 | 84·24 | 1 ,, 1 ,, = 84·488 |
| 10. | 82·0 | N.D. | 6 ,, 7 ,, = 82·360 |
| 11. | 79·0 | 78·43 | 2 ,, 3 ,, = 78·407 |
| 12. | N.D. | 73·04 | 1 ,, 2 ,, = 73·142 |
| 13. | 57·6 | 58·14 | 1 ,, 4 ,, = 57·656 |
| 14. | N.D. | 49·92 | 1 ,, 5·5 ,, = 49·756 |
| 15. | N.D. | 38·58 | 1 ,, 9 ,, = 37·701 |
| 16. | 29·5 | 29·59 | 1 ,, 13 ,, = 29·526 |
| 17. | 17·2 | 18·92 | 1 ,, 24 ,, = 18·492 |
| 18. | 8·7 | 8·7 | 2 ,, 56 ,, = 8·585 |
| 19. | 4·0 | 3·99 | 1 ,, 130 ,, = 4·021 |
| 20. | 1·0 | 1·06 | 1 ,, 510 ,, = 1·057 |
| 21. | 0·35 | 0·34 | 1 ,, 1500 ,, = 0·362 |
| 22. | 0·07 | 0·105 | 1 ,, 8000 ,, = 0·068 |

It will be noticed that by the analysis of the freezing-points the number of points of discontinuity in aqueous solutions of sulphuric acid was raised from 17 to 22. As the table shows, each of these 22 discontinuities was regarded by Pickering as proving the existence of a hydrate, although only three of these compounds could be crystallised out from the liquids by cooling.

R.S. 51. *The Theory of Osmotic Pressure and its Bearing on the Nature of Solutions.* *Phil. Mag.*, pp. 490–501 (June, 1890) (12 pp.).

This paper contains a criticism of Raoult's method of deducing the molecular weight of a dissolved substance from the depression of the freezing-point of the solution. Part of the criticism was directed against an obsolete view that the molecular depression was a constant (compare p. 46), and part was invalidated by ignoring the effects of dissociation (compare p. 86). It is therefore unnecessary to repeat Pickering's arguments, which have already been adequately discussed.

R.S. 52. *A New Form of Mixing-Calorimeter.* *Phil. Mag.*, vol. 29, pp. 247–253 (March, 1890) (7 pp.). (See p. 20.)

R.S. 53. *Note on the Gradual Alteration in Glass produced by altering its Temperature a few Degrees. Phil. Mag.*, vol. 29, pp. 289–291 (March, 1890) (2 pp.).

A pyknometer, kept at 18° during a period of six months, had a constant water capacity of 25·0070 gm., in spite of temporary heating to 38°; but when the room temperature was lowered to 8° its water capacity at 18° fell by about 0·001 gm., and continued to diminish over a period of a few weeks. This effect was attributed to a progressive shrinkage of the glass, but the effects are minute, not exceeding 1 part in 10,000, and would have been smothered by casual errors in the case of a less careful worker and would have passed unnoticed by one of less regular and systematic habits of work.

R.S. 54. *The Nature of Solutions. Phil. Mag.*, vol. 29, pp. 427–434 (May, 1890) (8 pp.).

Eight months before the appearance of Pickering's great paper on solutions (No. 49), the methods which he used were adversely criticised by Prof. Arrhenius (*Phil. Mag.*, vol. 28, p. 30 (1889)). This attack, and Pickering's reply to it, in the paper cited above, included the following questions :—

(*a*) *Smoothing of Curves.*—Arrhenius expressed the view that if, when seeking to detect discontinuities by differentiating the "smoothed" experimental curves, "Mr. Pickering had 'smoothed' his curve properly, he would evidently have removed these angular points or sudden changes of curvature" (p. 37). Pickering's reply, a part of which has already been quoted (p. 69), was that to adopt this view was merely begging the question, since the proposal was to prove the non-existence of discontinuities by continuing the smoothing until they had disappeared!

(*b*) *Concordance of Breaks in Different Experimental Curves.*—In order to establish the fact that the breaks which he had observed did not depend merely on inadequate smoothing of the experimental curves, Pickering laid stress on the fact that the same breaks had been observed in curves of the most diverse character, and laid down the criterion that the real existence of these breaks "can be established only by the concordance of the indications obtained from many independent sources" (p. 430). This point was emphasised by reproducing in a series of small-scale figures the various curves which he had analysed, and thus illustrating in a graphic manner the diverse character of the curves in which discontinuities *at identical concentrations* were discovered.

(*c*) *Uncertainty of Results as illustrated by Divergent Conclusions of Different Authors.*—Prof. Arrhenius's attack reached a climax in the statement that

" Mr. Pickering has deduced from the specific gravity quite different hydrates from Mendeléef, and from the electrical conductivity quite different hydrates from Crompton " (*loc. cit.*, p. 38).

In reply, Pickering was able to show that, in spite of these differences in detail, the final conclusions reached by the various workers showed a very satisfactory concordance, since his own list of discontinuities actually included all those mentioned by Mendeléef and Crompton, thus :—

| From densities. | | From conductivities. | | Mean from all sources. |
|---|---|---|---|---|
| Mendeléef. | Pickering. | Crompton. | Pickering. | Pickering. |
| About 84·5 | At 84·48 | About 84·5 | At 84·0 | 84·24 per cent. |
| ,, 73·1 | ,, 73·07 | ,, 73·1 | ,, 73 (?) | 73·04 ,, |
| ,, 47·6 | ,, 50·33 | ,, 47·6 | — | 49·92 ,, |
| — | ,, 18·5 | ,, 18·5 | — | 18·92 ,, |
| ,, 3·5 | ,, 4·15 | ,, 3·5 | ,, 3·5 | 3·99 ,, |

This concordance was a complete refutation of Arrhenius's criticism that different authors had reached different results by analysing the same curves ; and the fact that they had all detected breaks at identical compositions provided an additional argument for the real existence of these elusive phenomena.

R.S. 55. *The Expansion of Water and other Liquids. Phil. Mag.*, vol. 30, pp. 400–412 with 2 plates (November, 1890), (13 pp.).

By differentiating, and by using a bent lath, Pickering claimed to have detected in his own data for the expansion of water, and in those of other workers, changes of curvature at — 2·5°, 0°, 9 to 11°, 17 to 20° and 50 to 60°. Examination of Pierre's data for 11 other liquids gave " breaks " in the case of methyl and ethyl alcohol, ethyl ether, methyl iodide, and ethyl bromide, and negative results in six other cases.

Since, however, these results were not supported by examination of other properties, they were only put forward tentatively because of the strong evidence of discontinuities obtained in the experiments on sulphuric acid (compare p. 59).

R.S. 56. *Die vermeintlichen Alcoholhydrate. Zeitschr. physikal. Chem.*, vol. 6, pp. 10–15 (1890) (6 pp.).

Pickering concludes that the densities of solutions of alcohol give no proof of the existence of definite hydrates, and that Mendeléef was in error in assigning a linear character to the first differentials. A similar criticism of Mendeléef's

conclusions in reference to sulphuric acid and water is contained in Paper No. 49. He comments on the small range of densities (0·79 to 1) as compared with that available in the case of sulphuric acid (1·8 to 1).

R.S. 57. *The Theory of Dissociation with Ions and its Consequences.* *Proc. C.S.*, vol. 6, pp. 171–172 (1890).

A preliminary note ; compare R.S. 72.

R.S. 58. *Determinations of the Heat Capacity and Heat of Fusion of some Substances to test the Validity of Person's Absolute Zero.* *R.S. Proc.*, vol. 49, pp. 11–32 (1891) (22 pp.).

This paper was an experimental refutation of a suggestion of Person (*Ann. Chim. Phys.* [3], vol. 21, p. 315 (1847)) that the heat of fusion (which diminishes with falling temperature when the liquid has a greater heat capacity than the solid) falls to zero at a temperature of —160°. Pickering's data for this "constant" range from —160° C. for water to —992° C. for bromine, showing that the supposed regularity was non-existent.

This paper may be compared with a series of notes in the *Chemical News*, (Paper 24*d*, and R.S. 25, 26, 35), in which incorrect thermochemical notions were exposed and denounced.

R.S. 59. *Ueber das Kryoskopische Verhalten verdünnter Lösungen.* *Ber.*, vol. 24, pp. 1469–1475 (1891) (7 pp.).

R.S. 60. *Zur Frage, ob in Lösungen Association oder Dissociation stattfindet.* *Ber.*, vol. 24, pp. 1579–1591 (1891) (13 pp.).

Paper 60 (*a*). *Association versus Dissociation in Solutions.* *Chem. News*, vol. 63, pp. 290–291 (June 19, 1891).

An abstract of R.S. 60 (see p. 54, where quotations are given).

R.S. 61. *Starke Lösungen und die Dissociationshypothese.* *Ber.*, vol. 24, pp. 3317–3327 (1891) (11 pp.).

R.S. 62. *Das Kryoskopische Verhalten von Rohrzuckerlösungen.* *Ber.*, vol. 24, pp. 3328–3341 (1891) (14 pp.).

R.S. 63. *Die Theorie von der chemischen Residual-Affinität als Erklärung für die physikalische Natur der Lösungen.* *Ber.*, vol. 24, pp. 3629–3647 (1891) (19 pp.).

R.S. 64. *Note on Some Objections to the Work on Sulphuric Solutions. Chem. News*, vol. 64, pp. 1–2 (1891) (2 pp.).

A considered reply to a Discussion at the Chemical Society on June 4, 1891 (*Chem. News*, vol. 63, p. 305 (1891) ). Armstrong and Rücker had urged that any real discontinuities would be indicated on the curves drawn directly to represent the experimental results, without making use of the method of differentiation. Pickering replied that differentiation was only used to show more clearly breaks which would be recognised less easily in the original curves, and that during the preceding eighteen months he had been able to dispense entirely with differentiation and to rely entirely on an examination of the original curves.

In reply to Morley he writes that "a break at a particular hydrate by no means implies that this particular hydrate has only just begun to form there. Supposing there to be three hydrates : $CaCl_2$ with 7, 8 and $9H_2O$ respectively ; then, as water is added to $CaCl_2 . 7H_2O$ its effect will be to form some of the $CaCl_2 . 8H_2O$, and, as more water is added, the relative proportion of $CaCl_2 . 8H_2O$ present will be increased : as soon, however, as more water is added than is necessary to entirely form the $CaCl_2 . 8H_2O$, another hydrate $CaCl_2 . 9H_2O$, will begin to make its appearance, and the effect of adding more water now will be to increase the relative proportion of the latter and diminish the proportion of the $CaCl_2 . 8H_2O$ present : thus the effect of adding water to solutions stronger than $CaCl_2 . 8H_2O$ will be different from that produced by adding it to solutions weaker than $CaCl_2 . 8H_2O$ ; in other words, there will be a change in the rate of the effect at the composition of the $CaCl_2 . 8H_2O$ itself : this is just what is actually observed." This statement is perfectly true of non-dissociating hydrates ; but it is not necessarily true of a complex dissociating hydrate, since a large excess of water may be required to produce a maximum quantity of this hydrate quite apart from converting it into one of still greater complexity (see footnote 7).

The reply to Lupton is quoted fully on p. 71.

R.S. 65. *The Densities of Sulphuric Acid Solutions. Chem. News*, vol. 64, pp. 311–313 (1891) (3 pp.).

Paper 65 (*a*). *The Densities of Sulphuric Acid. Chem. News*, vol. 65, p. 50 (January 22, 1892).

This article and letter describe Pickering's controversy with Lunge (see pp. 10–12).

R.S. 66. *The Nature of Solutions as elucidated by a Study of the Densities, Heats of Dissolution and Freezing-Points of Solutions of Calcium-Chloride. Proc. Chem. Soc.*, vol. 7, p. 105 (1891).

A preliminary note of work subsequently published in German (see R.S. 84).

R.S. 67. *Note on a Recent Criticism by Mr. Sydeny Lupton of the Conclusions drawn from a Study of Various Properties of Sulphuric Acid Solutions. Proc. Chem. Soc.*, vol. 7, p. 105 (1891).

A preliminary note (compare R.S. 70).

R.S. 68. *Chemical Action and the Conservation of Energy. Nature*, vol. 43, pp. 165–167 (December 18, 1890).

R.S. 69. *Deduction from the Gaseous Theory of Solution. Nature*, vol. 43, pp. 488–489 (March 26, 1891).

R.S. 70. *Mr. Sydney Lupton's Method of Reducing the Results of Experiments. Phil. Mag.*, vol. 32, pp. 90–98 (July, 1891) (9 pp.).

A reply to the criticism of Lupton (*Phil. Mag.*, vol. 31, p. 418 (1891) ). The principal points raised have already been discussed, *e.g.*, the failure of Lupton's attempt to make one parabola cover two sections of the curve (p. 70) and the cumulative character of the evidence for the real existence of discontinuities (p. 72). The " minor objections," to which Pickering replies in a series of 12 numbered paragraphs, do not appear to be sufficiently important to call for a detailed summary. A paper by Mr. E. H. Hayes, dealing with the mathematical aspects of Pickering's method of analysis with a bent lath, and printed immediately after Pickering's own paper, has already been described (p. 67).

R.S. 71. *Chemical Action at a Distance. Phil. Mag.*, vol. 32, pp. 478–480 (November, 1891) (3 pp.).

Ostwald (*Phil. Mag.*, vol. 32, p. 145 (August, 1891) ) had described some electro-chemical experiments for which, in his opinion, " a satisfying explanation can be first gained on the ground of the *Theory of free ions*." Pickering shows that they are all in accord with the classical ideas of electro-chemistry and do not call for the intervention of free ions.

> " All these experiments seem to be on a par with one described some time ago by Prof. Ostwald, consisting in the production of a small amount of electrolysis by a current of electrostatic origin : experiments which are perfectly consistent with the old electro-chemical theory, dressed up in the

garb of the dissociation theory, and then presented to us as proof positive of this theory " (pp. 479–480).

R.S. 72. *The Theory of Dissociation into Ions and its Consequences. Phil. Mag.*, vol. 32, pp. 20–27 (July, 1891) (7 pp.).

A controversial paper which has already been cited very fully (pp. 50–53).

R.S. 73. *Das kryoskopische Verhalten schwacher Lösungen.* (i) *Ber.*, vol. 25, pp. 1099–1107 (9 pp.). (ii) *Ber.*, vol. 25, pp. 1314–1324 (11 pp.). (iii) *Ber.*, vol. 25, pp. 1589–1599 (11 pp.). (iv) *Ber.*, vol. 25, pp. 1854–1865 (12 pp.). (v) *Ber.*, vol. 25, pp. 2011–2017 (7 pp.). (vi) *Ber.*, vol. 25, pp. 2518–2524 (7 pp.). (vii) *Ber.*, vol. 25, pp. 3434–3440 (7 pp.).

These papers contain the data used by Pickering in the general discussion of Paper No. 78, together with tables showing the errors when the data are represented by one, two or three discontinuous curves. His claim to have detected, by means of breaks in the freezing-points of dilute solutions, a series of 18 hydrates, with 101 to 9100 $H_2O$ and analogous compounds with 156 and 1820 molecules of naphthalene, need not be accepted, since even if the changes of curvature are real there is no need to suppose that the composition at which they occur are those of definite chemical compounds.

R.S. 74. *The Contraction on mixing Sulphuric Acid and Water. Chem. News.*, vol. 65, pp. 14–15 (1892) (2 pp.).

Pickering shows that the maximum contractions on mixing sulphuric acid and water occur as follows :—

| Temperature. | Composition. | Maximum contraction per gram. | Composition. | Maximum contraction per c.c. |
|---|---|---|---|---|
| ° | Per Cent. | | Per cent. | |
| 38·203 | 70·1 | 0·059907 | 76·3 | 0·097957 |
| 28·064 | 69·1 | 0·061040 | 76·0 | 0·100010 |
| 17·925 | 67·5 | 0·061825 | 76·0 | 0·101585 |
| 7·978 | 67·0 | 0·062827 | 75·8 | 0·103595 |

" It will be noticed that the position of neither of these maxima agree with the composition of the dihydrate, which contains 73·14 per cent. of acid, nor with any of the hydrates, the existence of which I inferred from breaks in the curves representing various properties of the solutions, and it is scarcely necessary for me to point out again that a maximum point by no means necessarily coincides with a change of curvature. Prof. Lunge's

statement that the maximum does coincide with the dihydrate, and also Mendeléef's statement to the same effect (' Principles of Chemistry,' vol. 2, p. 237) cannot, therefore, be accepted as correct " (p. 15).

R.S. 75. *Osmotic Pressure. Nature*, vol. 47, pp. 175–176 (December 22, 1892).

R.S. 76. *The Density of Sulphuric Acid Solutions. Phil. Mag.*, vol. 33, pp. 132–144 (January, 1892) (13 pp.).

A reply to Rücker (*Phil. Mag.*, vol. 32, p. 304 (1891) ). This important paper has already been discussed very fully (pp. 76–78).

R.S. 77. *The Hypothetical Tetrachloride of Manganese. Phil. Mag.*, vol. 33, pp. 284–290 (March, 1892) (7 pp.).

A continuation of one of Pickering's early inorganic researches (R.S. 2). Vernon (*Proc. Chem. Soc.*, p. 58 (April, 1890); *Phil. Mag.*, vol. 31, p. 439 (1891)) had asserted that the higher chloride was $MnCl_4$ and not $Mn_2Cl_6$. Pickering now claims that Vernon's data support his own arguments on the following points :—

1. *The first half of the available chlorine is evolved much more rapidly than the second half.*

2. *The greatest amount of available oxygen obtained by decomposing the higher chloride by water is* 50 *per cent. of that present in the dioxide taken.*

3. *That the amount of higher chloride formed is largely increased by dissolving the dioxide in the presence of a molecular proportion of a manganous chloride.*

4. *Manganese sesquioxide dissolves in hydrochloric acid without the liberation of any free chlorine, and nearly the whole of the available oxygen in it can be removed on decomposing the solution with water.*

R.S. 78. *The Recognition of Changes of Curvature by Means of a Flexible Lath. Phil. Mag.*, vol. 33, pp. 436–466 (May, 1892) (31 pp.).

This paper has already been cited fully (pp. 68–69).

R.S. 79. *The Heat of Dissolution of Gases in Liquids. Phil. Mag.*, vol 34, pp. 35–46 (July, 1892) (12 pp.).

A study of the heat of dissolution of various vapours, in order to test the " physical " theory that substances in dilute solution are in the same condition as in the gaseous state (see p. 55).

R.S. 80. *Die Hydrate der Chlorwasserstoffsäure. Ber.*, vol. 26, pp. 277–284 (1893) (8 pp.).

This paper records the isolation by freezing of the new hydrate $HCl.3H_2O$, as predicted from a study of the properties of the solutions (see p. 40).

R.S. 81. *Die Gefrierpunkte von Chlornatriumlösungen. Ber.*, vol. 26, pp. 1221–1227 (1893) (7 pp.).

Controversial with H. C. Jones (see pp. 19 and 35).

R.S. 82. *Die Gefrierpunkte von Natriumchloridlösungen. Ber.*, vol. 26, pp. 1977–1979 (1893) (3 pp.).

Controversial with H. C. Jones (see pp. 19 and 35).

R.S. 83. *Die Hydrate der Iodwasserstoffsäure. Ber.*, vol. 26, pp. 2307–2310 (1893) (4 pp.).

In this paper Pickering records the separation from aqueous hydriodic acid of a *dihydrate*, a *trihydrate*, melting at — 48°, and a *tetrahydrate*, melting at — 36·5°. He also records a " break " in the ice-curve at about 30 per cent. HI, which would correspond with the hydrate III, $17H_2O$ (see p. 41).

R.S. 84 (*a*). *Prüfung der Eigenschaften von Chlorcalciumlösungen.*

R.S. 84 (*b*). *Untersuchung einiger Eigenschaften von Chlorcalciumlösungen.*

R.S. 84 (*c*). *Prüfung einiger Eigenschaften von Chlorcalciumlösungen. Ber.*, vol. 26, pp. 2766–2771 (1893) (6 pp.). *Ber.*, vol. 27, pp. 67–75 (1894) (9 pp.). *Ber.*, vol. 27, pp. 1379–1385 (1894) (7 pp.).

In these papers Pickering claims to have detected " breaks " in the curves representing the freezing-point, heat of solution and density of aqueous solutions of calcium chloride at compositions corresponding with 7·23, 8·10, 9·74, 12·8, 17·4, 28·7, 60·8, 145, 249 and 1534 $H_2O$. The only hydrates which could be crystallised out, however, contained $6H_2O$ and $4H_2O$. Since these were outside the range of compositions studied, their presence could not be detected by studying the physical properties of the solutions at atmospheric temperatures.

R.S. 85. *Note on the Refractive Indices and Magnetic Rotations of Sulphuric Acid Solutions. J.C.S.*, vol. 63, pp. 99–103 (January, 1893) (5 pp., with 1 plate).

The refractive indices (data of Van der Willigen) pass through a sharp maximum at the monohydrate $H_2SO_4, H_2O$ (84·5 per cent. $H_2SO_4$) which is more refractive than the anhydrous acid. " Breaks " were also detected at about 60 per cent. and 24 per cent. $H_2SO_4$. " These results, therefore, agree well in two cases with the molecular rotations, which showed breaks at 84, and 48 or 58 per cent.; the rotations, however, showed no break at a lower

percentage" (p. 101). The same three breaks, at 83·5, 60 and just under 30 per cent., were detected when the density data were plotted out in the form of "molecular volumes of $H_2SO_4$ in solution at 18°" (p. 102).

R.S. 86. *The Hydrate Theory of Solutions. Some Compounds of the Alkylamines and Ammonia with Water.* *J.C.S.*, vol. 63, pp. 141–195 (1893) (54 pp.).

The following maximum freezing-points were observed :—

| | | | | | |
|---|---|---|---|---|---|
| $NH_2Me$, $3H_2O$ | at | − 35·8° | $NH_2Pr$, $\frac{1}{2}H_2O$ | at | − 61·1° |
| $NHMe_2$, $7H_2O$ | at | − 16·85° | $NH_2Pr$, $8H_2O$ | at | − 13·5° |
| $NHMe_2$, $H_2O$ | about | − 68° | *iso*-$NH_2Pr$, $8H_2O$ | at | − 4·24° |
| $NMe_3$, $11H_2O$ | at | + 5·34° | $NHPr_2$, $\frac{1}{2}H_2O$ | at | − 17·20° |
| $NH_2Et$, $\frac{1}{2}H_2O$ | at | − 71·2° | $NPr_3$. | Limited solubility. | |
| $NH_2Et$, $5\frac{1}{2}H_2O$ | at | − 7·48° | *iso*-$NH_2Bu$. | Max. not reached. | |
| $NHEt_2$, $\frac{1}{2}H_2O$ | at | − 18·93° | *sec*-$NH_2Bu$. | ,, | ,, ,, |
| $NHEt_2$, $8H_2O$ | at | − 6·96° | $NH_2C_5H_{10}$. | ,, | ,, ,, |
| $NEt_3$, $2H_2O$ | at | − 19·2° | | | |

In addition, a number of "breaks" were detected in the curves for the freezing of ice or of a given hydrate.

R.S. 87. *Isolation of Two Predicted Hydrates of Nitric Acid.* *J.C.S.*, vol. 63, pp. 436–443 (1893) (8 pp.).

The hydrates were $HNO_3 . 2H_2O$ and $HNO_3 . 3H_2O$ (see pp. 38–39).

R.S. 88. *The Hydrates of Sodium, Potassium, and Lithium Hydroxides.* *J.C.S.*, vol. 63, pp. 890–909 (1893) (20 pp. with 1 plate).

The hydrates isolated and their freezing-points were as follows :—

| | | | |
|---|---|---|---|
| NaOH, $H_2O$ | + 64·3° | KOH, $H_2O$ | + 143° |
| NaOH, $2H_2O$ | + 12·5° | KOH, $2H_2O$ | + 35·5° |
| NaOH, 3·1 $H_2O$ | + 2·73° | KOH, $4H_2O$ | − 33° |
| NaOH, 3·5 $H_2O$ | + 15·55° | | |
| NaOH, $4H_2O$ | + 7·57° | LiOH, $H_2O$. | Max. not reached. |
| NaOH, $4H_2O$ | − 1·7° | | |
| NaOH, $5H_2O$ | − 12·22° | | |
| NaOH, $7H_2O$ | − 23·51° | | |

R.S. 89. *A Study of the Properties of Some Strong Solutions.* *J.C.S.*, vol. 63, pp. 998–1027 (1893) (30 pp.).

A study of the molecular depression of the freezing-point of water, benzene, and acetic acid, by various organic compounds; also of the freezing-point of

sulphuric acid by acetic acid and of naphthalene by benzene. In each case the molecular depressions were followed up to very high concentrations, *e.g.*, 8 mols. of solute for 1 mol. of solvent. Pickering noted a "general tendency for the molecular depression in the case of non-electrolytes to diminish considerably as the strength of the solution increases, in contradistinction to electrolytes, where, excepting in very weak solutions, the depression increases with the strength" (p. 1008).

R.S. 90. *Note on the Stereoisomerism of Nitrogen Compounds.* *J.C.S.*, vol. 63, pp. 1069–1075 (1893) (7 pp.).

In this paper Pickering suggests a triangular configuration of the hydrogens in ammonia, with another atom opposite each face of the triangle in quinquevalent nitrogen compounds.

R.S. 91. *Some Experiments on the Diffusion of Substances in Solution.* *Phil. Mag.*, vol. 35, pp. 127–134 (February, 1893) (8 pp.).

An attempt to test the supposed identity of osmotic pressure with gas pressure (see p. 56).

R.S. 92. *The Hydrates of Hydrogen Bromide.* *Phil. Mag.*, vol. 36, pp. 111–119 (July, 1893) (9 pp.).

This paper describes the isolation of a new trihydrate (see p. 41).

R.S. 93. *Die Knicke der Hydrattheorie.* *Ber.*, vol. 27, pp. 30–31 (1894) (2 pp.)

A reply to Meyerhoffer (p. 79).

R.S. 94. *Examination of Recent Freezing-Point Determinations.* *J.C.S.*, vol. 65, pp. 293–312 (1894) (20 pp.).

Controversial with H. C. Jones (see p. 19).

R.S. 95. *On the Freezing-Points of Sodium Chloride Solutions.* *Phil. Mag.*, vol. 37, pp. 162–164 (January, 1894) (3 pp.).

Controversial with H. C. Jones (see p. 19).

R.S. 96. *The Densities of Solutions of Soda and Potash.* *Phil. Mag.*, vol. 37, pp. 359–375 (April, 1894) (17 pp.).

A careful study of relative densities leading to the detection of "breaks" corresponding with hydrates already described in R.S. 88 (see pp. 12 and 44). Since the stock solutions were standardised only by titration, the absolute values of the density have not the same value as in the case of the earlier measurements with sulphuric acid (R.S. 49).

R.S. 97. *The Hydrates of Hydrogen Chloride. Proc. C.S.*, vol. 9, p. 45 (1893).

A preliminary note (see No. 80).

R.S. 98. *A Comparison of some Properties of Acetic Acid, and its Chloro- and Bromo-Derivatives. J.C.S.*, vol. 67, pp. 664-684 (1895) (21 pp. and 1 plate).

The properties measured were the heat capacities of the solids and liquids, the heats of dissolution, and of fusion of the solid acids, the freezing-points, freezing-point depressions of the acids by water, and of water by the acids, and finally the freezing-points of complete series of mixtures of water with acetic acid and with the three chloracetic acids.

R.S. 99. *The Unit of Heat. Nature*, vol. 52, p. 80 (May 23, 1895).

R.S. 100. *The Heat of Combination of Substances in the Liquid and Solid Condition. Phil. Mag.*, vol. 39, pp. 510-528 (June, 1895) (19 pp.).

The heat of formation of the hydrate $H_2SO_4$, $H_2O$ happens to be the same (6667 and 6530 cal.) in the liquid and solid states. This result is accidental, since no similar relation could be detected in other cases, *e.g.* :—

| | Liquid. | Solid. |
|---|---|---|
| $NaOH . H_2O$, $2{\cdot}5\ H_2O$ .. .. | 5832 | 3783 |
| $SnBr_4$, $8H_2O$ .. .. .. .. | 14906 | 9748 |
| $C_6H_{14}O_2$, $6H_2O$ (Pinacone) .. .. | 1365 | 3792 |
| $C_6H_4(NO_2)_2$, $C_{10}H_8$ .. .. .. | — 145 | — 12 |
| $C_7H_6(NO_2)_2$, $C_{10}H_8$ .. .. .. | 599 | 287 |
| $(C_6H_5)_2N_2$, $C_6H_6$ .. .. .. | — 1610 | — 369 |

R.S. 101. *Self-Recorded Breaks in the Properties of Solutions. Phil. Mag.*, vol. 40, pp. 472–476 (November, 1895) (5 pp.).

"Breaks" can be recorded automatically by allowing sulphuric acid (5 or 10 per cent.) to flow into water in a calorimeter and plotting the course of the time–temperature curve.

R.S. 102. *The Theory of Dissociation into Ions. Nature*, vol. 55, pp. 223–224 (January 7, 1897); vol. 56, p. 29 (May 13, 1897).

A discussion with Whetham in reference to (i) the osmotic pressure of mixtures of propyl alcohol and water; (ii) the freezing-points of solutions of sulphuric acid and water in acetic acid. In the first case Pickering claimed that, since either propyl alcohol or water could be drawn through a semi-

permeable membrane from the pure liquid into the solution, the membrane could not be impermeable to either component but only to complexes of the two substances in the solution. In the second case, Whetham admitted that the details given by Pickering showed "that combination does occur when sulphuric acid is dissolved in water," but regarded it as "strong evidence for the modification of the dissociation theory for which I am contending," namely, that "dissociation of the ions from *each other* does not forbid the assumption that the ions are linked with one or more solvent molecules" (see p. 33).

Paper 103. *Thermal Phenomena attending the Change in Rotatory Power of freshly prepared Solutions of certain Carbohydrates, with some Remarks on the Cause of Multirotation.* By Horace T. Brown, F.R.S., and Spencer U. Pickering, F.R.S. *J.C.S.*, vol. 71, pp. 756–783 (1897) (28 pp).

See pp. 26 to 27.

Paper 104. *Thermo-Chemistry of Carbohydrate Hydrolysis.* By Horace T. Brown, F.R.S., and Spencer U. Pickering, F.R.S. *J.C.S.*, vol. 71, pp. 783–795 (1897) (13 pp.).

See pp. 27–28.

Paper 104 (*a*). *Hydrates in Solution* (discussion). *Trans. Faraday Soc.*, vol. 3, pp. 169–170 (1907).

Paper 105. *Note on Arsenates of Lead and Calcium.* *J.C.S.*, vol. 91, pp. 307–314 (1907) (8 pp.).

A study of the precipitation of sodium arsenate by lead acetate, lead nitrate, calcium nitrate or calcium chloride, with a view to the use of the product as an insecticide.

Paper 106. *The Interaction of Metallic Sulphates and Caustic Alkalis.* *J.C.S.*, vol. 91, pp. 1981–1988 (1907) (8 pp.).

By adding caustic alkalis to aqueous solutions of metallic sulphates, the following basic sulphates were prepared :—

$5NiO, 3SO_3$

$\left\{\begin{matrix} 5NiO, 2SO_3 \\ 5Al_2O_3, 6SO_3 \end{matrix}\right.$

$\left\{\begin{matrix} 4CuO, SO_3 \\ 4CoO, SO_3 \\ 4CdO, SO_3 \end{matrix}\right.$

$\left\{\begin{matrix} 5CuO, SO_3 \\ 5NiO, SO_3 \\ 5ZnO, SO_3 \end{matrix}\right.$

$\left\{\begin{matrix} 10CuO, SO_3 \\ 10FeO, SO_3 \end{matrix}\right.$

Paper 107. *The Chemistry of Bordeaux Mixture.* *J.C.S.*, vol. 91, pp. 1988–2001 (1907) (14 pp.).

This mixture is made by addition of milk of lime to aqueous copper sulphate. Such mixtures may contain the following products:—

$4CuO, SO_3$ (with $0{\cdot}06\ CaSO_4$).
$5CuO, SO_3, 0{\cdot}25CaSO_4$.
$10CuO, SO_3, 1{\cdot}3CaSO_4$.
$10CuO, SO_3, 4CaO, SO_3$.

The object to be aimed at is to produce the first of these compounds.

When copper sulphate is precipitated by lime in presence of excess of sodium sulphate, the precipitate contains sodium sulphate as well as calcium sulphate. The most basic product is —

$10CuO, SO_3, 2(Na_2Ca)SO_4$, or $10CuO, SO_3, Na_2SO_4, CaSO_4$.

Paper 108. *Emulsions.* *J.C.S.*, vol. 91, pp. 2001-2021 (1907) (20 pp.).

This paper is cited on pp. 105–106.

Paper 109. *The Hydration of Precipitates.* *J.C.S.*, vol. 95, pp. 123–128 (1909) (6 pp.).

Recently formed precipitates will emulsify oils, and by adjusting the proportions of precipitate and oil, an emulsion can be obtained which is of the same density as the liquid. By measuring this density and determining the weight and volume of the oil, and of the precipitate after drying, it is possible to deduce the weight and volume of the water in the precipitate.

Paper 110. *The Carbonates of Copper and the Cupricarbonates.* *J.C.S.*, vol. 95, pp. 1409–1429 (1909) (21 pp.).

In addition to azurite, $3CuO, 2CO_2, H_2O$, and ordinary malachite, $2CuO, CO_2, H_2O$, the following carbonates were isolated:—

$5CuO, 2CO_2$.
$5CuO, 3CO_2$.
$8CuO, 3CO_2, 6H_2O$.

Attempts to prepare $3CuO, CO_2$, and more basic carbonates were not successful.

The basic carbonates dissolve in bicarbonates to form a double carbonate of copper and the alkali metal. This separates as a light blue double salt; but since it will not re-dissolve in the mother liquor, the solution probably contains an isomer, *e.g.*, NaO . CO . O CuO . CO . ONa contrast $Na_2CO_3, CuCO_3$. The copper in this solution is electro-positive, but has a colour 30 times more intense than

in copper sulphate. With excess of normal sodium carbonate, the copper becomes electronegative, an α-cupricarbonate $Na_2Cu(CO_3)_2 . xNa_2CO_3$ being formed, which oxidises dextrose and is formulated as containing quadrivalent copper directly linked to carbon. Excess of sodium hydroxide dissolves the basic carbonate, forming a deep blue solution of a β-cupricarbonate, $Na_2Cu(CO_3)_2$, $x$NaOH, which oxidises dextrose and dissolves cellulose. The latter property may, however, be attributed to the formation of a cuprate containing the group Cu(ONa)(OH).

Paper 111. *Cupricitrates.* *J.C.S.*, vol. 97, pp. 1837–1852 (1910) (14 pp.).

The products obtained were as follows :—

(1) Potassiocupric citrate, $(C_6H_5O_7)_2CuK_4$.
(2) A β-cupricitrate, $(C_6H_5O_7)_2K_4H_2CuO$.
(3) Potassium β-cupricitrate, $(C_6H_5O_7)_2K_4HKCuO$.
(4) Potassium β-cupricitrate, $(C_6H_4O_7)_2K_6Cu$, $6H_2O$.
(5) Potassium α-cupricitrate, $2(C_6H_5O_7)_2CuK_4$, $K_2Cu(CO_3)_2$.
(6) Tetrapotassio-cupric-β-cupricitrate, $(C_6H_5O_7)_2K_4Cu$, CuO.
(7) and (8) Dipotassio-dicupric-β-cupricitrate, $(C_6H_5O_7)_2K_2Cu_2$, CuO.
(9) Copper cupricitrate, $(C_6H_5O_7)_2Cu_3$, CuO.
(10) Basic copper citrate, $(C_6H_5O_7)_2Cu_3$, 4CuO.
(11) Potassio-cupric-β-cupricitrate, $(C_6H_5O_7)_3K_5Cu_2$, 2CuO.
(12) Potassium-γ-cupricitrate (not isolated).
(13) Potassio-cupric hydrogen citrate, $(C_6H_5O_7)_2K_4Cu$, $C_6H_5O_7KH_2$, $H_2O$.

Paper 112. *The Constitution of Basic Salts.* *J.C.S.*, vol. 97, pp. 1851–1860 (1910) (10 pp.).

Graphic formulæ containing quadrivalent copper are assigned to the complex products precipitated from aqueous copper sulphate by lime-water.

Paper 113. *Cupritartrates and Analogous Compounds.* *J.C.S.*, vol. 99, pp. 169–180 (1911) (12 pp.).

A series of cupritartrates, saccharates, mucates and quinates is described. The view is advanced that these " must be considered as substances in which CuO is added to the nucleus, and not as substances in which copper atoms displace hydrogen atoms." In these formulæ a tetrad atom of copper is linked directly to two atoms of carbon. " Another view, which is, perhaps, less open to objection, is that the hydrogen atoms of the alcoholic hydroxyls become displaced by CuOH groups " (p. 179).

Paper 114. *Potassium Cupricarbonates.* *J.C.S.*, vol. 99, pp. 800–811 (1911) (12 pp.).

"If potassium formed cupri-carbonates analogous to all those cupri-compounds which have been isolated, or suggested as existing, in other cases, eight different compounds of copper carbonate with potassium carbonate would exist: these eight compounds have all been isolated, as well as one additional compound. Two are dehydration products of others; one is a gelatinous substance; the other six are crystalline: all have well-marked physical, and, in some cases, chemical properties, differentiating them from each other. In only two cases is the evidence as to composition at all doubtful" (p. 800).

Paper 115. *Cupriglycollates.* *J.C.S.*, vol. 99, pp. 1347–1353 (1911) (6 pp.).

The composition of copper glycollate corresponds with the formula $HO.Cu.O.CH_2.CO.OK, H_2O$. Basic glycollates were also prepared.

Paper 116. *Copper Salts and their Behaviour with Alkalis.* *J.C.S.*, vol. 101, pp. 174–192 (1912) (19 pp.).

"Those cupri-compounds wherein the copper is in the non-carboxylic portion of the molecule contain it as CuOH displacing hydrogen in alcoholic hydroxyl . . . Alcoholic groups are necessary for the formation of such compounds," since, "in the nineteen cases in which no such group is present, no cupri-salt is formed by the action of alkali, but a basic salt is precipitated instead; whereas in the thirteen other cases, where alcoholic hydroxyl groups are present, a cupri-salt is formed; sometimes accompanied with the formation of some basic salt also, in amounts depending on the proportion of water present" (p. 174).

Paper 117. *Alkaline Cupri-Compounds.* *J.C.S.*, vol. 101, pp. 1614–1625 (1912) (12 pp.).

"Twenty-four substances, representing ten different types of compounds, have been obtained, and, with the exception of four salts representing one of these types, they are all crystalline" (p. 1614).

"The salts above described supply twenty-two instances in which the empirical formulæ necessitate the copper being present as CuO, and not as Cu displacing hydrogen; the average difference between the found molecular weights and those calculated on the former view is 1·5 per cent. (or algebraically, − 0·6), whereas on the latter view it is 7·8 per cent., all the differences being positive" (p. 1624).

Paper 118. *The Colour Intensity of Copper Salts.* *J.C.S.*, vol. 101, pp. 1625–1634 (1912) (10 pp.).

By working with columns of liquid differing only in the ratio 1 : 2, it was shown that the molecular colour intensity of copper sulphate is constant from 8 to 0·016 gram. in 100 c.c.

" With organic salts the intensity is greater, and diminishes with the dilution; this has been explained by postulating the presence of complex ions; copper acetate, for instance, ionising into $AcCu|Ac^-$ (Sidgwick, and Tizard). Such ionisation, to explain the facts, would have to *decrease* with dilution, and, moreover, is inapplicable in the case of salts of dibasic acids. Its existence seems to be definitely negatived by the results obtained on electrolysing certain cupric salts; for it has been ascertained that the highly coloured ion in such cases is not the cation, but the anion, just as it is in the case of the cupricitrates, cupritartrate and cupricarbonate; thus, with the malate and citrate, of which strong and highly coloured solutions are obtainable, electrolysis in a double vessel connected by a tube containing gelatin reveals a deep blue anion travelling in one direction, and a pale blue cation in the opposite direction " (p. 1631).

" On the view now suggested, dyad copper, or copper in an ordinary hydroxyl group, has always in solution the same colour intensity (unity), whilst tetrad copper, or copper in the electronegative portion of the molecule, has an intensity about nineteen times greater: the co-existence of these two forms of compounds in solutions of organic copper salts explains, not only the colour phenomena, but the results obtained on electrolysis also " (pp. 1631–1632).

" It is probable that some of the so-called normal salts are really the corresponding cupri-compounds. Nearly all the copper salts of organic acids are characterised by sparing solubility in water. . . . In strong contrast with these, we have the citrate, malate and glycerate, which are all excessively soluble. . . . Since the glycerate in question has been found to be the cupri-compound, the natural inference is that the other two also are cupri-compounds " (pp. 1633–1634). In a footnote Pickering adds, " This has now been established as regards the malate."

" Whether the deep coloration of the various compounds examined should be regarded as due to the copper in them being quadrivalent, or to its being in the electronegative portion of the molecule, is not certain; but the former explanation appears preferable. . . . That a considerable increase in colour intensity should accompany the change in function of an atom from a dyad to tetrad is . . . . rendered probable by the analogous behaviour

of the allied elements, iron and manganese, and such a change is, indeed, only an extension of the phenomena already presented by copper itself, when the univalent . . . and colourless atom in the cuprous salts becomes highly coloured on its assumption of bivalent functions. Judging by the ferrocyanides, great increased depth of colour is not correlated with a position in the electronegative portion of a molecule" (p. 1634).

Paper 119. *Note on Cupric Malate and Citrate.* *J.C.S.*, vol. 103, pp. 1354–1357 (1913) (4 pp.).

Paper 120. *Organic Ferric Salts.* *J.C.S.*, vol. 103, pp. 1358–1368 (1913) (11 pp.).

"The oxalate is a normal salt, but the tartrate, malate and citrate are ferri-compounds closely resembling the cupri-compounds: the iron is in the electronegative ion, does not give the usual reactions of iron, and possesses great colour intensity. The compounds are very soluble, and solidify in scale form" (p. 1367).

Paper 121. *The Colour Intensity of Iron and Copper Compounds.* *J.C.S.*, vol. 105, pp. 464–483 (1914) (20 pp.).

"Iron in ferric compounds may exist in five different conditions:—

"(1) Both atoms in the electropositive or hydroxyl position: colour-intensity very small, probably *nil* as regards yellow light.

"(2) Both atoms in the electronegative portion of the molecule, directly united to the nuclear element of this portion (ferri-compounds): intensity about 20.

"(3) One atom in each of the two above conditions: intensity 10.

"(4) As ordinary colloidal hydroxide by the hydrolysis of electropositive iron: intensity about 135.

"(5) As darker colloidal hydroxide, by the hydrolysis of electronegative iron: intensity about 280" (p. 483).

Paper 122. *Metallo-Compounds of Cobalt and Nickel.* *J.C.S.*, vol. 107, pp. 942–954 (1915) (13 pp.).

"Both cobalt and nickel form compounds closely analogous to the cupri-compounds, which are characterised by great depth of colour and solubility, and by containing the metal in the anion, as is proved by electrolysis."

"Organic salts of all three metals dissolve in alkali hydroxides, and yield

compounds of which the two which have been isolated in the case of cobalt are similar to two isolated in that of copper.

" The colour intensity of solutions of inorganic salts of the three metals is not affected (except in the case of very concentrated solutions of cobalt) by dilution, but that of the organic salts decreases on dilution."

" Two metameric forms of normal cobalt racemate have been obtained " (p. 954).

Paper 123. *Metallo-Compounds in Solution.* *J.C.S.*, vol. 107, pp. 955–959 (1915) (4 pp.).

" The great colour-intensity of solutions of copper salts of organic acids, and the variations in the intensity with the concentration of the solution, were explained by the co-existence in solution of two forms of the compound, the normal salt with low colour intensity, and a cupri-compound with a colour intensity about twenty times greater " (p. 955).

" Scales or glass are obtained from those compounds which, according to the colour intensity, are rich in the cupri-compound, and crystals from those which are rich in the normal salt " (p. 957).

Paper 124. *Compounds of Iron, Manganese, Lead and the Metals of Group II.* *J.C.S.*, vol. 109, pp. 235–250 (1916) (15 pp.).

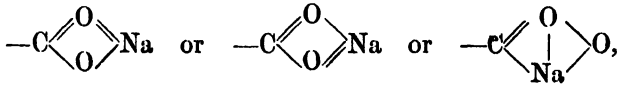
A study of the tartrates, citrates and malates of Mn, Fe, Pb, Mg, Cd, Hg, Ca, Sr, Ba. The conclusions from these observations have already been cited (pp. 114–115).

Paper No. 125. *The Detergent Action of Soap.* *J.C.S.*, vol. 111, pp. 86–101 (1917) (16 pp.).

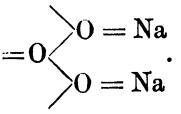
See p. 106.

Paper No. 126. *Problems bearing on Residual Affinity.* *R.S. Proc.*, A, vol. 93, pp. 533–549 (1917) (17 pp. and 1 plate).

This paper, which is almost the last of Pickering's formal publications, is mainly theoretical, although some of the points raised are made the subject of experiment. The paper is not easy to follow, since the ideas on which it is founded do not coincide with the normal canons of belief. In particular, modern chemical and physical theory finds no place for the tervalent sodium atom, which is the leading feature of formulæ such as those suggested for the carboxylates



of which the last is assigned to the metallato-compounds of sodium. In the same way Pickering postulates that the pyrophosphates contain the group



The views thus put forward have not been supported by later workers, and have not contributed substantially to current theoretical beliefs.

Paper No. 127. *Flocculation. R.S. Proc.*, A, vol. 94, pp. 315–325 (1918) (11 pp. and 1 plate). See pp. 107–108.

Paper No. 128. *The Explosion at Bailleul. Nature*, vol. 104, p. 5 (September 4, 1919).

The explosion of a munition dump at Bailleul was heard at Harpenden.

Paper No. 129. *Radiation Temperatures. Nature*, vol. 104, pp. 153–154, (October 23, 1919).

Paper No. 130. *Robert Warington* (Obituary notice). *Trans. C.S.*, vol. 93, pp. 2258–2269 (1908).

# PART II.—INVESTIGATIONS ON THE EFFECT OF EXTERNAL CONDITIONS ON THE GROWTH OF FRUIT TREES.

## CHAPTER I.

### ORIGIN, SCOPE AND METHODS ADOPTED AT THE WOBURN FRUIT FARM.

There is no logical connection between the two branches of Pickering's scientific work. The fruit investigations were wholly unrelated to those on physical chemistry and cannot have been even dimly suggested by them. The reason for the taking up of the new work must be sought deep down in his character. During the early 'eighties he began coming out from his mother's house in London to Harpenden, then a small and almost entirely rural village: he lodged with a labourer's family and worked in the fields with the labourers. The two accidents to his eye had necessitated its removal and left him far from robust in health, and he seems to have been much the better for these visits. But we may doubt whether this was his sole object. A resourceful person like Pickering, trained at Eton and Oxford and brought up in the then fashionable Bryanston Square, could have come into the country for the benefit of his health without living and working with labourers. It seems more probable that he had come under the influence of the humanistic teachings of William Morris, Toynbee and others then making themselves felt among the more serious minded of the younger men, and it was in response to impulses such as these that he broke away from his London laboratory and began his life in the country.

Whatever the reason may have been, the selection of Harpenden was fortunate, as it enabled him to work on the Rothamsted Experimental Plots and to acquaint himself with the possibilities of applying science to crop production. With Pickering this meant that he soon wanted to do experiments himself on the subject. How or why he came to think of fruit rather than any other crop as the outlet for his energies we do not know; he had no knowledge or experience of fruit growing. But he succeeded in interesting the Duke of Bedford, whom he had known both at school and at college, and the Duke, with characteristic energy, in 1894 set aside 20 acres of land for an experimental fruit farm, and from that date till 1919, a period of 24 years, bore all the expenses of the work. The purpose of the station was unexceptionable, and it is clearly

stated in the first report:—"The main object of this experimental station is to ascertain facts relative to the culture of fruit, and to increase our knowledge of, and to improve our practice in, this industry. Our object is not to provide a model of a commercial fruit farm, nor to induce farmers to adopt fruit farming instead of agriculture. We believe, it is true, that fruit farming might be successfully extended in this country, and that a certain though perhaps small percentage of those who now find agriculture an impossibility might be able to gain a fair livelihood by the culture of fruit: but if we are to aid any such extension, it will not be by the direct, or still less by an indiscriminative advocacy of the industry, but by increasing our knowledge of it, both from a scientific and practical point of view, so that those who may embark on it may be able to equip themselves better for their profession than they now can."

This was not only the first definitely experimental fruit farm to be established in Great Britain, it was the first attempt at scientific work on the growth of fruit trees in any country. Even the methods of experiment were unexplored. Very little was to be learned from abroad; in the United States there was only one station, that at Amherst, founded in 1889, and on the Continent there was nothing corresponding to the agricultural institutions then developing.

It must not be supposed, however, that this absence of scientific experimentation meant that horticulture was in a backward condition. On the contrary, its followers had by purely empirical methods achieved great advances and amassed much sound knowledge without invoking professional scientific aid. Indeed, the history of improvements, both in agriculture and horticulture, reveals the rather disconcerting fact that the greatest advances have with few exceptions been made by empirical rather than by scientific methods.

Pickering's lack of technical knowledge of fruit growing might have been overcome, but, unfortunately, he lacked also the feeling and the eye for a fruit tree which would have ensured him the sympathy of the practical man; in consequence, he was not able to make as much use of the accumulated empirical knowledge as he might otherwise have done. He never fully understood the fruit growers; indeed, it must be admitted that he did not try to do so, but as a keen controversialist freely challenged their methods, their canons and their beliefs. In return, they neither understood nor properly appreciated him, and they were not slow in challenging his results. Nor had he the gift of interesting them in the experiments. Perhaps the saddest feature of the giving up of the experiments by the Duke of Bedford, in 1918,

was the refusal of the fruit growers to take even the smallest action for the continuance of the work. The comment of one of their papers with a large circulation was quite definite: "Whilst regretting the cause, the writer was glad on the whole that the station was closed." This lack of co-operation with fruit growers was particularly unfortunate, for it can safely be said that no investigation in horticulture or in agriculture can be regarded as complete, even as a scientific exercise, until its results have been tested on the large scale by practical men. The rigid control of conditions in the experiment may bring about an altered grouping of factors and thus alter the nature of the problem, rendering the investigation somewhat artificial. In the large-scale test all the factors operating in the field, whether known or not, have full play, and any discrepancy between the results actually obtained and those expected may reveal some new and hitherto uninvestigated factor. There can be little doubt that the value and the certainty of Pickering's experiments would have been enhanced had he been fortunate enough to secure from the outset the interest and the co-operation of the best practical fruit growers.

But the fruit farm might then have lost its distinguishing characteristics. The lack of co-operation arose in part from Pickering's strongly developed experimental tendencies. He would accept no result, however well established it might seem, without putting it to the test of experiment. Had he been more in sympathy with the practical man, he might have been more willing to accept the settled convictions arrived at empirically, and then some of his most important results might never have been obtained. What the farm lost in one direction it probably gained in another.

*The Fruit Farm and the Laying Out of the Plots.*

Some fatality seemed to dog the footsteps of the earlier experimenters on fruit. At Amherst the topographical conditions were uneven: the orchard had been established on a somewhat steep slope sheltered on two sides by mature forest trees but exposed on the other two sides. The results, therefore, lacked uniformity and definiteness—a drawback which was intensified by the small number of trees in each unit, there being three only. At Woburn the subsoil, and over most of the farm the surface soil, was too heavy for the normal development of fruit trees; the field was not well drained, and its position rendered it very liable to spring frosts, which often killed the blossom.

The farm consisted of a single field of 20 acres, situated on the Oxford clay plain near the foot of the Lower Greensand ridge and close to the Ridgmont Station on the Bletchley and Cambridge line. It was not quite level, but

fell slightly to a brook which was liable to periodic flooding. It had been in ordinary arable farming, and it stood in bad repute, as water would not drain away, but lay on the land for weeks in a wet season. In his first report Pickering described the soil as a sandy loam, and attributed its heaviness to the very fine state of division of the sand rather than to any large amount of clay. Subsequent mechanical analyses showed that a sandy loam formed the top 9 inches of the upper part of the field, but that the whole of the remainder, including the subsoil of the upper part, consisted of heavy Oxford clay. The part of the field lying towards the brook had a still heavier surface soil, derived probably from the mud deposited from the brook in its periodic overflowings. The analysis of the soil is given in Table I.

Table I.—Analysis of the Soil of the Woburn Fruit Farm.

*Mechanical Analyses.*

*Upper Part of Farm.*

| | Mean diameter of particles. | 1st depth. 0–9 in. | 2nd depth. 9–18 in. | 3rd depth. 18–27 in. |
|---|---|---|---|---|
| Fine gravel | 3–1 | 2·1 | 5·2 | 0·8 |
| Coarse sand | 1–0·2 | 48·3 | 21·5 | 17·7 |
| Fine sand | 0·2–0·4 | 7·7 | 5·3 | 2·5 |
| Silt | 0·04–0·01 | 7·3 | 8·0 | 8·0 |
| Fine silt | 0·01–0·002 | 12·8 | 13·2 | 14·9 |
| Clay | below 0·002 | 15·3 | 35·0 | 44·8 |

*Lower Part of Farm.*

| | | | |
|---|---|---|---|
| Fine gravel | 0·3 | 0·6 | 0·3 |
| Coarse sand | 6·7 | 14·5 | 10·3 |
| Fine sand | 2·2 | 6·4 | 3·2 |
| Silt | 2·3 | 7·4 | 6·8 |
| Fine Silt | 21·4 | 13·9 | 14·1 |
| Clay | 51·5 | 41·0 | 52·8 |

*Chemical Analysis*: *Mixed samples*, not identical with those used above.

*Upper Part of Farm.*

| | 1st depth. | 2nd depth. | 3rd depth. |
|---|---|---|---|
| | 0–9 in. | 9–18 in. | 18–17 in. |
| Nitrogen | 0·139 | 0·086 | 0·067 |
| CaO | 0·34 | 0·58 | 1·53 |
| $K_2O$ soluble in HCl | 0·25 | 0·34 | 0·42 |
| $K_2O$ soluble in 1 per cent. citric acid | 0·025 | — | — |
| $CO_2$ from carbonates | 0·12 | 0·20 | 0·81 |
| $P_2O_5$ soluble in HCl | 0·14 | 0·13 | 0·13 |
| $P_2O_5$ soluble in 1 per cent. citric acid | 0·014 | — | — |
| Weight of 1 cubic foot after drying, lbs. | 95·2 | 108·2 | 101·4 |

*Lower Part of Farm.*

| | | | |
|---|---|---|---|
| Nitrogen | 0·29 | 0 17 | 0·105 |
| CaO | 1·01 | 0·97 | 0·64 |
| $K_2O$ soluble in HCl | 0·62 | 0·52 | 0·34 |
| $CO_2$ from carbonates | 0·12 | 0·06 | 0·07 |
| $P_2O_5$ soluble in HCl | 0·22 | 0·18 | 0·36 |
| Weight of 1 cubic foot after drying, lbs. | 74·2 | 70·6 | 80·0 |

The soil was not well suited for the purpose, and many of the trees gave neither the growth nor the yield of fruit expected in good commercial orchards. The sticky and tenacious nature of the subsoil and the liability of the lower ground to flood, and so to hold up water over the whole field, were serious defects. Not only did these factors adversely affect the trees, but they made cultivation very difficult; it was almost impossible to keep down the growth of weeds.

In these circumstances one cannot but admire the skill with which Pickering was able to deduce so much from the experiments carried out on such unpromising soil.

*The Trees used for Experiment.*

The scope of the experiments was very wide. Besides a large series of experiments on apple trees, there were smaller ones on bush fruit, strawberries, and potatoes; in addition, collections were begun of varieties of pears, plums, cherries, etc. The most important investigations were those on apples, and it is these with which we shall be mainly concerned. The experiments involved

no less than 1800 three-year-old apple trees, most of which were described as "dwarfs on an English broad-leaved Paradise stock."

It was not then realised that the term "Paradise stock" is very indefinite, and is applied to all stocks raised vegetatively, in contradistinction to the "crab" and "free" stocks raised from seed—the former from wild crab apples and the latter from garden varieties. Even the "English broad-leaved Paradise stock" includes at least five varieties which are botanically and horticulturally distinct. Hatton and Barker have both shown that variation in the stock greatly affects the behaviour of the tree, the different varieties of Paradise stock varying in behaviour under similar conditions. The measurements from the different trees from one and the same plot at Woburn showed considerable discrepancies which cannot now be smoothed out. This failure to recognise the necessity for uniformity in the stocks vitiated the results, and considerably reduced the value of many of the elaborate measurements.

During the course of the work certain defects were revealed in the details of the experiments. In the experiments with dwarf apple trees six trees formed a unit; this constituted a considerable advance on the Amherst experiments, in which there had only been three, but Pickering realised later that the number was still insufficient for the study of fruit yields; instead of six, he considered that there should have been from twelve to eighteen; and we should now add that all trees should be of the same stock.

The distance between neighbouring trees was 11 feet, except in the experiments on Bramley's seedling, where it was 13 feet 6 inches, and Stirling Castle, where it was 6 feet 6 inches. These distances were found to be too small; Pickering recognised afterwards that the trees should have been planted at least 20 feet apart. The manurial experiments were seriously prejudiced by this closeness of planting. The manured rows alternated with the unmanured. This arrangement had the advantage of revealing irregularities in the ground, but it invited the criticism, which it is now impossible to traverse, that the roots of the unmanured trees would strike into a manured plot as soon as they had pushed out more than 5 feet 6 inches from the tree. In such circumstances one would expect the lack of manure to show its effect for the first few years, but not afterwards. We shall find that this actually happened.

### *The Measurement of the Results.*

If Pickering's lack of technical knowledge hampered him in the laying out of the plots and the planting of the trees, it certainly had no such effect in the designing of methods to measure the resulting growth and yields. Nothing

approaching his elaboration of treatment had been attempted before, and the correlations which he found between one measure and another have never seriously been called in question; they still stand as safe guides to future experimenters. He early recognised the distinction between fruiting and vegetative growth, and he recorded data bearing on both types of plant activity.

The best measure of vegetative growth would have been to weigh each tree annually, but this would have involved lifting the tree, a course which would soon have killed it. Other means had, therefore, to be adopted. He took instead measures of leaf size and growth of new wood, and finding that these were correlated he ceased to measure the new wood and confined himself to leaf size only, and regarded this as a measure of the total vegetative growth of the tree. He soon realised, however, that two trees might make equal amounts of growth, and yet differ considerably in character; one might be a "weedy" growth with long, weak, spindly shoots of no value for fruit production, while the other might make shorter but sturdier and much more vigorous shoots that would lead to heavy growth of crops. He found, in fact, that there were two factors concerned in tree growth which it would be necessary for him to evaluate separately as far as possible—the vigour of the tree and the actual amount of growth. Finally, therefore, he used leaf size as the measure of vigour at the time being, and the spread and growth of the tree as the measure of growth.

It was impossible to take rigid and unexceptionable measures of any of the quantities involved; a conventional treatment was necessary, bringing with it some degree of artificiality with the inevitable openings for criticism. It was, of course, impossible to carry out measurements of leaf growth with strict completeness; he obviously could not measure every individual leaf on the tree. He began by selecting what appeared to be an average-sized leaf from a branch and determining its length and breadth; this was repeated about one hundred times on each tree. After the first year he measured instead the sixth leaf from the end of each of six shoots disposed at about equal intervals round the tree—36 measurements in all for each tree—and assumed that the value thus obtained was the true mean for the tree. The mean lengths and breadths being found, the mean leaf area was shown to be approximately, and taken to be actually, three-quarters of the product of these two quantities. The probable error of the results was shown to be less than $\pm 5$ per cent. From 1897 onwards he varied the method somewhat: ten leaves were taken from each tree, the sixth from the end of each of ten shoots; these were kept

for some months till thoroughly air dried, and then weighed; the weight was taken as a measure of the average size of the leaves.

Later experimenters have found the difficulties of selection so great that they have not adopted this particular measurement.

Two other leaf measures were occasionally taken: the total leaf area and the total leaf weight. The number of leaves on the tree was counted and then multiplied by the mean area or mean weight, ascertained as just described. But the counting of the total number of leaves was laborious and uncertain, and the results hardly justified the trouble involved.

The measurement of wood growth was a more definite operation than the leaf measurements, since it involved no personal selection. The shoots formed in any particular season are easily distinguished from the growth of the previous year, though the purely mechanical difficulties of measurement are considerable. Each shoot was measured and the total length and the number of shoots was recorded. The variation in growth of similarly treated trees was considerable, amounting not infrequently to 200 or 300 per cent.; this may be attributed to differences in the original stock on which the scions were grafted.

The labour involved in the measurement of the new shoots was very great, and as the young trees grew up it became prohibitive. Pickering then substituted the mean leaf area because he considered that "leaf size" and "growth" as measured by lengths of new shoots were affected in the same way by the different treatments. Pickering's comparison is given *in extenso* in Table II, which should be studied in some detail as showing the way in which he utilised the data.

The figures in the table give the differences between the measurements for the "normal" plots (1, 10, 21, 34, and such treated plots as Pickering came to regard as virtually normal), and the particular treated plot, the normal being put at 100. The differences in column VI are simply algebraic; a + or − sign indicates that the treatment has acted in the same way on both leaf and shoot growth, but a + sign shows that it produced a larger effect on the shoot growth, and a − sign that the larger effect was produced on the leaf growth. Where no sign is given, the treatment has acted in one way on the leaf size and in another on the shoot growth.

Pickering classified the differences into four groups given in the last column. In those marked A the treatment has produced a measurable effect (more than 10 per cent.) on both leaf and shoot growth, and the "agreement of the two properties is as good as could reasonably be expected, the differences between the numbers being less than three times the mean difference." In those marked

A′ the effect on one character is much larger than on the other. B indicates that no appreciable effect on either leaf or shoot, while C shows that leaf is apparently affected in one way and shoot in the other. Pickering concludes from the table that out of 29 cases there are 22 showing satisfactory concordance, 5 showing less satisfactory concordance, while in 2 cases only—those marked C—are the results discordant.

Table II.—Effect of Various Treatments on Leaf Size and Growth, measured as described on pp. 164, 165. Season 1896. (First Report, 1897, pp. 79 and 80.)

| Plot. | Treatment. | Leaf size. Normal = 100. | Growth. Normal = 100. | No. of shoots. | Difference between III & IV. | Type of agreement. |
|---|---|---|---|---|---|---|
| I. | II. | III. | IV. | V. | VI. | VII |
| 2 | Cut back at end of 1st year | +20 | +76 | +16 | +56 | A |
| 3 | Cut back; not pruned | +18 | +35 | -11 | +17 | A |
| 4 | Not cut back nor pruned | −27 | −76 | −53 | +49 | A |
| 9 | Summer pruning | − 9 | −63 | −32 | +54 | A |
| 14 | Root pruned | −39 | −91 | −62 | +52 | A |
| 17 | Grass grown | −35 | −87 | −63 | +12 | A |
| 18 | Ground hardened | −17 | +11 | +26 | 28 | C |
| 19 | Weeds grown | −44 | −85 | −72 | +41 | A |
| 20 | Dug near roots | − 8 | + 2 | + 8 | 10 | B |
| 22 | No phosphate | − 6 | − 3 | +16 | − 3 | B |
| 23 | No potash | + 1 | − 2 | − 5 | 3 | B |
| 24 | No nitrate | 0 | + 4 | + 1 | 4 | B |
| 27 | Dunged before planting | 0 | − 5 | + 4 | 5 | B |
| 32 | No manure | −23 | −11 | − 7 | −12 | A |
| 33 | Half-dose of manure | −11 | −13 | −10 | + 2 | A |
| 40 | Nitrate in summer | − 8 | +47 | +13 | 35 | A′ |
| 42 | Badly planted | −25 | +31 | +19 | 56 | C |
| 43 | Neglected and restored | −10 | −20 | −32 | +10 | A |
| 44 | Neglected | −56 | −94 | −70 | +38 | A |
| 45 | Ground not trenched | −17 | + 2* | +37 | 19 | A′ |
| 46 | Three-feet holes | + 8 | +41* | +32 | +33 | A |
| 48 | Planted too high | − 7 | −13* | − 3 | 6 | B |
| 49 | Planted too low | − 7 | +36* | +37 | 43 | A′ |
| 53 | Peat | + 4 | +68 | +78 | +64 | A′ |
| 55 | Compost | +16 | +75 | +57 | +59 | A |
| 56 | Replanted November, 1895 | −53 | −92 | −63 | +39 | A |
| 57 | Planted in winter | + 4 | +58 | +51 | +54 | A′ |
| 58 | Planted in spring | + 7 | +13 | +19 | + 6 | B |
| 59 | Blossoms removed | − 2 | +47 | +60 | 49 | A′ |

* Bramley omitted.

The fruit from each tree was weighed and recorded separately. Even this apparently simple operation had its difficulties, for Pickering realised that weights alone would be misleading to the practical man unless he could give some estimate of value also. A given weight of fruit might be of high value if the individual fruits were shapely, of the proper size and of good appearance;

or almost worthless if they were small and not good looking. In addition, therefore, to the weights he worked out a " value " number. The fruits were put into three grades conforming more or less to the market classification. It was found that average weights of single fruits in these grades was roughly in the proportion of 4 : 2 : 1 ; Pickering further assumed that the value to the grower (*i.e.*, market value *less* cost of picking and marketing) of equal weights of each of these three grades was also in the proportion of 4 : 2 : 1 ; and so arrived at the values for single apples of the respective grades in the proportion of 16 : 4 : 1. The " value " number was therefore arrived at by adding together the number of apples in the first grade, the quarter of the number of those in the second grade, and the sixteenth of those in the third grade.

The method of treating the results was in some ways rather special.

There were six " normal " plots uniformly distributed over the ground, and on these the treatment was similar ; the experimental plots lay in between. The results of the normal plots were set out on curves, three of which are here reproduced (fig. 1), and each curve is assumed to give the values which would be obtained on any intervening plot had the treatment there been normal.

This calculated value was then compared with the actual value and the difference stated as a percentage of the normal value. Thus, if the actual value for leaf size on one of the plots was 90, when compared with the value indicated by the curve as 100, the effect of the treatment was said to be —10. In the published reports all the data are thus expressed as percentage differences : the actual measurements are not given.

The method employed was very ingenious, but it suffers from two defects. It assumes a continuous variation in the soil, where the variation may quite well have been discontinuous, and it takes no account of the variation in the trees themselves. In the actual curves, the points between 50 and 60 are not strictly comparable with the rest, as the trees had, in fact, received other than normal treatment. Even if a curve were permissible, it would be possible to draw alternative curves that would give results different from those actually recorded.

A more serious objection to the method is that it gives no indication of the magnitudes of the various quantities. The published reports gave no statements of actual fruit yields until 1921, when the last was issued, and at the writer's urgent request the figures were given. It was then obvious that the yields throughout had been much lower than could reasonably have been expected from trees of the age and variety grown. The average yields obtained, together with those ordinarily expected, are given in Table III.

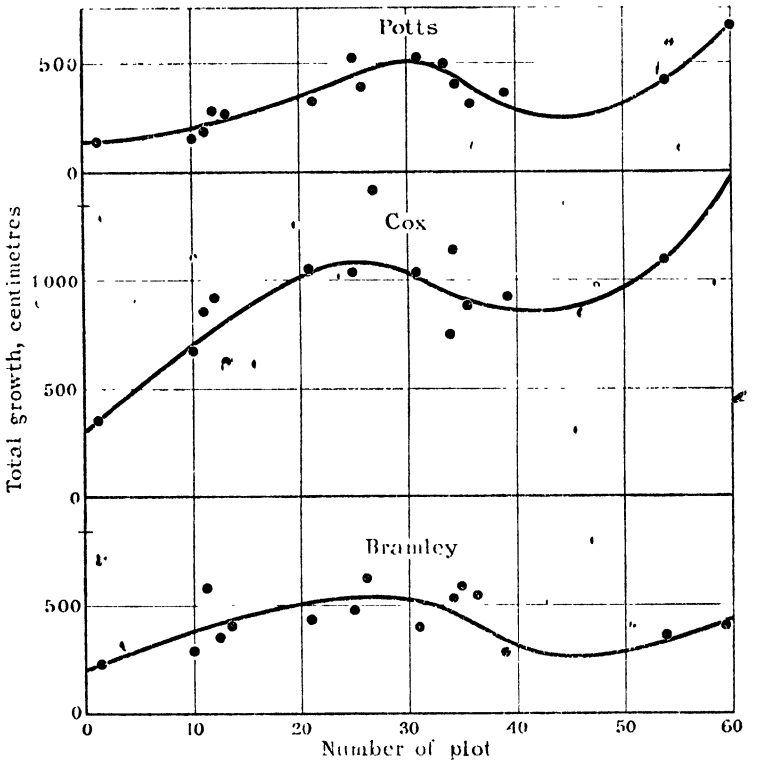



FIG. 1.—Total length of new wood formed in 1896 by the dwarf apple trees in the normal plots: showing method of treating the results.

Table III.—Trees planted in the winter of 1894–95, being then three years old: the average yields per tree in lb. per annum were :—

| | | | A good grower would expect of a 15-year-old tree :— |
|---|---|---|---|
| 1898–1908 | Cox's orange | 2·4 (omitting 1901 and 1907 = 1·3) | 50–70 |
| 1897–1904 | Pott's seedling | 4·8 | 80–100 |
| 1899–1911 | Lane's Prince Albert | 6·6 | |
| 1897–1919 | Stirling Castle | 21·6 | |
| 1904–1919 | Bramley's seedling | 64·9 (1896–1903 — 1·3) | |
| 1911–1919 | Bramley's standards | 155·5 | 150 |
| 1911–1919 | Varieties | 22·9 (1904–10 = 2·6) | |

The varieties were worked *in situ* in 1899, and are therefore 8 years younger than the other trees.

These results show clearly that some limiting factor was operating to keep down the yield of fruit, excepting in the case of the Bramley's seedling. Pickering refers a good deal to late frost as adversely affecting the crops; the

soil type and the difficulty of drainage were no doubt important also. Unfortunately, the results were not discussed from this point of view. We shall see later on that the addition of manures to the trees gave no marked additional crop. Pickering therefore argued that fruit trees needed but little manure, and that the dressings sometimes given in horticultural practice are unnecessary. It is, however, equally possible that the manures never had a chance to act, seeing that the limiting factor was still in full operation.

These various objections to the methods adopted at Woburn are stated at the outset, so as to show the limits within which the data and the conclusions are likely to be of value. Experiments on fruit trees are much more difficult than experiments on agricultural crops. The factor of plant individuality is more in evidence, since the experimenter works with 5, 10 or 20 trees only, while the agriculturist works usually with thousands of plants. Each experiment takes much longer to carry out; it may, indeed, require 10 or 20 years for completion, while an agricultural experiment is usually made in one season. In the history of investigations on growing plants, the first design of an experiment has rarely proved to be the best. Lawes and Gilbert found it necessary to recast the whole of their field work at the end of the first eight years. Pickering realised the desirability of recasting his experiments, but he could have done it only by giving up Woburn altogether after 15 or 20 years of work and starting afresh somewhere else, a course which was not open to him. He rendered, however, to future experiments the valuable service of discussing the difficulties of the work in his book "Science and Fruit Growing."

## CHAPTER II.

### The Planting and Pruning of Fruit Trees.

*Trenching.*

At the outset Pickering had followed the conventional lines in planting most of the fruit trees. The land was trenched, *i.e.*, the top "spit"—the depth to which the spade is driven—was removed, the lower "spit" broken up, and then the top "spit" was replaced; holes were then dug and the trees carefully placed in them with the roots spread out evenly; finally the soil was replaced with every precaution to avoid injury to the roots. Plots 42 to 45, however, were not trenched, but dug only one "spit" deep; in plots 42, 43, and 44 the trees were also carelessly planted. Certain differences were soon manifested; the trees on the untrenched plots showed a diminution of leaf size for the first three years and perhaps longer, but the other growth factors showed increases. But as time went on the differences disappeared, and over the whole period the effect of the trenching appeared to be small.

The matter is of some technical interest, because trenching is often done in gardens at great expense; if it is really ineffective, much would be saved by omitting it.

In conjunction with the present writer the experiments were repeated and extended to four distinct types of soil—the light Millbrook sand, two rather heavy loams—one from the fruit farm at Ridgmont and the other from the north piece of Broadbalk field at Rothamsted—and a heavy clay from the fruit farm. Monthly determinations were made of the moisture and nitrate contents of the trenched and untrenched soils, and observations were made on the growth of the trees.

Trenching had very little effect on the moisture content of the soils. There is some indication that it facilitates percolation from the surface to the subsoil on heavy loams and clay, and that it somewhat increases the subsoil moisture. It appears, however, to be only a minor factor in determining the water supply to the plant.

Nor did trenching lead to any marked increases in the store of nitrate in the soil. There were small gains on the sand and rather larger gains on the clay, which persisted over all the four seasons, but these never much exceeded the error of the experiment. Trenching did not appear to alter the distribution of the nitrate between the surface and the subsoil.

The behaviour of the plants furnishes a sensitive index to the changes in the soil. Here, however, the indications are no more definite than those given by the determinations of water and nitrate. As compared with untrenched land an increased leaf size (generally small) is shown in three out of the four trenched sets, but in the fourth there was a reduction; an increased growth was recorded in three, but a reduction in two, sets; whilst the two records of crop yield (the only ones taken) were both larger on the untrenched ground. The effect on the growth of trees appeared to depend largely on the character of the seasons following trenching and planting; thus on the Ridgmont clay the results of 1906, 1907 and 1908 were somewhat in favour of trenching, whilst those of 1912 were more definitely against it. On the Ridgmont loam, the trenching done in 1894 had practically no effect on trees planted immediately afterwards, while that done in 1910 benefited the trees then planted, which, however, belonged to a different variety. The results cannot now be explained, but form a problem for future workers.* It seems clear, however, that bastard trenching done without addition of manure to the bottom spit is unlikely to effect sufficient change in the soil to justify the expense involved. If there is a pan to be broken the case is different, but, in absence of a pan, the main use of bastard trenching is apparently to afford an opportunity for adding manure or other fertilising material to the bottom spit. Unless this is done, the real benefit of the process is missed.

### *Mode of Planting.*

The trees which had been planted carelessly in the original set of experiments behaved completely differently from what the conscientious gardener would have expected; they grew better, and, when they were lifted after three to five years, were found to be considerably heavier than those planted in the conventional way. At first Pickering thought that the severe root injury brought about by the careless planting had stimulated new root growth, but he soon rejected this view. He therefore set out a series of experiments in which he separately tested the various processes in the careless planting—the huddling of the roots together into a small hole, the stamping of the roots into the ground, the injury to the roots caused by fraying at the ends, the placing of the roots in a vertical position instead of spreading them out, and the removal of one-third and two-thirds respectively of the roots. The results were not concordant; some trees died and some trees flourished. The cutting off of two-thirds of the roots was distinctly harmful, and, for the rest, the

* *Journ. Agric. Sci.*, vol. 5, pp. 483-496 (1913).

stamping in alone seemed to be usually beneficial; the other forms of ill-treatment—injury to the roots and huddling of the roots together—were sometimes harmful, sometimes beneficial, and sometimes without effect. "We fear," said Pickering, "that by taking trees that were unsuitable for transplanting in the hope of obtaining more marked results, we have only obfuscated these results, the individual plants being more affected by the condition in which each happened to be than by the treatment which it received on planting."* He was preparing "to abandon the subject as being an insoluble paradox," when another and rather casual experiment gave him the key to the problem. Trees had been planted at various depths, and those deeply planted had, on the whole, made better growth than those more normally planted, *but their old roots were dead, and new roots had formed near the surface.* Pickering therefore concluded that the transplanting of a tree killed the roots, and the speed of recovery was determined by the rate at which new roots formed. In planting trees, therefore, it was useless to try and save the old roots, as was attempted in the current method; they should be allowed to perish quickly, and the new ones should be induced to start.

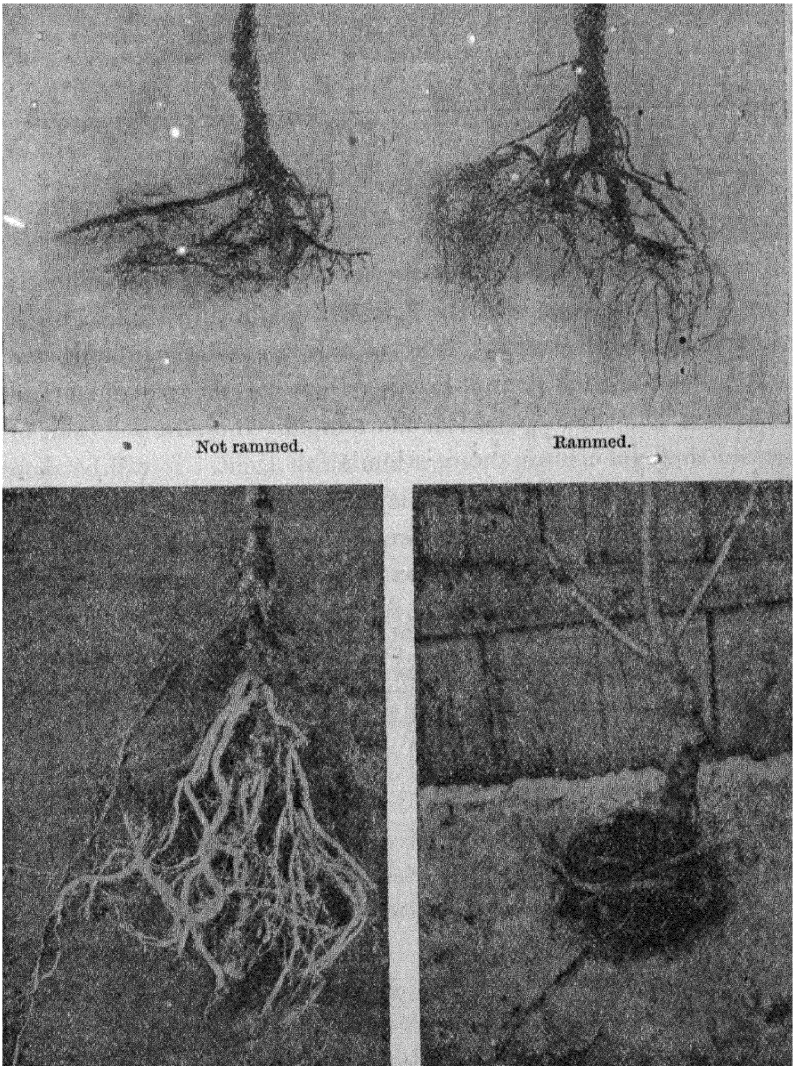
These revolutionary ideas brought the Fifth Report into great prominence among the "expert" writers of the day, who gave it a somewhat acrimonious reception. Pickering felt bound to furnish more evidence, and he did so.

The experiments on various forms of root enquiry were carefully repeated.† Ramming the roots was consistently beneficial; trimming them with a knife and injuring them (within limits) by breaking them roughly with a spade was not. He therefore extended the "rammed" series, planting the trees in the most unorthodox fashion possible. "A few forkfuls of earth were removed, so as to make a shallow hole; into this the tree was put, with the roots just as they happened to come; the earth was shovelled over them and rammed with a heavy rammer till the whole was thoroughly puddled and shook like a jelly at each stroke. As one of our critics said, it is planting trees gatepost fashion, and we cannot improve on his graphic description of the process: certainly any workman who had been found planting a tree in this fashion a few years ago would have been promptly dismissed, and the tree would have been considered as doomed."

"The consolidation of the earth round the roots is such that the ground generally remains hard for the next twelve months, and even during the second and third years it is perfectly easy to recognise which trees have been rammed

* *5th Report*, p. 69.
† *9th and 15th Reports.*

by merely pressing the ground with the foot."* In order to reduce the possibility of mistake, he alternated these "rammed" trees with others planted in the usual way. The result was invariably the same: the first effect of ramming was either negligible or harmful, but by the second season the rammed trees




Rammed: new roots painted white. Not rammed.

FIG. 2.—Ramming the trees into the soil much increases the growth of roots.

[*By courtesy of MacMillan & Co.*]

* *9th Report*, pp. 7–8.

had grown much more than the others. Pickering repeated the experiments at other centres, and as a rule obtained similar results. Examination showed that more roots were formed on the rammed than on the unrammed trees; a photograph is given in fig. 2 (Plate II, *9th Report*, p. 23). Some of the final results showing gains of rammed over unrammed trees were*—

| | Excess of weight of new roots. | Excess of weight of new branches. | Excess of length of new branches. |
|---|---|---|---|
| Gascoyne's No. 8.... .... | + 141 | + 131 | + 144 |
| M. Louise No. 40 ... .... | + 133 | + 118 | + 128 |

Pickering saw that this stimulation of root development by ramming was not caused by any improvement on the soil, but was a direct effect on the tree. The ordinary method of planting does not ensure as close contact between soil and roots as does ramming, and, arguing from certain experiments which in his view proved that seeds germinate more rapidly in moist soil than in water, he suggested that soil contains some stimulating agent. It will be shown later that the germination experiments do not prove this, and Pickering's suggestion, while it may be correct, has no experimental basis. There is, however, no doubt that "ramming" is beneficial and does in some way stimulate root development, but the precise action is not known.

*Pruning.*

Much attention was devoted at the Woburn Fruit Farm to this important operation, and it is discussed in several of the Reports.

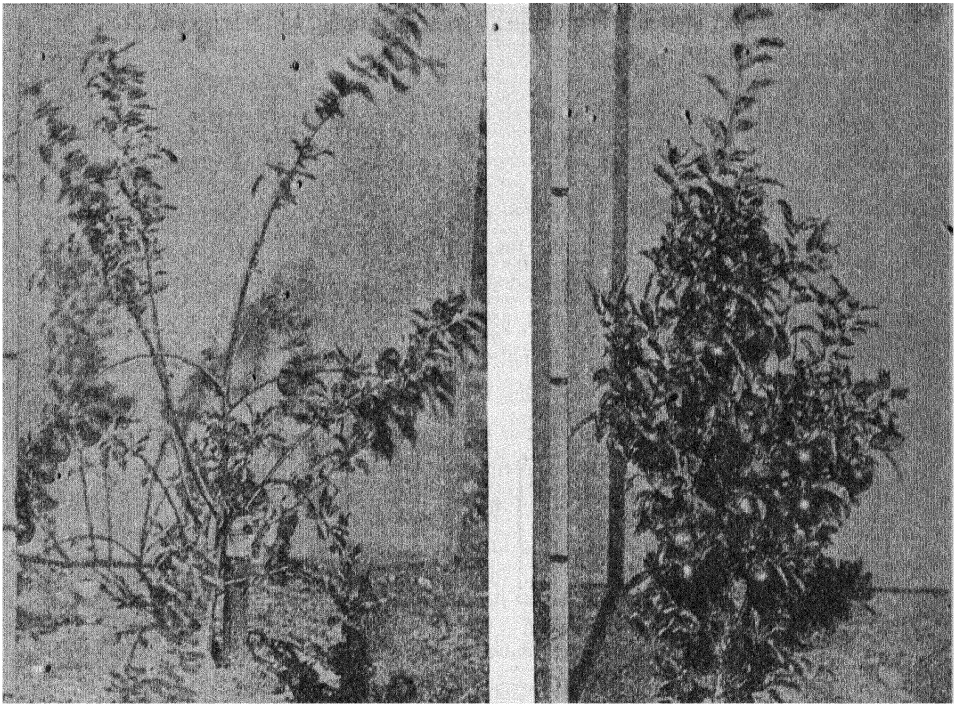
Some of the trees were left unpruned from the time of planting throughout the whole experiment. Buds developed only at the ends of the shoots: the branches thus became long, straggly, and incapable of carrying the weight of the fruit; there was also less leaf growth, the deficiency amounting in some cases to 24 per cent.

Cutting back the shoots at the time of planting caused a distinct improvement: it stimulated the buds behind the cut into activity and led to a compact sturdy growth. Fig. 3 (figs. 15 and 16, *1st Report*, p. 102) shows two Cox's orange apple trees two years after planting, one of which had been cut back at planting while the other was left untouched. The difference in growth is very marked.

* *9th Report*, p. 23.

This experiment throws no light on a question which has led to much controversy in horticultural circles—whether it is better to prune at the time of planting, as was done here, or in the following year.

Pickering uses the word "pruning" in a rather restricted sense, confining it to the removal of thin straggling wood, and of much of the new wood formed in the preceding year. A tree pruned in this way certainly looks well in the



Coxe's Orange Pippin.—Plot 4.
Not cut back nor pruned. 1896.

Coxe's Orange Pippin.—Plot 1.
Pruned. 1896.

FIG. 3.—Effect of proper pruning.

rather formal fruit and vegetable garden, and a gardener with a keen eye for shapeliness may be forgiven if he seeks justification in other directions for a process which he really enjoys carrying out. Gardeners always maintain that pruning not only gives the shapely tree, but also causes "fruit" buds to start, and therefore increases the amount of fruit.

Pickering conceded the point in regard to shapeliness, and even admitted that the tree gained in sturdiness through being more compact, but he did not

agree that the fruit was increased; on the contrary, he maintained that it was diminished.*

| | Value of Crops during 10 Years. |
|---|---|
| No pruning .. .. .. .. .. | 158 |
| Moderate pruning .. .. .. .. | 100 |
| Hard pruning .. .. .. .. .. | 49 |

Another set of results is given in diagram form in fig. 4 ("Science and Fruit Growing," fig. 12, p. 65).

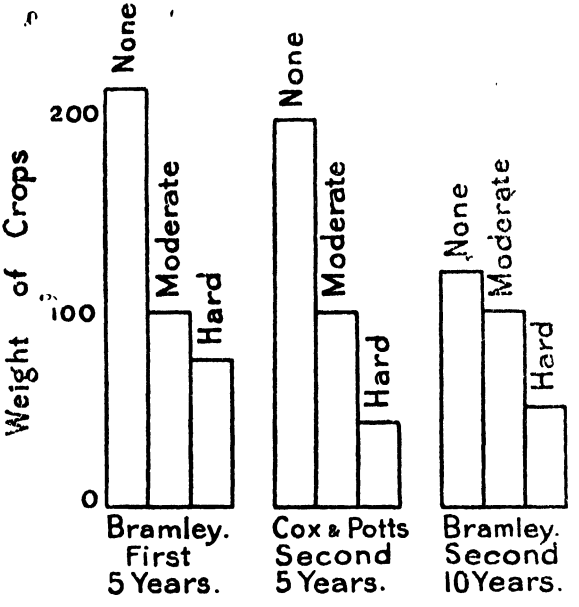



FIG. 4.—Weights of crops from trees pruned to different extents.

Pickering recognised that he could not advise growers to dispense with pruning entirely, especially of young trees. A fruit tree "has been developed by selection and cultivation until it has become abnormal in certain respects, and consequently requires abnormal or unnatural treatment. It has been developed so as to bear a much heavier crop than it would naturally do, and to bear it at an earlier age: such crops are in many cases greater than the branches can carry without distortion or injury, and, hence, if pruning is dispensed with, the tree may be ruined. The conclusion, therefore, is that pruning should be reduced so far as is consistent with the formation of a well-shaped

* *5th Report*, p. 117; also "*Science and Fruit Growing*," p. 67.

tree, capable of carrying such a crop as it is likely to produce. The pruning will, of course, retard the development of the tree, but the extension of the branches is arrested more than the filling out of the branches, and hence a more compact and sturdier tree will be produced."*

He obtained, however, somewhat different results with older trees; while pruning checked fruiting it also stimulated the growth of new wood :—

| | New Wood.† Relative Lengths. |
|---|---|
| Not pruned .. .. .. .. .. | 54 |
| Moderately pruned .. .. .. .. | 100 |
| Hard pruned .. .. .. .. .. | 104 |

| | Actual Lengths per Tree.‡ *Bramley.* | *Stirling Castle.* |
|---|---|---|
| Not pruned .. .. | 2,179 in. | 1,126 in. |
| Moderately pruned .. | 6,694 ,, | 1,495 ,, |
| Hard pruned .. .. | 6,940 ,, | — |

The result of this alteration in behaviour as the tree grows older is that the moderately and the hard pruned trees tended after some years to overtake the unpruned trees, so that the differences observed in early years became reduced. Thus the relative sizes of the trees planted in 1904 were, at various subsequent dates§ :—

| | No pruning. | Moderate pruning. | Hard pruning. |
|---|---|---|---|
| 1904 . . | 106 | 100 | 82 |
| 1908 .. . | 105 | 100 | 83 |
| 1911 ... . . . | 100·5 | 100 | 86·5 |
| 1914 .. ... .. | 101·5 | 100 | 88·5 |

It is unnecessary to go into the technical details of these trials. The time of year when the operation was performed made little difference to the result, but there were disadvantages in summer pruning. Nor was the manner of pruning of much importance: secateurs and knives were equally effective, and it was immaterial whether the cut was made in the conventional way—upwards and outwards and just beyond an outside bud pointing away from

* "Science and Fruit Growing," pp. 67 and 69.

† *Ibid.*, p. 69.

‡ *7th Report*, pp. 9, 42.

§ *Science and Fruit Growing*, p. 70.

the centre of the tree—or whether the cut sloped in some other way and was made above an inside bud. Only one thing seemed to produce any effect: if the cut were an inch above a bud the new shoot lost in vigour. Pickering supposed that the formation of the callus was retarded and vigour thereby diminished.

*Root Pruning.**

Whenever a tree is producing too much wood the fruit grower can have recourse to root pruning, but the process is too troublesome to be performed frequently in the commercial plantation. Pickering's measurements entirely confirmed the popular view that root pruning seriously interferes with growth. When done every year it checked all growth, and ultimately killed the trees; root pruning every other year brought growth almost to a standstill, while when done every fourth year it still caused severe reduction in growth. So long as the operation was not repeated too often, however, the effects appeared to be beneficial; there was a loss of fruit in the first season, but a gain in the second. He regarded root pruning as "an operation which should be practised with extreme moderation, and only in those cases where excessive branch growth calls for stringent measures."†

*The Growers' Criticisms of the Results.*

Pickering's work on planting and pruning was confined entirely to measurements of the growth and yields obtained; it was not followed up by physiological studies of the tree. It is interesting to compare his results with those obtained by practical fruit growers.

The work on trenching is in accordance with good experience; and the best practice in gardens is to add turf or other manurial substance to the lower spit when the operation is carried out. Trenching is too costly to be undertaken in ordinary commercial plantations.

The necessity for hard ramming at the time of planting is now recognised, especially for trees on free-rooting stocks, as also is the futility of trying to save all the roots. Indeed, it has since been pointed out‡ that this was known by the gardeners of the seventeenth century; it is recorded by La Quintinye§ in France and by Laurence‖ in England. Laurence advocated "taking off

* *2nd Report*, p. 155; *5th Report*, p. 38.

† "Science and Fruit Growing," p. 46.

‡ E. A. Bunyard, *Journ. of Pomology*, vol. 1, No. 1.

§ John de la Quintinye, "Instructions pour les Arbres Fruitiers," English translation by John Evelyn, 1693.

‖ John Laurence, "The Clergyman's recreation, showing the pleasure and profit of the art of gardening" (1714).

all the small Fibres intirely" and shortening the bigger roots to 6 inches. No hole was dug, but the tree was simply pressed to the ground, its roots covered with earth, and it was tied to a stake. An American horticulturist, Henry Martyn Stringfellow (1839–1912), cut away all the side roots, then sharpened the main root and drove the tree into the ground: vigorous growth took place just as had happened with Robinson Crusoe's palisade treated in the same way. None of these practices was recognised by good horticulturists, nor do the seventeenth and eighteenth century writings in any way detract from the importance of Pickering's observations.

Pickering was not correct in supposing that the old roots always die after transplanting; it has been shown at Long Ashton that the original fibrous roots may continue to function for years, and even form the foundation for the whole root system. But in the main the success of transplanting probably depends, as Pickering insisted, on the ease with which new roots develop.

Considerable criticism has been levelled against Pickering's sweeping conclusion: "That pruning encourages growth is, except under special conditions, one of the fallacies prevalent in horticulture. . . . From every point of view it would appear that pruning is disadvantageous to a fruit tree, and the more it can be reduced the better." It was no doubt justifiable to emphasise the harmful results of hard pruning, but, as one of the critics pointed out, this drastic statement is not a promising beginning for a discussion with men who prune for the special purpose of encouraging growth, and who know that they obtain better growth. Much of the trouble arose from Pickering's method of averaging all his results, which assumed that all varieties were equally affected, and that the differences were of statistical importance only and had no biological significance. The assumption is known to be incorrect: Bramley's seedling is notoriously susceptible to pruning and its results cannot legitimately be averaged with those given by Cox's Orange and Stirling Castle.

Pickering ignored the difference in purpose between the pruning of standards and of dwarf trees. In the production of standards growth is controlled by pruning so as to cause branching at about 6 feet above the ground; after which the tree is left very much to itself, weak wood only being removed. A dwarf tree, however, is treated differently; it must be kept low and restricted in growth. Regular pruning is therefore essential.

There still remains room for a detailed study of pruning, in which the different purposes of this operation and the effects on different varieties of trees are kept sharply distinct.

## CHAPTER III.

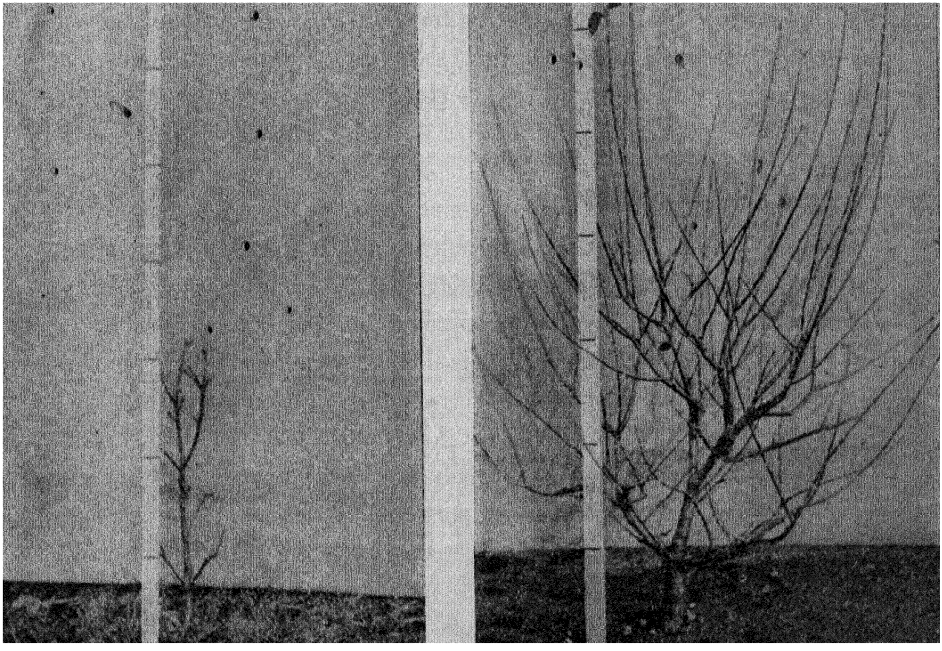
### The Influence of Growing Grass on Fruit Trees.

Among the first experiments started at Woburn was one to determine the effect on fruit trees of growing grass around them. Plot 17 contained the usual set of six Bramley's, Cox's and Potts' varieties of apple trees, manured with the full normal fertiliser, but differing from all the others in that grass was sown to a distance of 5½ ft. round each of them: four years later the intervening spaces were grassed so that the whole plot formed a continuous grass strip. The grass was cut two or three times in the season and allowed to lie on the surface to rot.

An immediate effect was produced, much more striking than anything else shown at Woburn. The young trees suffered intensely, much more so than on those on the badly planted and completely neglected plots: indeed, no method of ill-treatment tried at Woburn had anything like so bad a result. Even trees which were lifted annually and root-pruned before being replanted, though more stunted and enfeebled than the grassed trees, nevertheless showed none of their peculiar symptoms. During the first four years—from 1894 to 1898—the trees surrounded by grass increased by only two-thirds of their weight, while their neighbours kept free from grass had increased ten to thirteen fold in weight. (fig. 5.) Nor did the effect pass off: as time went on the differences remained at least as great; the standards were as much affected as the dwarfs, and the old trees as the young ones. Recovery began, however, directly the roots extended beyond the grassed area, but it ceased as soon as the grass was extended. Trees eight years of age which had been raised on cultivated land and were doing well had their growth and their leaf weights cut down very soon after grass was grown. Besides the reduction in growth, there were certain peculiar qualitative effects produced on the tree. There was a deficiency of green colouring matter, which showed itself in several rather striking ways. The leaves became light and unhealthy in colour all through the season and they assumed their autumn tints quite a fortnight sooner than those in the tilled soil. The bark also was distinctly bright in colour, while the apples, which were normally green, became waxy yellow or brilliant red, so that even expert growers failed to identify them.* The roots were darker, less succulent and thinner than in tilled soil: their

* 3*rd Report*, p. 50.

direction of growth was not affected, however, and they showed no tendency to strike deeper into the soil. The number of new roots was reduced, but nothing like so much as the development of those which started into growth. The leaf buds burst more early in the spring. These effects were still produced, though to a smaller extent, when grass only partially covered the roots. There was this interesting modification, however, that a certain degree of covering appeared to be advantageous to the grower, inasmuch as the checking of the



In Grass. Tilled Ground.

FIG. 5A.—Bramley's Seedling Dwarfs, in grassed and tilled soil. Four years after planting.

[*By courtesy of Messrs. Macmillan.*

growth of the trees when not too severe tends to heavy cropping, while the brilliant coloration of the fruit enhanced its market value. Some of the trees near to growing grass and partially affected by it gave respectively, 98 per cent. and 138 per cent. more crop during the first ten years than others on wholly cultivated land.* But this critical point is not easy to strike exactly and Pickering definitely advised fruit growers that growing grass was harmful to trees. Similar results were obtained with cherries, pears, plums and forest trees.

* "Science and Fruit Growing," p. 272.

This was contrary to the experience of many growers, and once again Pickering found himself in the position of attacking established practice. Many of the best orchards in the country are grassed over: in Kent and other counties sheep are grazed in them, thus giving the farm a double return: Pickering contended that the trees would probably have done even better had there been no grass, though he admitted that in the light loams favoured by fruit growers the roots might extend downwards and so grow out of the range of the

In Grass. Tilled Ground.

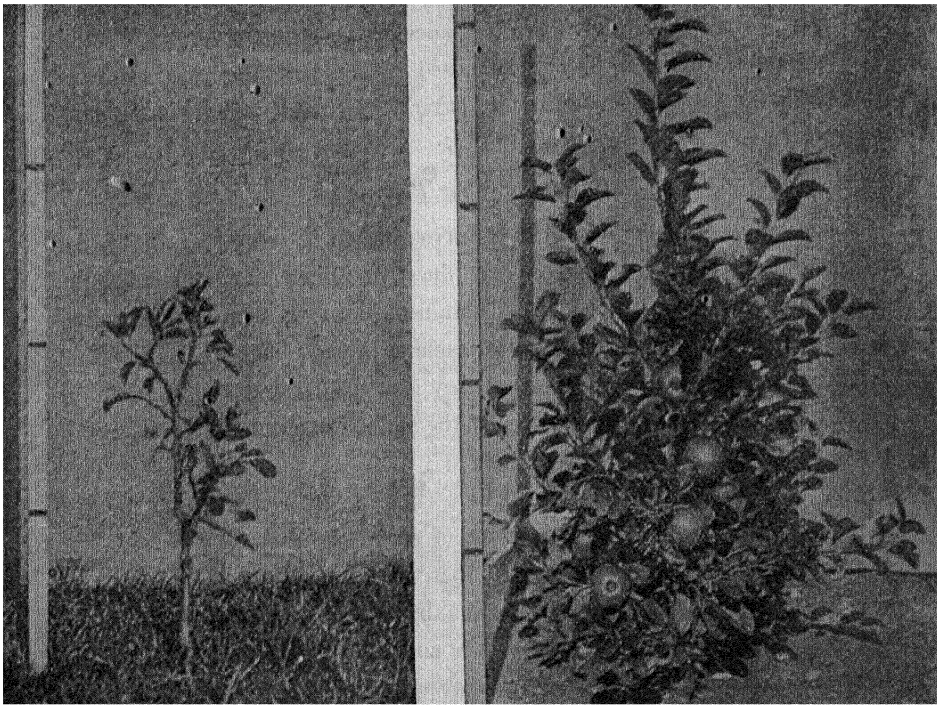
FIG. 5B.—Bramley's Seedling on crab stock, 1899. Planted December, 1895.

[*By courtesy of Messrs. Macmillan.*

grass action, thus setting up conditions favourable to the partial effects already indicated.

There was considerable confusion in the controversy; each side had more of the truth than the other recognised. Pickering's trees were practically all on Paradise stock, while practical growers use either the crab or the free stock in grassed orchards. The Paradise stock (which are raised vegetatively, as shown on p. 163) do not survive the competition of grass; Pickering's result is true for them. But the crab or free stocks, being seedlings, are not only more

vigorous, but as a rule more deeply rooting: they survive in grass, although their growth is reduced. Pickering ignored this difference. Grassed orchards have several advantages over tilled orchards in practice. The grass can be grazed and thus brings in a return: the tilled land costs a great deal for cultivation even when it is stocked with pigs. Even the reduction in the amount



Potts' Seedling.—Plot 17.

Properly planted and tended, except that grass is grown round the tree. 1896.

Potts' Seedling.—Plot 40.

As Plot 17, except that the land is tilled.

FIG. 5C.

of growth brought about by the grass is not necessarily disadvantageous: it reduces the amount of pruning necessary and it stimulates fruiting. In a certain commercial orchard where tilled and grassed plantations are both maintained, the cost of pruning on the tilled land is about 6d. per annum per tree, while on the grassed land it averages only about one-third of this amount.

The injury done by growing grass to trees has been further studied at the

National Fruit Research Station at Long Ashton,* by Hedrich in New York State,† and by the Howards‡ at Pusa.

In Pickering's experiments the grass usually killed the trees: obviously this is not a general result, otherwise forests could hardly have grown up over large areas of land. Indeed, at Rothamsted grass cannot withstand the competition of trees, so that grass land left unattended becomes ultimately woodland devoid of grass. There are, however, conditions in which grass survives and trees do not: these give rise to glades in the forest or to great treeless areas such as the prairies. The injury caused by the trees to the grass is complex, there being a light effect in addition to other actions such as those investigated by Pickering.

*The Causes of the Phenomena.*

Pickering spent many years in endeavouring to ascertain why grass had so harmful an effect on fruit trees, but illness prevented him from completing his investigations. The results he obtained, however, are so important—and, if they are substantiated, so far-reaching in their effects in agricultural, botanical and ecological science—that they must be dealt with at considerable length. At the outset he proceeded by the method of elimination to ascertain the general nature of the factors involved.

The possibilities first investigated were that the grass might interfere with the supplies of water, of nutrients or of air to the roots of the trees In the first report he inclined to the view that the water supply was affected; in the second report, he suggested that the air supply was an important factor; but before long he gave up these views and brought forward an altogether new explanation. As the investigation proceeded, the experimental work became highly ingenious, as might be expected from Pickering.

*Water Supply.*

The growth of the grass undoubtedly reduces the amount of moisture in the soil, and to this extent curtails the supply to the tree. Into some of the grassed plots§ were sunk iron pipes, four per plot, to a depth of 6 inches from the surface, and at a distance of 1 foot from the tree. Water was poured down these each week in quantities equivalent to three-quarters of the previous

* *National Fruit and Cider Inst. Reports* (1908, 1909, 1911); *Journ. Bath and West Agric. Soc.*, vol. 8, p. 140 (1911).

† New York Agric. Expt. Station, *Bull.*, pp. 314, 375, 383 (1909 and 1914).

‡ *Bull.* 16, Agric. Research Institute, Pusa (1910).

§ 3*rd Report, Woburn Expt. Farm*, p. 30.

week's rainfall on an area of a circle 4 feet in diameter. No amelioration, however, was produced in the condition of the tree; the grass was just as harmful whether additional water was supplied or not. The results are given in Table IV.

Table IV.—Leaf-Weights of Trees in Grass, etc., compared with Trees in Open Soil.

| | 1900. | 1901. | 1902. |
|---|---|---|---|
| | Per cent. | Per cent. | Per cent. |
| 813, Grass | − 25 | − 43 | − 30 |
| 815, Grass watered | − 23 | − 46 | − 43 |

Equally harmful effects of grass were seen in pot experiments, where the supply of water was more closely controlled.

It was therefore concluded that the injury done by grass to the tree is not due to any restriction of the water supply. Confirmatory evidence was obtained from the observation that the grass effect was quite different from that of drought, and it was shown at least as markedly in a wet as in a dry season.

Pickering's evidence on this point seems to be satisfactory, though it would have been more convincing had he allowed for a bigger root spread than 4 feet.

*Air Supply.*

A hoop of sheet iron 4 feet in diameter and 18 inches in depth was placed over a tree, the stem of which was at its centre; it was then driven into the ground till the upper edge was flush with the surface of the soil. A layer of cement, 2 inches in thickness, was then laid over the surface from the edge of the hoop right up to the stem of the tree, thus enclosing the roots in every direction excepting from the subsoil, which is here a stiff Oxford clay and apparently a perfect seal.

Six trees were so treated and no harmful effects were observed; on the contrary, for the first two years there was an actual improvement in growth—the leaf-weight was larger (Table V), the fruit was particularly clean, well formed, and highly coloured, while the trees were among the very few on the whole farm which did not suffer from aphis and fungoid attacks.

Table V.—Leaf-Weights of Trees in Grass, etc., compared with Trees in Open Soil.

| | 1900. | 1901. | 1902. |
|---|---|---|---|
| | Per cent. | Per cent. | Per cent. |
| 813, Grass | − 25 | − 43 | − 30 |
| 817, Cement | + 6 | + 23 | − 38 |

Later on, however, the vigour of the trees declined, but even after ten years they were much better than corresponding trees growing in soil which had been covered with grass.

Similar results were obtained in pot experiments where the surface of the soil was sealed up with paraffin wax.

Pickering regarded this as sufficient proof that the grass effect was not connected with soil aeration, but the experiment loses in value because no clear distinction is made between the two very different factors involved—the negative effects of cutting off oxygen, and the positive poisoning effects resulting from an increased concentration of carbon dioxide in the soil gases. His experimental work took account only of the reduced oxygen supply; it ignored altogether the effects produced by the carbon dioxide continuously evolved from grass roots. He made a determination of the amount of carbon dioxide in the soil air under grass and in cultivated land, and found less in the former than in the latter. It is highly improbable that this was the normal condition. Casual measurements of soil factors are very apt to mislead, and nothing short of frequent regular measurements can be trusted to give a faithful picture of the normal conditions in a soil. It will appear later on that the harmful effects are produced only when the surface of the soil is wholly or partly covered with a mat of growing roots. Removal of the grass, even to a space of 6 inches round the stem of the tree, led to a sensible mitigation of the harmful grass effects.* This part of the investigation seems to have been insufficiently developed.

*Supply of Nutrients.*

The grass growing round the tree removes some of the nutrients from the soil, as is shown by the percentages of substances soluble in the 1 per cent. citric acid given in Table VI.

* "Science and Fruit Growing," p. 273.

Table VI.—Analysis of Soil after Drying at 100° C., by Digestion* with a 1 per cent. Citric Acid Solution.

| | Plot 814. Open Soil. | Plot 815. Grassed Soil. |
|---|---|---|
| | Per cent. | Per cent. |
| Lime (CaO) | 0·116 | 0·084 |
| Phosphoric acid ($P_2O_5$) | 0·0135 | 0·0084 |
| Potash ($K_2O$) | 0·0245 | 0·0135 |
| Magnesia (MgO) | 0·0086 | 0·0079 |

Pickering, however, did not attach great weight to this factor, and he judged from several observations that the harmful effect of grass could not be attributed to any withdrawing of nutrients from the tree. The effect was, in his view, too pronounced, and shown too soon after the grass was laid down. More direct evidence was obtained by adding fertilisers to the water supplied to the roots in an experiment similar to that described on p. 184. No mitigation of the grass effect was produced. Further, he planted a tree in white sand not supplied with fertilising substances: the tree grew perfectly well, although the sand was highly deficient in plant nutrients, containing only 0·0003 per cent. of phosphoric acid soluble in 1 per cent. citric acid, and 0·0056 per cent. of potash, soda and magnesia, while there was no measurable amount of nitrogen. The tree flourished for at least two years, having apparently been able to mobilise reserves of nutrients stored up in its own tissues.

This last experiment has been repeated at Long Ashton by Wallace, who finds that growth will continue for two or three years, as stated by Pickering, but it is much less than for fully fed trees, and after a time it ceases.

Pickering's experiments do not rule out the possibility of interference with the nitrogen nutrition of the tree. He left nitrogen out of account in the analyses just quoted, but even had he brought it in he could not have assumed that the amount of nitrogen in the grass was a measure of the amount that had disappeared from the soil. Nitrates are very liable to be decomposed or taken up by micro-organisms. Lyon, Heinicke and Wilson† have recently reinvestigated this harmful effect of grass on fruit trees, and attribute it mainly to nitrogen starvation. In their experiments there was not only less nitrate in the grassed than in the arable soil, but less even than was expected after allowing for the quantity taken up by the grass; in some way or other the

* *3rd Report, Woburn*, p. 26.

† T. L. Lyon, A. J. Heinicke and B. D. Wilson, 'Cornell Memoir,' 63 (1923).

grass favoured the removal or destruction of nitrates by micro-organisms. This action went so far as to render the supply of nitrate in the grassed land insufficient for the tree. In the Eastern United States apple growers are more and more allowing the orchards to become covered with grass, thereby reducing the cost of cultivation, and overcoming the ill effect on the trees by annual applications to each one of 5 to 10 lbs. of nitrate of soda or sulphate of ammonia.

While admitting that Pickering did not adequately study this possibility, and that nitrogen starvation may have been an important factor, it does not appear to explain all the phenomena.

### *A Toxic Excretion from the Grass Roots.*

Pickering's experiments led him to the view that the effect of grass was " not merely a question of starvation in any form, nor of any simple modification of the ordinary conditions under which a tree can thrive, but that the grass has some actively malignant effect on the tree, some action on it akin to direct poisoning."* He therefore planned a set of experiments which, for simplicity and directness, would be difficult to surpass.

The first experiments, made in 1895, were designed to find out whether the effect of grass could be reproduced by watering the trees with water which had passed through growing grass, and had thus been in contact with its roots. Grass was grown in perforated trays containing sand, to which no additional plant nutrients had been supplied ; it was washed with water and the leachings collected. Three sets of pot experiments were made, using crab stocks grown in sand : in one the sand was covered with growing grass, in the remaining two there was no grass, but one set was watered with grass leachings and the other with pure water. The whole experiment was duplicated in pots of soil. In the sand experiments the grass leachings were harmful, though not as much as grass itself : in the soil experiments they did no harm ; on the contrary, they seemed to be advantageous. After two years the averages of growth measurements were† :—

| | In earth. | In sand. |
|---|---|---|
| No grass nor grass leachings .. .. | 100 | 100 |
| Growing grass .. .. .. .. | 41 | 48 |
| No grass, but grass leachings .. | 130 | 83 |

* *3rd Report, Woburn*, p. 48.
† *13th Report, Woburn*, p. 87.

Pickering therefore concluded that the toxic excretion from grass roots, if there be one, must be very unstable and capable of changing rapidly into a plant nutrient. Certain observations seemed to support this view. Trees speedily began to recover from the deleterious influence of grass once the grass was removed. Further, young trees planted in soil previously grassed, but from which the grass was removed, flourished better than others in tilled soil. Finally, as already shown (p. 184), trees near to grass actually seemed to benefit therefrom. The deleterious agent, therefore, could not be permanent.

Ten years later (1914—see *17th Report*, p. 14) he repeated the experiment with other crops and confirmed the loss of deleterious effect by exposure, though he obtained no increase in growth.

The next set of experiments was much more complete. Pickering had never made a crucial test to find out whether the effect of grass was to remove from the soil something beneficial to the tree, or whether it was to add something harmful. He now supplied evidence that the grass injury was produced whether the roots mingled with those of the tree or whether they were sharply separated. Apparently, therefore, the injury was caused by addition of something harmful. The pots were so arranged that the grass roots could take neither food, water nor anything else out of the soil in which were the tree roots, yet the harmful effect was sharply marked. Perforated iron trays, annular in shape, were fitted into the pots, leaving a central circular space in which the tree could grow. The tray was filled with sand in which grass was sown. The experiment was modified by filling the pot entirely with soil which was sown with grass ; there was no tray : in one series some fine gauze was inserted in the soil at a few inches depth to prevent the grass roots mingling with the tree roots ; in the other there was no gauze. In a control set, trees were grown by themselves with no grass.

The general mean of the results was :—

| | Amount of tree growth. |
|---|---|
| Control : no grass | 100 |
| Grass growing in soil : no gauze or trays | 60 |
| Grass grown in trays | 73 |
| Grass : gauze partition | 71 |

It thus appeared that the effect of the grass was just as marked whether the roots were allowed to mingle with those of the tree or whether they were kept sharply distinct by means of a gauze partition or tray. The simplest explanation was that the water that had passed the grass roots carried with it something toxic to the tree.

*General Nature of the Phenomenon.*

Pickering's next step was to find whether the phenomenon was general or confined only to grass and fruit trees. Experiments both in the field and in pots showed that the injury was general and reciprocal, the grass suffering from the effects of the tree. Field experiments showed that "all trees were affected, whether forest or fruit, and all kinds of grass are capable of doing the injury. It is true that the more vigorously growing trees were less affected, and that some kinds of grass seem more harmful than others, the strong-growing, deep-rooted grasses, such as cocksfoot, having a worse effect than the shallower-rooted, weaker-growing fescues; but there is no difference in kind, only in degree."* Various other plants were tested in pot experiments: all showed an adverse effect on other plants, not only of different kinds, but even of the same kind.

More extended experiments were then begun. The pots were improved; the iron tray of the earlier series was replaced by one of glazed earthenware, the same material as the pot itself; in the check experiments, *i.e.*, those in which there was no surface crop, the trays were filled with soil only (fig. 6). All the water given to the plant was run through the earth in trays. The crops were varied, always, however, with the same general result: "Tobacco, for example, did badly with grass growing in the trays, but it was almost killed when clover took the place of grass. When the same plant was grown in pots and trays, the action was even more marked than when plants of a different kind were grown (Table VII). There was, however, this interesting difference between trees and softer plants. In every case examined the softer plants finally recovered from the effect of the surface crop, and except in one case, where they had been almost killed, they outstripped the duplicate plant without a surface crop. From the results obtained by grassing mature trees, this recovery cannot be attributed to the age of the plants; it is attributed to a counteracting of the evil effects of the toxin by the beneficial effects of its oxidation product as this accumulates in the soil."†

There was no depression of growth when the perforations in the trays were closed up so that water could no longer pass from the tray to the pot; the effect, therefore, must be due to something in the water passing out, and could not be attributed to any aerial factor.

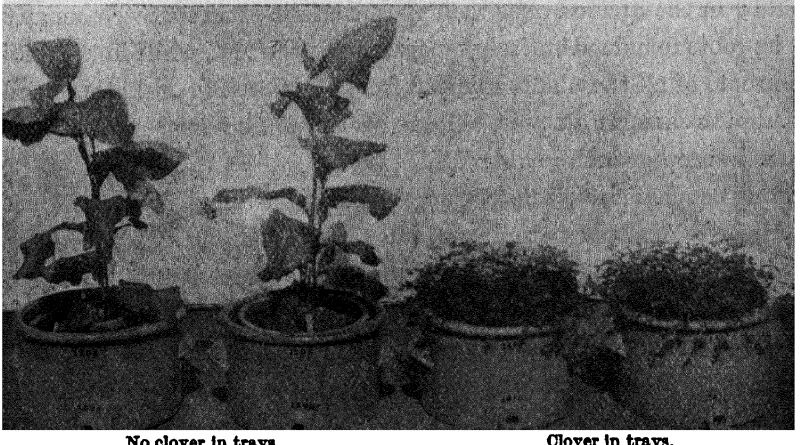
* *14th Report, Woburn*, p. 59.

† *14th Report, Woburn*, pp. 64–65; *Journ. Agric. Sci.*, vol. 6, pp. 136–151.

Festuca in trays. No festuca in trays.

Festuca pretensis.

No grass in trays. Grass in trays.



No clover in trays. Clover in trays.

Tobacco.

FIG. 6.—The effect of one crop upon another. 'Journ. Ag. Sci.,' 1914, vol. 6, p. 136.

[*By courtesy of the Cambridge University Press.*

Table VII.*—Harmful Effect of Surface Crop and Subsequent Partial Recovery. The weight of the crop in the check pots with no crop in the trays = 100.

| Plant in pot. | Plant in tray. | Relative weights of plants under surface growth. | |
|---|---|---|---|
| | | A. Earlier date. | B. Later date. |
| Tobacco | Grass | 60 | 127 |
| ,, | Clover | 3 | 21 |
| Mustard | Grass | 46 | 62 |
| ,, | Mustard | 11 | 11 |
| Tobacco | Grass | 66 | 72 |
| ,, | Tobacco | 26 | 46 |

Pickering saw that if one plant could injure another of the same kind, it must also injure itself. He proceeded to make a series of experiments and to draw conclusions which seemed to widen the idea of toxicity so much as virtually to render demonstration impossible. "If," he argued, "the toxin affects the plant itself as potently as it affects its neighbours, it should make no difference—with certain minor reservations—whether several plants are in the same mass of soil with free communication between their roots, or whether they are separated from each other, as they might be by driving partitions down into the soil so as to confine each plant in a compartment of its own."† In order to test this possibility, he grew plants in rectangular glazed pots, 6 in. by 9 in. surface and 9 in. depth, some of which were divided into six compartments of 3 in. by 3 in. surface, while others were left undivided. In each pot he grew six plants; in the divided ones each plant had its own separate compartment, so that its roots remained entirely separate from the rest, while in the undivided pots the roots of all the plants mingled freely. Watering and other conditions were made the same in all pots, and, as Pickering had surmised, there was no difference in crop growth (Table VIII).

Pickering concluded, therefore, that "with a given number of strictly similar plants in the same bulk of soil, root-interference has no effect." He drew a further conclusion: "When different numbers of plants are grown in the same amount of soil and this amount is insufficient for the full development of the plants, the resulting plant growth will be the same whatever be the number of plants present. Root-interference, as has been shown, does not affect the results,

* 17*th Report, Woburn*, pp. 10 and 11 (1920).
† *Ibid.*, p. 39.

Table VIII.—Six Plants grown in Divided and Undivided Pots.* Relative weights, the actual weights (after drying) being entered in brackets.

1914.

| Plant. | Divided pots. | | Undivided pots. | |
|---|---|---|---|---|
| Barley | 98 | 100 (7·1 grms.) | 100 | 98 |
| ,, | 104 | | 92 | |
| ,, | 99 | | 102 | |
| Mustard | 94 | 100 (6·5 ,, ) | 103 | 100 |
| ,, | 103 | | 99 | |
| ,, | 103 | | 96 | |
| Tomatoes | 101 | 100 (8·6 ,, ) | 109 | 103 |
| ,, | 99 | | 106 | |
| ,, | 100 | | 100 | |
| Tobacco | 94 | 100 (5·6 ,, ) | 114 | 113 |
| ,, | 97 | | 112 | |
| ,, | 109 | | 112 | |

and the sole limiting factor, therefore, will be the amount of nutrient available in the soil; when this is limited, it will be entirely used up and should produce the same amount of plant growth, whatever be the actual number of plants growing in it."† The experimental data are given in Table IX.

Table IX.—Different Numbers of Plants grown in the Same Weight of Soil.

*Tobacco.*

| | 1 plant. | 2 plants. | 4 plants. | 16 plants. |
|---|---|---|---|---|
| | Grams. | Grams. | Grams. | Grams. |
| Weight per pot— | | | | |
| Actual | 120 | 122 | 131 | 128 |
| Relative | 100 | 102 | 109 | 106 |
| Weight per plant, relative | 100 | 51 | 28 | 6·6 |

*Mustard.*

| | 1 plant. | 4 plants. | 16 plants. | 64 plants. |
|---|---|---|---|---|
| | Grams. | Grams. | Grams. | Grams. |
| Weight per pot— | | | | |
| Actual | 56 | 78 | 89 | 91 |
| Relative | 100 | 138 | 159 | 162 |
| Weight per plant, relative | 100 | 35 | 10 | 2·5 |

These results agree with those already obtained at Rothamsted.

* *Ibid.*, p. 40.

† 17*th Report, Woburn*, pp. 40 and 41.

It must be admitted that the apparent elimination of toxic effects in these experiments introduces difficulties, and suggests that the phenomena are more complex than the first experiments indicated. Some further observations, which Pickering never followed up, support this view: he found considerable differences in plant growth, even when every plant was grown in a separate pot, according as the pots were near together or separated. There appeared to be an above-ground or aerial interference which might vary with such external conditions as temperature, degree of isolation, etc.* Pickering carried out one experiment which seemed to indicate that his main results were not affected by this factor, but so important a matter could not be eliminated by a single test. Other interesting observations are recorded in the *17th Report*. In the main they arise out of unfinished experiments and are therefore not reproduced here.

*Pickering's View of the Nature of the Toxic Substance.*

In the *17th Report* (1920) Pickering set out his views as to the nature of the toxic substance. He began by eliminating two obvious possibilities. At an early stage it had come to his notice that the growth of plants in water cultures brought about an alkaline reaction in the medium, due to the larger net absorption of the nitrate radical than of the base. The Rothamsted workers were at this period making a study of the phenomenon, and they showed that it was not confined to water cultures, but occurred also in natural soils. A set of pot experiments was therefore put up in which the reaction of the soil was varied from distinct acidity to distinct alkalinity. The growth of the tree was adversely affected by the higher dose of potassium carbonate; but even when 0·04 per cent. was present, the reduction in growth was only 20 per cent. against 50 per cent. reduction on the grassed plots. Pickering therefore concluded that the induced alkalinity was not the prime cause of the toxic effect.

In another series of experiments he tested and rejected the hypothesis that the causal agent was carbon dioxide from the grass roots. The experimental evidence was much less convincing than one would have liked. He did not picture the toxic agent as an exudation from the root of a substance actually poisonous to other plants. "The facts, as they stand at present, merely warrant the conclusion that a plant, in growing, leaves something in the soil which, until it becomes decomposed and oxidised, is detrimental to growth of other plants, and necessarily, therefore, to that of itself. What this some-

* This above-ground interference has been studied by W. E. Brenchley at Rothamsted, 'Ann. Applied Biology,' vol. 6, p. 142 (1920).

thing is we do not yet know, but it is very probably only the organic débris of the roots as they push themselves through the soil. How such débris acts so as to be prejudicial to plant life is another matter, and presents a problem which it may be difficult to solve. The prejudicial substance is evidently soluble in water, and it is equally evident that it is easily oxidised or, in chemical language, it must be a reducing agent. A certain supply of oxygen is required for the healthy development of plant roots, and it might be suggested that this substance absorbs the oxygen in the soil, and does not leave enough for use of the roots. Such an explanation, however, would imply the continued presence of a larger amount of the reducing substance than seems possible. A more probable explanation is that processes of oxidation occur normally in the root cells of healthy growing plants, and that such processes are interfered with when a reducing agent, even in minute quantities, finds its way into the cells."*

Reviewing the whole investigation, the case for a toxic substance appears to be none too well founded. The evidence on which interference with soil aeration or with the nutrition of the plant was ruled out seems insufficient. Moreover, as in all Pickering's work, no account is taken of the fact that the chemical changes in the soil are mainly the result of the activities of micro-organisms. There is some evidence that these activities are affected by plant growth: apparently nitrates are less rapidly formed, or are more liable to be decomposed under a growing crop than in uncropped cultivated land. In view of these considerations it seems highly desirable that the whole subject should be carefully re-examined. An important factor in plant growth is undoubtedly at work, and Pickering's observations make a good starting-point for further investigation.

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* 17*th Report*, p. 20.

## CHAPTER IV.

### The Manuring of Fruit Trees.

At the time that the Woburn experiments began in 1894 there was little systematic knowledge of the effect of manures on fruit trees, although a general similarity in nutrition and fertiliser requirements between fruit trees and agricultural crops seems to have been widely assumed. In the practical handbooks available in 1894 it was taken for granted that farmyard manure will give good results, and, if they are mentioned at all, it is assumed that the so-called artificial fertilisers will also increase the crops by producing the same effects as on agricultural crops. Pickering himself must have been familiar with these effects, since he had worked as a labourer on the Rothamsted plots and knew the Rothamsted workers well.

It is not surprising, therefore, that the Woburn manured plots were laid out closely on the lines of the Rothamsted experimental plots. They included the following, among others :—

(1) No manure.
(2) Farmyard manure.
(3) Complete artificials.
(4) As 3, but without nitrogen.
(5) „ „ phosphate.
(6) „ „ potassic fertiliser.

It is a great tribute to Pickering's clear and unbiassed powers of observation that he was not in the least perturbed when the results turned out contrary to expectation. Instead of calling them absurd and attributing them to local peculiarities, as others did and he might well have done, he boldly called in question the whole of the fruit growers' manurial practice, thereby raising a great storm of controversy which lasted as long as the work continued.

In laying out any series of manurial experiments it is necessary to decide at the outset the quantities of the different fertilisers to be used. Pickering adopted for this purpose a method which he recognised to be faulty, it having been destructively criticised by Lawes and Gilbert nearly fifty years previously; but he was unable to devise a better method, and, indeed, it is difficult to see what else could have been done. From published analyses of the composition of the ash of apples and an assumed average crop of 50 lbs. of apples per tree,

he calculated the weights of potassium sulphate, superphosphate, magnesium sulphate and sodium nitrate that would be required to replace the amounts of potassium, phosphorus, magnesium and sodium withdrawn from the soil. He then doubled these quantities in order to allow for loss by drainage and so arrived at a mixture to be given to each tree each year.

The data were :—

*Ash Constituents in Fresh Apples.*

| | Per cent. |
|---|---|
| $K_2O$ | 0·13 |
| $P_2O_5$ | 0·05 |
| MgO | 0·03 |
| $Na_2O$ | 0·09 |

*Fertiliser Mixture to replace Twice the Amount of Ash Constituents contained in 50 lbs. of Apples per Tree.*

| | Per Tree. Lb. | Per Sq. Metre. Grams. | Per Acre. Lb. |
|---|---|---|---|
| Potassium sulphate | 0·26 | 9·7 | 94 |
| Superphosphate | 0·42 | 15·8 | 152 |
| Magnesium sulphate | 0·09 | 3·3 | 32 |
| Sodium nitrate | 0·27 | 10·0 | 97 |

The first three substances were applied each November and the nitrate of soda each February.

While recognising the doubtful validity of the method by which he had arrived at the mixture, Pickering found some support for it in the circumstance that "the relative proportions of the constituents present in it are very similar to those mixtures which in the experiments of Lawes and Gilbert have yielded some of the best results with a number of farm crops."†

The scheme of experiment was rather ambitious, and it included a number of plots which were discarded later. The two most important series were those where complete artificials were tested against farmyard manure and against no manure, and those designed to show the effects of specific fertilisers—nitrogen, phosphorus or potassium—or of supposed fertilisers—such as manganese and iron salts.

* Taken from E. Wolff, *Aschenanalysen*, p. 129 (Berlin, 1871), and J. König, *Die menschlich Nährungs- u. Genussmittel*, p. 815 (Berlin, 1893).

† 1*st Report*, p. 11.

As Pickering interpreted the results, they fall sharply into two divisions :—

1. Results obtained during the first period of the life of the tree (p. 164), when it is simply making growth.

2. Those obtained in the second or fruiting period.

1. *Effect of Manures on Apple Trees during the First or Growing Period.*

The effect of complete artificials was manifest at once in the growth of the trees. On leaf size, growth and number of shoots, the artificials produced a marked effect quite as good as that of dung ; further, the use of only half the amount of artificials led to only one-half the increase. This was in accordance with expectation. But wholly unexpected results were obtained when any single ingredient was omitted from the mixture of artificials. There was no depression of yield : any three of the fertiliser constituents behaved exactly like the mixture of all four. It appeared, therefore, that no one of them had any specific action : the results are given in Table X.

Table X.—Mean Results obtained by Different Methods, 1896.*

| Plot. | Treatment. | Leaf size. | Growth. | No. of shoots. | Remarks. |
|---|---|---|---|---|---|
| I. | II. | III. | IV. | V. | VI. |
| 21 | Normal (complete manure) | | | | |
| 22 | No phosphate | − 6 | − 3 | + 16 | Effect not significant. |
| 23 | No potassium | + 1 | − 2 | − 5 | |
| 24 | No nitrate | 0 | + 4 | + 1 | |
| 27 | Dunged before planting | 0 | − 5 | + 4 | |
| 28 | Dunged every year | | + 4 | 0 | |
| 32 | No manure | − 23 | − 11 | − 7 | Reduction significant. |
| 33 | Half dose of manure | − 11 | − 13 | − 10 | Reduction less, but significant. |

Pickering never accounted for this curious phenomenon, nor indeed is it clearly explained yet. Since these experiments were carried out, however, results have been obtained with agricultural crops on clay soils where artificial manures have given crop increases, but it seemed immaterial what particular manures were used. It is possible that the added salts may affect the colloidal properties of the soil, but there may also be a limiting factor effect, as indicated later.

Pickering was surprised at the failure of the farmyard manure to act better than the artificial manures. Whether it was dug in before planting, as in Plot

* 1*st Report*, pp. 79, 80.

27, or applied as a mulch, as in Plot 28, it gave no increase over the complete fertiliser mixture applied to the "normal" plot. His attention was diverted from the phenomenon by the circumstance that the effect of the complete manure began to be much less marked after the fruit trees had passed the young stage. Already in the *2nd Report* (1900) he finds the total omission of manure has reduced the growth only by 5·5 per cent., while halving the dressing has brought it down only by 3·5 per cent.—quantities too small to be observable to the naked eye. Since the growth of the unmanured plot had not progressively decreased, he attributed the earlier results to some accidental circumstances attendant on the special season (1896) in which the measurements were made.

Further work indicated, however, that the results were probably sound. Some years later, when the experiment was concluded and the apple trees were removed, he planted several thousands of crab and Paradise stocks on these same plots, and, weighing them after they had been growing for two years, he found that the manures had increased their growth. The relative amounts of growth were :

| *Less than Normal Manure.* | *Normal Manure.* | *More than Normal Manure.* |
|---|---|---|
| 85 | 100 | 114 |

As a result of all his work, Pickering concluded that the liberal supply of manure to ground used for nursery stock, which is the usual practice among nurserymen, is justified.*

2. *Effect of Manures on Apple Trees during the Second or Fruiting Period.*

After the trees had passed the period of rapid growth and had settled down to the second or fruiting period, Pickering began to obtain much smaller differences on the different plots. He had now a large number of measurements, and for purposes of discussion he grouped his plots together according as they had less or more manure than that applied to the normal plots. Table XI shows a typical summary of his measurements.

* "Science and Fruit Growing," p. 93.

Table XI.—Effect of Quantity of Fertiliser on Tree Growth.*

| | Less than normal manure. | Normal manure. | More than normal manure. |
|---|---|---|---|
| Leaf-weights | 93 | 100 | 98 |
| Size of trees | 100 | 100 | 99 |
| Weight of trees | 103 | 100 | 101 |
| Weight of fruit | 93 | 100 | 106 |
| Size of fruits | 103 | 100 | 95 |
| Value of crops | 98 | 100 | 102 |
| Annual growth | 87 | 100 | 88 |
| Mean | 96·7 ± 1·5 | 100 | 98·4 ± 1·3 |
| Without annual growth | 98·3 ± 1·25 | 100 | 100·2 ± 1·17 |

These results were quite unexpected and were severely criticised: it was freely stated that the soil must be abnormal. Pickering therefore laid out two new sets of experiments. He grew two market garden crops—potatoes and onions—and found that they responded in the usual way to fertilisers; he therefore concluded that the results with apple trees were not due to abnormality in the Woburn soil or the method of experiment, but were really characteristic of the tree. Secondly, he started a somewhat similar set of experiments on apple trees at Millbrook, on the light soil of the Lower Greensand, about five miles from Woburn. Here, however, the effect of the fertilisers was distinctly marked and wholly in the direction expected from the results of agricultural experiments. The results are summarised in Table XII, taken from the *16th Report* (p. 33).

Table XII.—Effect of Different Doses of Artificials and Dung on Apples at Millbrook.

| | Nil. | Dose of artificials. | | | Dose of Dung. | | |
|---|---|---|---|---|---|---|---|
| | | Single. | Double. | Treble. | Single. | Double. | Treble. |
| Prunings, 1903, '4, '5, and '6 | 100 | 147 | 125 | 163 | 151 | 213 | 227 |
| Weight of crops, 1902, '3, '4, '5, '6, '7, and '11 | 100 | 141 | 142 | 168 | 156 | 186 | 242 |
| Size of fruits, 1905, '6, '7, and '11 | 100 | 132 | 142 | 163 | 191 | 272 | 251 |
| Mean | 100 | 140 | 136 | 165 | 166 | 224 | 240 |
| Relative value if artificials = 100 | — | — | — | — | 119 | 165 | 146 |
| | | | | | | 143 | |

* "Science and Fruit Growing," p. 91.

The experiment was also designed to show the effects of particular fertilisers, and the results shown in Table XIII were very striking.

Table XIII.—Effect of omitting one of the Constituents of the Artificial Manures.

| | No manure. | Potassium omitted. | Phosphate omitted. | Nitrogen omitted. | Complete manure. |
|---|---|---|---|---|---|
| Prunings, 1903–6 . . | 68 | 65 | 121 | 103 | 100 |
| Weight of crops, 1902,* '5, '6, '7, and '11 | 71 | 37 | 111 | 98 | 100 |
| Size of fruits, 1905, '6, '7, and '11 . . . . | 76 | 99 | 129 | 108 | 100 |
| Mean .... . | 72 | 67 | 117 | 103 | 100 |

The marked effect of potassium is strictly in accordance with expectation on a light sandy soil, since potassic fertilisers tend to prolong the growing period of the plant and thus serve to counteract the shortening effect of the general conditions of a sandy soil, which naturally reduces the amount of growth. The crops receiving nitrogen and phosphate only, but no potassium, are even smaller than those without manure: this result has been obtained with gooseberries at Long Ashton and with apples at Hutton. It is under investigation at Long Ashton. A similar result with potatoes is being studied at Rothamsted. The effect of phosphate in reducing growth is intelligible, since phosphates tend to shorten an already short growing season. The results are of further interest as showing a relationship with the chemical composition of the soil: at Millbrook there is only a small proportion of soluble potash but a larger amount of soluble phosphate, while at Ridgmont the position is reversed :—

| *Millbrook.* | *Ridgmont.* |
|---|---|
| *Potassic fertiliser beneficial.* | *Potassic fertiliser without effect.* |
| Per cent. soluble† $K_2O$ in soil = | |
| 0·006 | 0·024 |
| *Phosphatic fertiliser harmful.* | *Phosphatic fertiliser beneficial.* |
| Per cent. soluble† $P_2O_5$ in soil = | |
| 0·024 | 0·014 |

Pickering seems to have regarded the Millbrook results as abnormal and the Ridgmont results as more nearly normal. The land at Millbrook, he says, is

* 16*th Report*, p. 36.

† In Dyer's 1 per cent. citric acid solution.

" of a light sandy, and decidedly poor character, having, owing to its poorness, been abandoned for agricultural purposes many years ago ; it is not, of course, land which a commercial fruit grower would be likely to select" (*16th Report*, p. 29). Hence he did not attach as much weight to them as to the Ridgmont results, and he argued generally that the manuring of apple trees was not economical, since substantially the same results would be obtained if no manure were applied. As time went on he somewhat modified this attitude : he recognised that " the crops at Ridgmont were light, owing to circumstances independent of the soil.* . . . Under other circumstances the average cropping might have been three or four times as great as it was, and probably in such a case the soil could not have borne the drain on its resources without the addition of manure." But in the main he stuck to his position.

The conclusion was not accepted by practical fruit growers, the best of whom manure their trees liberally. As they are shrewd, observant men with a keen eye to business, it must be supposed that they feel themselves justified in so doing. It is unnecessary to go into the controversy that followed, but it must be admitted that Pickering's case was not very strong. Several objections can be raised.

It has been pointed out by Mr. Edward A. Bunyard† that the unmanured row was adjacent to rows receiving manure and distant only 11 ft. from them. Now the roots of trees extend some distance in the soil, and there seems no reason why the roots should have remained in their own plots. So also, the " no potash " plot (23) joins a " no phosphate " plot (22), and if the roots of trees on 23 invaded 22 (as is quite possible), they would obtain potassium while in turn the trees in 22 by invasion of 23 would obtain supplies of phosphates. There is considerable force in this criticism, and fruit experts now realise that in repeating this experiment a considerable alteration in design would be necessary. Pickering himself later on advised that 20 ft. should be the minimum distance between the trees.

The difference in results between Ridgmont (Oxford Clay) and Millbrook (Lower Greensand) has already been mentioned. At Ridgmont Pickering considered there was no appreciable effect from manures, while at Millbrook the results were in accordance with the expectations of agricultural science—farmyard manure being very effective, potassic fertilisers also proving effective, while phosphates were not only ineffective, but detrimental to the growth

* It is difficult to agree that the lightness of the crop was independent of the soil and subsoil.

† *Journal of Pomology*, vol. 1, No. 1.

of the trees. Neither soil is altogether typical of fruit land. Much of the fruit produced in this country is grown on loamy or even sandy soils: the great fruit districts of Kent are situated on the Thanet beds or Oldhaven sands in the Newington, Teynham and North Kent area, and on the Lower Greensand in the Maidstone area. The Wisbech fruit area is on loam, and so also are many of the fruit districts of the West. Much fruit is, however, grown on heavier soils—on Lias clays in the Pershore, Evesham, Cheltenham, and Martock districts; on heavy loams of the Old Red Sandstone in Hertfordshire; and on the medium to heavy loams of the Keuper Marls scattered over Worcestershire, Gloucestershire, and Somerset.

The mechanical analyses of some of these soils are set out in Table XIV.

Table XIV.—Mechanical Analysis of Woburn Soils compared with Soils from Good Fruit Orchards in Kent.

*Surface Soils.*

| | Ridgmont. | Millbrook. | Good fruit soils in Kent. | | |
|---|---|---|---|---|---|
| | | | Newington. | Greenhithe. | Loddington, Maidstone. |
| Fine gravel | 2·1 | 4·3 | 0·5 | 0·3 | 3·5 |
| Coarse sand | 48·3 | 70·4 | 16·9 | 2·0 | 10·2 |
| Fine sand | 7·7 | 7·2 | 57·3 | 68·1 | 33·5 |
| Silt | 7·3 | 1·7 | 8·2 | 3·6 | 14·6 |
| Fine silt | 12·8 | 6·8 | 3·9 | 4·8 | 14·9 |
| Clay | 15·3 | 6·0 | 6·0 | 11·6 | 12·2 |

*Subsoils.*

| | | | | | |
|---|---|---|---|---|---|
| Fine gravel | 5·2 | 7·0 | 0·2 | — | 2·6 |
| Coarse sand | 21·5 | 76·1 | 16·7 | — | 9·8 |
| Fine sand | 5·3 | 5·0 | 58·5 | — | 30·2 |
| Silt | 8·0 | 1·8 | 6·8 | — | 17·5 |
| Fine silt | 13·2 | 4·7 | 4·0 | — | 15·5 |
| Clay | 35·0 | 2·9 | 6·9 | — | 15·3 |

The Millbrook soil is lighter than any of the fruit soils, and the Ridgmont surface soil is not unlike that of Loddington, but there is a great difference in the subsoils. At Loddington the subsoil is but little heavier than the surface soil: water and roots easily penetrate. This condition is very necessary for fruit trees. At Ridgmont, on the other hand, the subsoil is markedly heavier than the surface soil, containing the very high proportion of 35 per cent. of

clay—neither water nor roots* could penetrate. These conditions are known to be very unfavourable to the growth of fruit trees. Pickering records† that a considerable number of the trees and bushes were killed by the water-logging of the soil in the wet seasons 1903 and 1904 : the survivors can hardly fail to have suffered in other seasons.

On looking over the whole of the Woburn results, one seems driven to the conclusion that some factor was severely limiting the growth and fruiting of the trees. Most of the apparent abnormalities are explicable on this view, including :—

1. The inability of farmyard manure or of complete artificials to raise growth above that of the incomplete mixtures.
2. The fact that no further effect on the growth of the tree was produced by any manure after the first two or three years.
3. The low yield of fruit on some of the varieties which, as already shown, fell far below that expected in a good garden.

There is evidence that the factor limiting the growth and development of the trees was the nature of the subsoil. All the facts are in accordance with this view : the waterlogging ; the failure of the roots to penetrate ; the weakening of the growth of the trees as shown by the decline in leaf size (*4th Report*, p. 65) ; the bad cankering of the Potts' Seedling, and the poor condition of the Cox's Orange (*16th Report*, p. 8). Of the varieties grown, only Bramley's Seedling would be expected to do well in adverse soil conditions. Reference to Table III, p. 168, shows that Bramley's Seedling is the only one that produced yields of the magnitude expected, and, therefore, was the one least affected by the harmful limiting condition. Pickering did not recognise this fact, but in his discussions grouped all his different varieties together, attaching equal weight to each of them.

If, as seems reasonable, Bramley's Seedling is treated separately from the rest, some interesting results are obtained. Disregarding the first seven years (first period, active growth), where the fruit yields are negligible, the results for the whole fruiting period are set out in Table XV.

* *16th Report*, pp. 3, 72 ; *9th Report*, p. 69.
† *4th Report*, p. 2.

Table XV.—Yields of Fruit, Kilos. per Tree, Bramley's Seedlings, Dwarfs.

*Effect of Artificials.*

| Year. | Complete artificials. Plot 21. | Without phosphate. Plot 22. | Without potash. Plot 23. | Without nitrogen. Plot 24. | Complete artificials. | |
|---|---|---|---|---|---|---|
| | | | | | Plot 25. | Plot 26. |
| 1904 | 36·3 | 19·7 | 32·2 | 36·2 | 33·2 | 34·6 |
| 1906 | 6·9 | 3·4 | 6·7 | 19·5 | 14·3 | 5·6 |
| 1907 | 26·6 | 48·3 | 57·2 | 40·8 | 50·5 | 18·7 |
| 1908 | 23·0 | 2·4 | 7·1 | 7·2 | 5·6 | 19·2 |
| 1909 | 91·8 | 55·9 | 90·6 | 78·5 | 68·3 | 114·4 |
| 1910 | 12·2 | 3·9 | 7·3 | 1·8 | 4·6 | 3·3 |
| 1911 | 87·1 | 58·1 | 79·3 | 55·1 | 91·4 | 72·6 |
| 1913 | 96·4 | 46·7 | 50·1 | 55·9 | 48·5 | 84·5 |
| 1915 | 124·7 | 82·6 | 65·4 | 78·0 | 70·6 | 111·6 |
| 1916 | 0·5 | 0·3 | 0·2 | 0·9 | 0·9 | 0·2 |
| 1917 | 119·3 | 70·3 | 68·8 | 71·1 | 98·8 | 135·6 |
| 1918 | 1·2 | 8·3 | 4·8 | 49·4 | 0·7 | 4·2 |
| 1919 | 116·2 | 70·6 | 56·3 | 49·9 | 71·0 | 95·3 |
| 1920 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mean | 53·0 | 33·6 | 37·6 | 38·9 | 39·5 | 50·0 |

Mean of "complete artificial" plots: 47·5.

*Effect of Farmyard Manure with and without Artificials.*

| Year. | Complete artificials. | | No artificials. | | |
|---|---|---|---|---|---|
| | Farmyard manure 1894 only. Plot 27. | Farmyard manure every year. Plot 28. | Farmyard manure every year. | | |
| | | | Plot 29. | Plot 30. | |
| | | | | (*a*) | (*b*) |
| 1904 | 25·0 | 30·7 | 17·0 | 21·7 | 29·0 |
| 1906 | 3·6 | 2·9 | 10·8 | 8·1 | 12·0 |
| 1907 | 46·0 | 46·6 | 29·3 | 41·6 | 55·1 |
| 1908 | 5·0 | 9·2 | 1·0 | 4·3 | 3·8 |
| 1909 | 112·4 | 121·5 | 53·9 | 85·5 | 85·6 |
| 1910 | 1·8 | 8·4 | 10·9 | 7·7 | 10·7 |
| 1911 | 95·1 | 97·7 | 41·0 | 89·4 | 102·6 |
| 1913 | 86·3 | 105·0 | 38·9 | — | 74·4 |
| 1915 | 90·7 | 112·1 | 32·1 | — | 102·2 |
| 1916 | 0·8 | 0·5 | 0·2 | — | 0·0 |
| 1917 | 129·2 | 155·8 | 40·7 | — | 106·2 |
| 1918 | 6·0 | 11·8 | 4·7 | — | 7·1 |
| 1919 | 82·5 | 103·9 | 21·4 | — | 103·2 |
| 1920 | 0·0 | 0·0 | 3·3 | — | 0·3 |
| Mean | 48·88 | 57·6 | 21·8 | 37·04 | 49·43 |

The figures in column (*a*) are for all six trees; those under (*b*) are for the three trees to which the plot was ultimately reduced.

* 18*th Report*, Appendix, pp. xvi *et seq.*

Table XV—(contd.).

*Effect of Varying Quantities of Manure.*

| Year. | No Manure. Plot 32. | Farmyard Manure only. Plot 31. | Complete artificials. Half normal dressing. Plot 33. | Normal dressing. Plot 34. | Three times normal dressing. Plot 35. | Ten times normal dressing. Plot 36. (*a*) | (*b*) |
|---|---|---|---|---|---|---|---|
| 1904 | 11·1 | 10·7 | 33·0 | 23·1 | 18·2 | 26·8 | 33·1 |
| 1906 | 3·9 | 2·0 | 6·1 | 3·6 | 2·9 | 5·3 | 7·9 |
| 1907 | 32·6 | 33·3 | 21·7 | 36·6 | 31·3 | 51·9 | 37·5 |
| 1908 | 4·2 | 12·8 | 6·1 | 2·0 | 4·1 | 5·7 | 6·0 |
| 1909 | 64·8 | 87·8 | 91·4 | 75·6 | 54·1 | 91·9 | 65·1 |
| 1910 | 4·1 | 5·2 | 1·9 | 5·4 | 6·9 | 10·7 | 15·4 |
| 1911 | 68·3 | 58·7 | 72·2 | 70·0 | 50·6 | 75·8 | 48·4 |
| 1913 | 51·5 | 58·7 | 70·6 | 62·1 | 61·6 | 58·4 | 49·1 |
| 1915 | 71·4 | 82·6 | 87·4 | 84·5 | 79·8 | 52·7 | 47·7 |
| 1916 | 0·2 | 0·8 | 0·3 | 0·3 | 0·5 | 1·1 | 1·0 |
| 1917 | 60·9 | 85·9 | 76·5 | 76·7 | 86·6 | — | 44·8 |
| 1918 | 3·4 | 0·5 | 5·1 | 4·5 | 1·8 | — | 1·5 |
| 1919 | 51·1 | 51·3 | 76·3 | 71·8 | 56·9 | — | 38·8 |
| 1920 | 1·4 | 0·0 | 0·0 | 0·0 | 0·2 | — | 0·0 |
| Mean | 30·63 | 35·73 | 39·20 | 36·89 | 32·53 | 38·03 | 28·30 |

The figures in column (*a*) are for all six trees; those under (*b*) are for the three trees to which the plot was ultimately reduced.

The figures in the table seem to show conclusively that manuring has influenced the yield of the trees. The summarised data are as follows:—

Average Yield of Fruit.

| | Kilos. per annum. |
|---|---|
| Trees without manure | 30·6 |
| With farmyard manure | 35·7 |
| With artificials:— | |
| Half dressing | 39·2 |
| Full dressing | 36·9 |
| Three times dressing | 32·5 |
| Ten times dressing | 38·0<br>28·3 |

The absence of further response to quantities exceeding the "half dressing" presents no difficulty: it suggests a limitation by some other factor.

The omission of any of the single ingredients of the complete artificial manure depresses the yield, and, as happened for growth, the depression is very similar in amount, whether the omission be of nitrogen or of potassium, though there is evidence of a greater reduction when phosphates are omitted, as, indeed, would be expected from the general properties of a clay soil in contradistinction to those of a sand, as at Millbrook.

Apparently, therefore, the figures indicate a response of apple trees to manures similar in kind to that shown by other crops. The difference between this conclusion and that drawn by Pickering lies in the circumstance that he averaged the whole of his results, attaching, as far as can be discovered, the same value to a tree giving a poor yield, and, therefore, in an abnormally poor condition, as he attached to a tree giving the normal yield.

It must be at once admitted, however, that the response of fruit trees to fertilisers is much less than that of agricultural crops. On these the effect of manures is generally striking; on fruit trees it is readily masked by other conditions. Apple trees at East Malling are little, if at all, affected by manures, even over a period of six years, though annual crops grown between the trees respond readily. Nor are definite and incontrovertible crop increases obtained in the extensive trials made in the United States. In the main these are carried out in commercial orchards, where it is notoriously difficult to secure uniform conditions of soil or uniform trees. Among the earliest tests are some on peach trees begun in New Jersey in 1884* and continued for several years, the results of which varied from year to year. Later work on apples† indicated favourable returns from potassic and phosphatic fertilisers. An important series of experiments was begun by the late Dr. C. A. Goesmann at Amherst in 1889, and carried on by W. B. Brooks and J. K. Shaw‡; these are still being continued. The results are not very decisive; farmyard manure has, however, produced an effect, and the growth of the trees has been improved. Mr. Hatton, who has recently visited the orchard, informs the writer that there are only three trees in each set, that the plots are not duplicated, and that the ground is not level, but on a slope. The indefiniteness of the results, therefore, is not conclusive evidence of the ineffectiveness of manures.

In the Geneva experiments (New York State), begun by Hedrick§ in 1896,

* *New Jersey Experimental Station Report*, p. 102 (1887); p. 132 (1889).

† *Report*, p. 75 (1911).

‡ The latest summary is given in *Mass. Agric. Coll. Bull.*, p. 209 (1922).

§ *New York State Bull.*, p. 339 (1911).

an attempt was made to obviate the difficulties revealed by the earlier workers. The ground was carefully selected; the plots were separated by "buffer" rows; each treatment was duplicated, and there were four control plots; and efforts were made to secure uniform trees. There are, however, still no very definite results with fertilisers, the smallness of the population and the individuality of the tree causing variations in results even under the same treatment.

A still later series of experiments was started by J. P. Stewart in 1907* on an extensive scale in the orchards of Pennsylvania. The results are again inconclusive. Again, however, the experiments are not altogether satisfying; they have been drastically criticised by R. D. Anthony and J. H. Waring, who show† that insufficient attention was paid to topographical factors, to the individuality of the trees, to the selection of varieties, etc.

None of these fertiliser experiments gives any clear indication of the effects of fertilisers on fruit yields; even the best of them proved unsatisfactory because of the great variation in individual trees. Pickering's trees suffered from the same defect, and it may safely be asserted that this is the greatest stumbling-block in the way of the fruit experimenter. A serious attempt to overcome it is being made by Anthony: whether successfully or not remains to be seen. Perhaps the only definite conclusion to be drawn from the work is that the effects of fertilisers are not usually very great, so that they are easily masked by individual variations in the trees themselves.

The experience of fruit growers in this country is that in grassed orchards, at any rate, manuring is advantageous, but this is best done through the agency of sheep. These animals are turned in to graze, and they are given cake or corn, in addition to the grass; their excretions manure the land. Where there is no grass, but the land is kept cultivated, it is usual to apply manure, usually farmyard manure, or some organic material such as shoddy, and in view of the persistence and cost of the practice there is difficulty in believing that it is ineffective, especially when the trees are yielding well.

*Manurial Experiments with Bush Fruit and Strawberries.*

Of these experiments the most important were on gooseberries, and their main feature was the extraordinary effect of farmyard manure in increasing first the growth, then the crop, and finally the longevity of the bushes. Several series of experiments are recorded—one in which the plots were maintained

* *Penn. Bulls.*, p. 91 (1909); p. 100 (1910); p. 121 (1913); *Report*, p. 423 (1914).
† *Penn. Bull.*, p. 173 (1922).

from 1897 to 1911, by which time most of the unmanured bushes were dead, though those receiving farmyard manure were still flourishing; and a second series which ran from 1912 onwards. The weights of crops and of bushes, as deduced from a row lifted after five years, were as follows* :—

| Series. | No Manure. | Artificials equivalent to | | Dung. | |
|---|---|---|---|---|---|
| | | 12 tons dung. | 30 tons dung. | 12 tons. | 30 tons. |
| 1. 1900–07: weight of fruit .. ... | 100 | 70 | 113 | 446 | 644 |
| 2. 1913–17: weight of fruit ..... | 100 | 87 | 140 | 315 | 726 |
| 3. Weight of bushes ..... ..... | 100 | 92 | 124 | 210 | 696 |

In these experiments the effect of artificial manures is difficult to determine, owing to the circumstance that the smaller dressing has apparently decreased the crop, while the larger one has increased it—a very exceptional result. In another series of experiments, the effect of the artificial manures is more definite, though, as happened with young apple trees, the omission of nitrogen or potassium has no obvious effect, but the omission of phosphate increases the crop† :—

*Relative Value of Crops.*

| | |
|---|---|
| No manure ..... | 100 |
| Complete artificials..... | 203 |
| Artificials without nitrate..... | 219 |
| ,, ,, potassium ..... | 198 |
| ,, ,, phosphate ..... | 297 |

Currants and raspberries gave similar results.

This marked effect of farmyard manure is being studied by Hatton; it was not followed up by Pickering, but it can be paralleled elsewhere. Citrus trees at the Riverside Experiment Station, California, continue to flourish when farmyard manure is supplied, but not when artificial manures alone are given. The Rothamsted and Woburn experiments show that farmyard manure has certain special effects on agricultural crops, particularly on clover. The problem is now being studied at Rothamsted.

Strawberries behaved somewhat differently from gooseberries. The average

* "Science and Fruit Growing," p. 96.

† *Ibid.*

yield of fruit per plant on the unmanured plot was not high, being only 115 grams over the best five years (1898–1902), and there was considerable scope for improvement, yet the increases given by manure were only small.

| | |
|---|---|
| No manure | 100 |
| Farmyard manure, 12 tons | 125 |
| ,, ,, 30 tons | 127 |
| Artificials equivalent to 12 tons farmyard manure | 123 |
| Artificials equivalent to 30 tons farmyard manure | 105 |

Pickering recognised that the Ridgmont soil was not favourable to strawberries, and he attached but little importance to these experiments.

The experiments on gooseberries, however, deserve repetition, as they seem to indicate some special reaction to farmyard manure which might open up interesting problems in plant physiology.

## CHAPTER V.

### Pests and Diseases of Fruit Trees: Insecticides and Fungicides.

Pickering's attention was early drawn to the significance of insect and fungous attacks by a severe outbreak of the currant gall mite (*Phytoptus ribis*), which occurred within a year of planting the black-currant bushes in 1895 (*2nd Report*). No method of eradication was discovered and the bushes were simply cut down. Such drastic treatment extended to other crops would soon have brought the experiments to an end, and he found it necessary to study the more important insects and fungi attacking the trees, even if only to ensure the continuance of the experiments.

At the outset he disclaimed any special knowledge of mycology or entomology, but this did not prevent him from making some interesting observations, which will be found recorded in the *6th*, *8th* and later *Reports*. In most cases the observations cannot well be summarised, and they will therefore not be reproduced here. His work on silver-leaf disease, however, is more important and must be dealt with at some length.* This disease has long been known in Great Britain, and it appears to be spreading; it has made the growth of some of the finer plum trees almost impossible in many gardens. Its most striking symptom is a silvering of the leaf; the whole branch is affected and ultimately dies; finally, the tree itself dies. The causal organism was diagnosed as *Stereum purpureum* by Percival,† but his proof did not entirely convince mycologists.

Pickering began by showing beyond doubt that the introduction of *Stereum* into the tree was usually followed by the disease; inoculation of the stem was most harmful, but it was also effective in the root or the branches. Different trees varied in susceptibility, the order being:—

| | | | |
|---|---|---|---|
| Plums | 70 | per cent. | affected.‡ |
| Apples | 26 | ,, | ,, |
| Laburnums | 17 | ,, | ,, |
| Laurels | 25 | ,, | ,, |
| Pears | 11 | ,, | ,, |

* *6th and 12th Reports;* "Science and Fruit Growing," p. 231.

† *Linn. Soc. Journ.*, vol. 35, p. 390 (1902).

‡ "Science and Fruit Growing," p. 236.

but it was immaterial whether the fungus used for inoculation was derived from plum, apple or laburnum; in other words, there was nothing to show that the fungus was modified by its host, or that it varied in potency according to the source from which it was derived. No evidence could be obtained that trees which had been infected, and had recovered, were immune to subsequent attack.

Pickering considered that the fungus entered the tree through wounds. He could find no evidence that it travelled underground, as Percival had suggested, nor that it was carried on the pruning knife (except, perhaps, from very badly infested trees), nor that it entered by way of the leaf through wounds made by aphids, etc. Like other workers, he was unable to find a remedy, and his advice was to diminish the chance of infection by cutting out and burning affected wood, and to diminish the chance of acceptance by tarring all wounds immediately they are made.

The practical deductions, while not particularly helpful, are no doubt sound, but mycologists are by no means convinced that *Stereum purpureum* is the sole cause of the disease, for silver-leaf has occurred where no *Stereum* could be found; and, conversely, in the United States *Stereum* is quite common, but silver-leaf is not. There is still room for considerable work on this subject.

### *Fungicides and Insecticides.*

Most of the diseases and pests observed by Pickering had already been studied by others, and remedial measures in the form of washes or sprays had been devised and were, indeed, in common use. But there was a great amount of confusion, and anyone who set out to prepare a wash or spray was faced with a multiplicity of recipes, for many of which it was difficult to see any justification. With his characteristic scorn for Government enterprise, he hunted through the leaflets of the Board of Agriculture and found no less than 13 different recipes for making one and the same wash,* and comments thus :—

"It is, no doubt, necessary that emulsions of different strengths should be used for different purposes and under different conditions, but research has not been so complete yet as to show that every insect requires a special strength of emulsion, or that its requirements vary from year to year; and the only conclusion must be that such recommendations were based on mere fancies by those advocating them, and not on the requirements of the case as determined by direct experiment."†

Fortunately for the Board, he found as many other conflicting recipes issued

* *6th Report*, p. 19.

† "Science and Fruit Growing," p. 152.

by other authorities, one at least of which was somewhat dangerous. Even for the simple alkaline wash used to remove lichens and moss from fruit trees in winter, there were discordant and unintelligible prescriptions. Fruit growers were invited to mix caustic soda and caustic potash, but no reason was given, nor could any be discovered; moreover, it was not at all clear whether potassium hydrate or potassium carbonate was meant, and some growers used the one and some the other. Pickering revelled in an empirical tangle of this sort, and one of the liveliest passages in all his Reports is that* in which he makes his entry into the field, castigating the slipshod worker of the past, while admitting that his own first experiments, "made with saucepans and teacups on an office table, are apt to lack in exactness what they may gain in simplicity." This difficulty, however, he overcame by erecting a laboratory at his own house in Harpenden, where he examined the problem on physico-chemical lines reminiscent of those adopted in his earlier days.

His first problem was to study the alkali wash, and he soon found, as he expected, that the potassium hydrate served no useful purpose; he therefore discarded it in favour of the cheaper and more effective sodium hydrate. His final recommendation was a 2¼ per cent. solution, which he found to destroy moss, eggs of mussel scale, etc.

A more difficult problem was presented by the washes containing paraffin. Pickering showed that it was necessary to define the paraffin, since the low-boiling paraffins had nothing like the toxicity of those of higher boiling-point. He finally chose a commercial fraction known as "Royal Daylight"—a lamp oil supplied by the Anglo-American Oil Company.

The paraffin could not be used undiluted: it had to be made into an emulsion, an operation which had caused much difficulty to his predecessors. His study of the process of emulsification was very characteristic. The experiments were simple and the results strikingly unexpected. He churned paraffin oil with water by means of a syringe and showed that it was broken up into minute globules, which, however, coalesced almost at once to form an unbroken layer of oil. When a little soap was added the globules did not coalesce and the liquid in consequence remained milky in appearance. On standing, the oil rose to the surface, but this time in the form of a cream composed of separate globules of paraffin which do not coalesce but remain emulsified. In a completely packed emulsion the mass of globules, assuming they continue spherical, occupy 74 per cent. of the volume of the cream, the remaining 26 per cent., the interstices between the globules, being occupied by the soap solution. But he found that water

* *6th Report.*

separated from this mixture, indicating that the globules were losing their spherical shape and assuming more flattened or angular forms, which allowed of closer packing. By churning the cream with more paraffin he was able to produce thicker and thicker emulsions, till finally with 99 per cent. of paraffin he obtained one almost as solid as a blanc-mange. It formed a translucent jelly with a bluish tinge, and was exhibited at the Royal Society's Soirée where it caused much interest. To see almost pure paraffin standing up solidly in this way was a novel and striking experience.

Previous workers had assumed that the soap formed an emulsion because it altered the surface tension between the water and the oil, but Pickering could not accept this explanation. He claimed to obtain emulsification in cases where there was no alteration in surface tension. Further, he showed that the power of emulsifying does not increase, like the change in surface tension, with the amount of soap used.

An attempt to prepare an alkaline emulsion led him to quite a different explanation.* A mixture of lime and paraffin had been used for spraying in the United States; he found that it was not a true emulsion but a mixture of the kind known as a quasi-emulsion. On addition of more water there was a separation, some of the lime falling to the bottom carrying with it a little oil, while most of the oil rose to the surface carrying with it some of the lime. But emulsification became perfect on the addition of a little copper sulphate or iron sulphate. He could not attribute this change to an alteration in the surface tension; all that had happened, he considered, had been the precipitation of a finely divided insoluble basic sulphate. He suggested, therefore, that emulsification resulted from the coating of the oil globules with minute solid particles, which thus kept the globules apart. He produced satisfactory emulsions by the use of finely divided clay and other solids, including the insoluble basic sulphates of iron, copper and other metals. Solids failed to act, however, if they were wetted more easily by the oil than by the water, for in that case they entered the globules instead of remaining on the surface. Instances were afforded by sulphur and purple of Cassius. In order to explain the presence of solid particles in the soap solution Pickering supposed that the soap decomposed partially in solution forming an insoluble "acid" soap, which remained suspended in the form of very fine particles; it was these that caused the emulsification. The solid is not very stable, however, and is perpetually redissolving

* *Trans. Chem. Soc.*, vol. 91, p. 2001 (1907). Somewhat similar results had already been obtained by Ramsden (*Roy. Soc. Proc.*, vol. 72, p. 156 (1903), but Pickering did not see this paper until he had completed the work here described.

and being reprecipitated; hence the oil particles occasionally had an opportunity of coalescing, thereby causing an apparently spontaneous de-emulsification. This did not occur with solids such as the basic sulphates, and the emulsions produced by them persisted for years without visible change.

This discovery allowed him to make a mixed wash containing both paraffin and basic copper sulphates: the former constituent was toxic to insects and the latter to fungi. If further experience justifies its use, this wash would be of considerable practical value, since labour forms the main item in the total cost of spraying. The application of two washes together instead of separately is an obvious economy.

*Bordeaux Mixture.*

The investigations on Bordeaux mixture were more detailed, and possibly of even greater practical importance, though they led to nothing so spectacular as his jelly containing 99 per cent. of paraffin. As in the case of other washes, there was no uniformity in the recipes offered to the practical grower, nor had there been any systematic chemical examination of the reactions taking place, although the mixture had been in use since 1882, at first to make growing grapes look distasteful to small boys, and then as a fungicide when the treated grapes were seen to remain free from mildew.

Bordeaux mixture is made by adding milk of lime to a solution of copper sulphate. It was often supposed that the product was copper hydroxide, but Pickering had already, as a student at Oxford, investigated the basic sulphates of iron* and was not prepared to accept this explanation. He investigated the action by adding lime water to solutions of copper sulphate, removing the precipitate, and determining the quantities of the constituents left in solution. The precipitation of copper was complete when the quantity of lime sufficed to form the basic sulphate, $4CuO.SO_3$, but the reaction did not end here. Addition of more lime caused further change, with formation of a basic sulphate $10CuO.SO_3$. Still further additions made the liquid alkaline and gave a compound, $10CuO.SO_3$, $3CaO$, and finally $10CuO.30CaO$. In each case, however, some calcium sulphate is present, and Pickering considered that it formed part of the complex molecule. The formulæ finally given are† :—

1.— $4CuO.SO_3$, $0{\cdot}06\ CaSO_4$,
2.— $5CuO.SO_3$, $0{\cdot}25\ CaSO_4$,
3.—$10CuO.SO_3$, $1{\cdot}3\ CaSO_4$,
4.—$10CuO.SO_3$, $4CaO.SO_3$,

and finally 5.—$CuO.3CaO$.

* *Trans. Chem. Soc.*, vol. 37, p. 807 (1880).

† *Trans. Chem. Soc.*, vol. 91, p. 1988 (1907); *Journ. Agric. Sci.*, vol. 3, p. 171 (1909).

These various basic sulphates were all produceable in the various methods for making Bordeaux mixture, though as a general rule the third and fourth predominated; and the question arose which was the best fungicide.

Pickering adduced evidence that the fungicidal action was due to a decomposition of the basic sulphate by carbon dioxide with production of the normal sulphate, which then dissolved and entered and killed the spore or mycelium. In favour of this view he argued that the poison could act only in solution, and he showed that a soluble copper compound was formed by the action of carbon dioxide. There was, however, some delay if basic sulphate were present, which he attributed to a preferential interaction between this substance and the carbon dioxide. The fourth compound was therefore unsuitable. As between the remainder, the choice was determined by the amount of copper rendered soluble during interaction with carbon dioxide. He expressed the reactions as follows:—

$$10CuO\ 2{\cdot}5\ SO_3 + 3{\cdot}75\ CO_2 = 3{\cdot}75\ (CuO)_2\ CO_2 + 2{\cdot}5CuSO_4.$$
$$10CuO\ SO_3 + 4{\cdot}5\ CO_2 = 4{\cdot}5\ (CuO)_2\ CO_2 + CuSO_4.$$

Thus, from a given weight of copper in the form of the basic sulphate $4CuO\,.\,SO_3$ he obtained $2\frac{1}{2}$ times as much copper sulphate as from the compound $10CuO\,.\,SO_3$, and he therefore considered it to be the best for use as a fungicide. Experience showed, however, that it was too dense in character to form a satisfactory spray, and therefore at some sacrifice of economy he aimed at a mixture of the two and proceeded to issue a new formula for the making of this old mixture.* But he went farther than this. Up to this time growers had had to make their own Bordeaux mixture, always a troublesome business and fraught with risk in case of error. Pickering, however, taught a manufacturer of fungicides how to make this basic sulphate, and he put it on the market in the form of a solid which needed only to be mixed with water.

Some controversy arose on the results. Gimingham† doubted whether the decomposition of Bordeaux mixture in the air proceeded as Pickering had outlined it, while Barker and Gimingham‡ maintained that the fungus itself acted on the Bordeaux mixture, rendering soluble some of the copper, which forthwith poisoned it. Pickering's reply§ was that the substances used by Barker and Gimingham were somewhat soluble in water and therefore their

* Pickering learned afterwards that the formula had been adopted in Italy many years before.

† *Journ Agric. Sci.*, vol. 4, p. 69 (1911).

‡ *Ibid.*, vol. 4, p. 76.

§ *Ibid.*, vol. 4, p. 273.

experimental evidence was vitiated: also that dormant spores could not excrete any solvent, yet they were killed. Barker and Gimingham adduced further evidence,* and their subsequent experience has strengthened them in their view.

During the discussion Pickering made the interesting observations that copper could be taken up by plant leaves from solutions of its salts, but that it displaced iron, which entered the solution; and also that some of the constituents of apple-tree leaves could dissolve certain copper compounds which were insoluble in water.

*Burgundy Mixture.*

As a variant on Bordeaux mixture, some growers prefer to precipitate the copper with sodium carbonate in place of lime. The product is known as Burgundy mixture, and has given good results in Ireland; but again there were considerable variations in the different formulæ and no definite basis existed for discrimination between them.

A study of the reaction between copper sulphate and sodium carbonate† satisfied Pickering that this was simpler than that between copper sulphate and sodium or calcium hydrates, in that the solution became alkaline immediately and the precipitate carried no sodium sulphate in combination. The product consisted of $5CuO.2CO_2$, and this forms the active constituent of Burgundy mixture.

It is not, however, very stable, but changes rapidly into malachite, $2CuO, CO_2, H_2O$, the minute spherical particles of which settle rapidly and are, therefore, entirely unsuitable for spraying; moreover, they are too inert to possess any important fungicidal value.

A disadvantage of Burgundy mixture is that the other products of the reaction, sodium bicarbonate and sodium sulphate,‡ injure the leaves, while the corresponding product in Bordeaux mixture—calcium sulphate—is too insoluble to cause damage.

Further investigations by Mond and Heberlein§ have shown that the reaction is considerably more complex than Pickering supposed, and that the composition of the mixture is subject to great variations.

* *Ibid.*, vol. 6, p. 220 (1914).

† *Trans. Chem. Soc.*, vol. 95, p. 1409 (1909).

‡ Pickering gives the following equation to represent the change:—

$$5CuSO_4 + 8Na_2CO_3 + 3H_2O = 5CuO, 2CO_2 + 6NaHCO_3 + 5Na_2SO_4.$$

"Science and Fruit Growing" p. 184.

§ *Trans. Chem. Soc.*, vol. 115, p. 908 (1919).

*The Effectiveness of Woburn Washes.*

Pickering himself recognised that his work required the co-operation of a mycologist and an entomologist, without which no unexceptionable test could be made on the organism it was desired to destroy. His recommendations to fruit growers were based on the assumption that he had correctly picked out from the components of the various mixtures the particular basic salts or emulsions that were effective. As the assumption was not subjected to the final mycological or entomological test, it might easily be mistaken, and then his particular formula would be no better than any other. In point of fact this is what happened. His Bordeaux mixture has been tried, both in England and in Ireland, and it has not proved more, and has in many tests been less, effective than certain of the older ones. Pickering had dissolved 0·64 lb. copper sulphate in water, precipitated with lime water, and made up to 10 gallons. In England, the common formula is that known as the 4 : 4 : 50, in which 0·8 lb. copper sulphate and 0·8 lb. of lime are mixed in 10 gallons of water. This formula still remains one of the most effective, and many growers prefer it to the Pickering mixture. In Ireland, an extensive series of trials was made in the years 1909 and 1910, in which Pickering's mixture was tested against the mixture ordinarily adopted in Ireland, viz.,—2 lb. copper sulphate, 1 lb. quicklime, 10 gallons water—potato blight being the test subject. The results are summarised in the Department's Journal,* and are uniformly unfavourable to the Woburn mixture. Against these, however, must be set the results obtained in the United States, in which the Pickering wash proved more effective in certain cases than the standard American wash made by mixing 1 lb. copper sulphate and 1 lb. lime in 10 gallons of water, and, of course, it required less copper sulphate.†

Summing up this rather complex mass of evidence, one seems driven to the conclusion that the subject is more complex than Pickering assumed, and it does not appear that any one formula will universally prove to be the best. The experts of the Ministry of Agriculture now recommend three different mixtures—one for potatoes, another for apple foliage, and a third for dormant peach buds.‡ Pending fuller investigations, this is probably the safest course to adopt.

Perhaps the most permanent practical result of Pickering's work on Bordeaux

* A. W. Oldershaw, *Journ Dept. Agric.*, Ireland, vol. 11, p. 450 (1911); G. H. Pethybridge *ibid.*, vol. 15, p. 492 (1915).

† F. C. Cook, *U.S.A. Dept. Agric. Bull.*, p. 866 (1920).

‡ See Ministry of Agriculture Leaflets, Nos. 23, 131 and 120, respectively.

mixture is the fact that, when made as he suggested, it can be stored in a solid form for relatively long periods without deterioration, so that it can be prepared by a chemical manufacturer to a definite standard of purity and stored by the grower until it is wanted. This is undoubtedly an advantage, especially to the small man. The large grower, however, has his own appliances for making the mixture and sees no advantage in purchasing it; moreover, he considers his own recipe gives better results. It would, however, be very unfair to judge Pickering's work on the particular formulæ he suggested. Its great value lay in his pioneering studies of the reactions involved in preparing a series of washes which, on the whole, have proved effective, and his description of the various compounds which he supposed to be formed. His descriptions and recommendations require amendment, but the material forms a useful starting-point for an investigation by a chemist, a mycologist and an entomologist into the very difficult problem presented by insecticides and fungicides.

## CHAPTER VI.

### External Conditions affecting the Yield of Fruit Trees.

The yields of fruit at Woburn were frequently disappointing, a circumstance which Pickering often put down to late frosts occurring just about the time of blossoming. It is well known that such late frosts cause much loss to fruit growers, and the site of a modern orchard is carefully selected so as to reduce to a minimum their possible occurrence.

Late frosts may arise from two causes, cold wind, or radiation on clear calm nights. The effect of cold winds can be mitigated by arranging shelter hedges, as was done at Woburn, but the radiation frost presents greater difficulties. Usually its effects are most marked at the bottom of slopes; the cold air from the higher ground sinks to these lower positions and is replaced by the warm air therefrom. The cold air then causes a precipitation of dew, or—if its temperature be low enough—an actual frost. Various methods have been suggested for preventing the trouble, such as the lighting of bonfires in the orchard to keep the temperature of the surrounding trees above the freezing-point, but there has been no systematic work in England on the subject, and it appealed very much to Pickering. Unfortunately, in absence of self-recording and self-starting appliances he was reduced to hand labour: the farm manager had himself to watch for frosts and to take the night observations, and, as Pickering records, "the work was cut short owing to the exposure entailed in taking observations having proved nearly fatal" to him. When at the Wye Agricultural College, the writer attempted, and had to give up, a similar investigation: favourable conditions for experiment come only occasionally and without much warning in each season, and, unless elaborate instruments are available, the experimenter is compelled to spend many cold dreary nights n the orchard waiting for frosts that do not arrive.

The meteorological records showed that late frosts were not alone responsible for the low yields often obtained. Pickering therefore examined the possibility, which is expressed as a definite rule by many fruit growers, that there might be a regular alternation in yields of fruit trees, a heavy crop in one year being succeeded by a light one in the next; this again by a heavy one, and so on. Examination of the results, this time made in conjunction with Dr. R. A. Fisher, Head of the Statistical Department at the Rothamsted Experimental Station, revealed an undoubted alternation. To give a single instance: the

yields from one of the plots of Bramley's Seedling apples for the years 1903 to 1920 inclusive were, in kilos. per tree, as follows :—

| | Yield, kilos. per tree. | | Yield, kilos. per tree. |
|---|---|---|---|
| 1903 .. .. .. | 0 | 1912 .. .. .. | 0 |
| 1904 .. .. .. | 10·6 | 1913 .. .. .. | 37·0 |
| 1905 .. .. .. | 0 | 1914 .. .. .. | 0 |
| 1906 .. .. .. | 0·4 | 1915 .. .. .. | 80·4 |
| 1907 .. .. .. | 13·8 | 1916 .. .. .. | 9·8 |
| 1908 .. .. .. | 2·2 | 1917 .. .. .. | 98·5 |
| 1909 .. .. .. | 33·0 | 1918 .. .. .. | 0·6 |
| 1910 .. .. .. | 5·0 | 1919 .. .. .. | 93·5 |
| 1911 .. .. .. | 71·1 | 1920 .. .. .. | 0 |

Inspection of all plots where the trees were producing any significant amount of fruit showed a similar alternation, the data being :—

| | Alternation occurred in | Per-centage. | Probable error. |
|---|---|---|---|
| Stirling .. .. .. | 18 cases out of 21 .. | 86 | ± 7 |
| Bramley .. .. .. | 18 „ „ 21 .. | 86 | ± 7 |
| Bramley Standard .. | 12 „ „ 13 .. | 92 | ± 8 |
| Varieties .. .. .. | 12 „ „ 13 .. | 92 | ± 8 |

For the establishment of a definite tendency to alternation, 85 per cent. of the total cases available should show alternation : this happens for all four varieties.*

Three other sorts, Cox's, Potts' and Lane's, showed no clear alternation, nor did the Bramley's in the early years, but the yields were too small to allow of close discussion.

When the results for the four yielding varieties are set out in detail (Table XVI), those for Stirling Castle (the earliest to come into bearing) divide themselves into two periods, one from 1897 to 1908, where the prolific years all occur in years of even denominations, the other from 1911 to 1919, where the prolific years are of odd denominations ; the period of uncertainty, wherein the change of step occurs, is of three years' duration, from 1908 to 1911.

* See 18*th Report.*

Table XVI.—Weight of Fruit per Tree and Number of Fruits per Tree in Various Plantations.*

Relative values, those for 1911 being taken as 100.

| Year. | Weight of Fruit. | | | | Number. | |
|---|---|---|---|---|---|---|
| | Stirling. | Bramley. | Bramley Standard. | Varieties. | Stirling. | Varieties. |
| 1896 | 0 | 0·9 | — | — | 0 | — |
| 1897 | 5 | 0·1 | — | — | 3 | — |
| 1898 | 42 | 0·2 | — | — | 31 | — |
| 1899 | 10 | 0·2 | — | — | 0 | — |
| 1900 | 56 | 0·4 | — | — | 3 | — |
| 1901 | 27 | 4·7 | — | — | 52 | — |
| 1902 | 57 | 1·1 | — | — | 141 | — |
| 1903 | 0 | 0 | — | — | 0 | — |
| 1904 | 78 | 35 | 10 | 10 | 117 | — |
| 1905 | 1 | 0 | 0 | 0 | 0 | 0 |
| 1906 | 145 | 9 | 0 | 10 | 154 | 10 |
| 1907 | 13 | 47 | 7 | 37 | 31 | 68 |
| 1908 | 108 | 10 | 1 | 30 | 94 | 26 |
| 1909 | 176 | 70 | 22 | 32 | 137 | 41 |
| 1910 | 220 | 9 | 1 | 12 | 257 | 14 |
| 1911 | 100 | 100 | 100 | 100 | 100 | 100 |
| 1912 | 57 | 0 | 0 | 5 | 42 | 6 |
| 1913 | 123 | 89 | 47 | 137 | 237 | 161 |
| 1914 | 6 | 0 | 0 | 0 | 7 | 0 |
| 1915 | 336 | 100 | 180 | 422 | 588 | 436 |
| 1916 | 0 | 4 | 2 | 10 | 0 | 8 |
| 1917 | 304 | 121 | 115 | 334 | 329 | 202 |
| 1918 | 0 | 7 | 19 | 23 | 2 | 19 |
| 1919 | 174 | 108 | 268 | 214 | 227 | 206 |
| 100 = | 11·06 | 66·5 | 87·07 | 7·5 | 131·5 | 81·6 |

A similar change in step is indicated with Bramley, but at an earlier date.

As already stated, Pickering at first attributed the alternation to the incidence of spring frosts, but he was forced to discard this idea. He does not seem to have put forward any other suggestion: the examination of the data was unfortunately not completed until the early stages of his last illness.

For fruits other than apples, the Woburn data are less complete. The results are as follows† :—

* 18*th Report*, p. 10.

† 18*th Report*, p. 18.

| | Alternation occurred in | Per cent. | Probable error. |
|---|---|---|---|
| Pears | 20 seasons out of 25 | 80 | ± 6 |
| Plums | 14 ,, ,, 19 | 74 | ± 7 |
| Gooseberries | 19 ,, ,, 26 | 73 | ± 6 |
| Red currants | 10 ,, ,, 13 | 77 | ± 8 |
| Raspberries | 6 ,, ,, 12 | 50 | ± 8 |
| Strawberries | 6 ,, ,, 8 | 75 | ±10 |

In no instance is the necessary 85 per cent. reached, but for pears the figures certainly suggest alternation, especially in later years, and their good and bad seasons synchronise with those for apples. For the other fruits there is no clear evidence of alternation, and an extensive series of experiments with strawberries afforded strong evidence against it; the yield appeared to be dependent solely on the peculiarities of the current season and not on the yield of previous years.

Thus, it appears that apples and probably pears, unlike plums and the bush fruit, are subject to some factor which causes a low yield to follow a heavy one, and vice versa. This statement is true of the Woburn plantation as a whole, but not of individual trees when compared with each other. Of two trees A and B, if the yield of A was above that of B in one year, it was not necessarily below it in another year; all the trees kept step in their yields (Table XVII). Pickering argued that this result went to disprove the existence of any tendency in the individual tree towards alternating fruiting, such as would be expected if, for instance, fruiting is conditioned by the gradual accumulation of some substance in the tree which becomes exhausted by a heavy crop and is only slowly renewed. For, if there were such an innate tendency, there should have been many trees giving high yields and many giving low ones, so that over the whole orchard the yields would show no systematic alternation. It seemed clear to him, therefore, that the alternation shown by the entire orchard was caused by some external condition. No correlation with external conditions could be detected, but this objection is not fatal. Dr. Fisher's comparison seems apt; he likens the process to the swaying of the bough of a tree which shows a definite rhythm or alternation, and yet a person wholly unfamiliar with the mechanism of the process might have considerable difficulty in connecting it with the movements of the wind. Pickering made no suggestion as to the nature of the factor bringing all trees into step, but he inclined to the view that it was some favourable season causing all to give a heavy yield, after which the small yield would follow, and the alternation would then set in regularly.

Table XVII.—Yields of Individual Trees at Woburn showing Alternations of Seasons, All Trees Keeping Step.

*Bramley's Seedlings—Dwarf.*

*Weight of Fruit in Kilos. per Tree.*

| Year. | (1) | (3) | (5) | (2) | (4) | (6) | (1) | (3) | (5) | (2) | (4) | (6) | (1) | (3) | (5) | (2) | (4) | (6) | (1) | (3) | (5) | (2) | (4) | (6) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1904 | 35 | 32 | 50 | 69 | 33 | 0 | 63 | 49 | 36 | 64 | 64 | 38 | 24 | 33 | 11 | 25 | 2 | 5 | 0 | 9 | 0 | 56 | 35 | 44 |
| 1905 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1906 | 11 | 27 | 13 | 68 | 15 | 0 | 44 | 42 | 16 | 57 | 41 | 26 | 26 | 13 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 21 | 17 | 15 |
| 1907 | 94 | 72 | 84 | 43 | 85 | 79 | 93 | 59 | 67 | 45 | 51 | 94 | 56 | 37 | 51 | 15 | 3 | 24 | 26 | 36 | 20 | 64 | 42 | 76 |
| 1908 | 14 | 4 | 5 | 72 | 0 | 0 | 0 | 7 | 0 | 39 | 5 | 5 | 3 | 5 | 8 | 0 | 5 | 2 | 1 | 11 | 13 | 11 | 0 | 0 |
| 1909 | 101 | 78 | 59 | 68 | 52 | 34 | 136 | 87 | 47 | 100 | 52 | 95 | 87 | 72 | 58 | 67 | 9 | 23 | 72 | 90 | 60 | 104 | 37 | 109 |
| 1910 | 1 | 6 | 9 | 95 | 7 | 24 | 3 | 2 | 6 | 42 | 7 | 4 | 2 | 10 | 11 | 6 | 6 | 4 | 2 | 8 | 13 | 14 | 21 | 10 |
| 1911 | 79 | 57 | 132 | 74 | 98 | 57 | 91 | 56 | 65 | 85 | 84 | 96 | 70 | 83 | 95 | 69 | 58 | 86 | 51 | 80 | 43 | 89 | 69 | 89 |
| 1912 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1913 | 68 | 80 | 116 | 112 | 114 | 49 | 101 | 73 | 75 | 80 | 89 | 56 | 47 | 80 | 95 | 54 | 11 | 46 | 19 | 81 | 67 | 61 | 86 | 74 |
| 1914 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1915 | 123 | 97 | 217 | 133 | 160 | 165 | 134 | 65 | 139 | 125 | 146 | 110 | 43 | 97 | 144 | 59 | 61 | 120 | 52 | 109 | 144 | 33 | 115 | 159 |
| 1916 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 3 | 0 | 19 | 10 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1917 | 93 | 121 | 241 | 114 | 107 | 114 | 124 | 67 | 142 | 74 | 83 | 91 | 46 | 63 | 128 | 89 | 58 | 148 | 11 | 102 | 41 | 53 | 125 | 98 |
| 1918 | 11 | 1 | 0 | 2 | 6 | 3 | 4 | 2 | 0 | 3 | 4 | 8 | 1 | 7 | 1 | 2 | 0 | 0 | 17 | 3 | 13 | 7 | 0 | 51 |
| 1919 | 0 | 69 | 196 | 83 | 94 | 153 | 51 | 30 | 95 | 50 | 83 | 85 | 20 | 47 | 81 | 46 | 76 | 158 | 25 | 92 | 111 | 41 | 74 | 150 |
| 1920 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |

(From 18*th Report* (1921), where many other data are given.)

Pickering directed attention to a further remarkable result: "It appears that there is an independent correlation, not merely between consecutive seasons, but between any one season and those preceding it in the third and fourth places; so that we must conclude that fruit trees have, so to speak, long memories, and that their behaviour in any particular season is conditional, not merely by immediately antecedent circumstances, but by their previous behaviour during at least the three foregoing seasons."

These results are extraordinarily interesting and deserve full investigation by a plant physiologist. The observations made at Woburn are not entirely in accordance with those made elsewhere: at East Malling such alternations as occur are associated with the individual trees, so that the bearing virtually becomes biennial; the trees of any one variety usually fall into two groups, some being in their "on" year and some in their "off" year. Here the alteration is apparently brought about, not by any external factor, but by some internal condition. The results are not necessarily antagonistic to those of Pickering if it could be assumed that the internal causal agent could be constrained in certain directions by sufficiently potent external factors.

The possibility of some such action is suggested by the results with Stirling Castle, where on one plot (188) the trees were disblossomed each year for several years, and thus prevented from fruiting; they were then allowed to fruit, and for two or three years gave crops out of step with the rest. They then fell in step, and remained so to the end. The constraining effect of the external factor is shown also by the change of step in the whole orchard which occurs about 1909.

Alternation of yield is unknown for agricultural crops; but there is a remarkable parallelism with the periodicity observed by Mr. D. W. Cutler and Miss L. M. Crump in the numbers of a flagellate (*Oicomonas termo*, Martin) in the active state in the Rothamsted soil. Here also there is a regular periodicity maintained by a whole population, with a very occasional change in step when the whole population passes from the odd to the even periods. No correlation with external conditions can be found, and no satisfactory explanation of the phenomena is yet forthcoming.

*Date of Flowering of Apple Trees and its Relation to Fruiting.*

Careful observations were made of the date at which the trees came into blossom, but no very definite results emerged. Pickering summarised his conclusions as follows:—

"Apples which are early in ripening, blossom, on the average, two or three

days earlier than late varieties; but this is only a general rule, to which there are many exceptions. The character of the fruit (dessert or cooking) has no effect on the relative date of blossoming. The actual date on which blossoming commences has no definite effect on the period over which the coming into blossom of a number of different varieties will extend; this seems to be determined solely by the weather conditions prevailing at the time. Some varieties habitually blossom earlier or later than others, but in the majority of cases such late habits are so little marked that, on the average, they exercise only about one-third as much influence in determining the order of blossoming as do the weather conditions at the time, so that it is futile to attempt to draw up any precise list of the order of blossoming of a large number of varieties. On the average, the same variety will occupy a place in such a list, $2\frac{1}{2}$ days different in one season from what it occupies in another, whereas two different varieties selected at random will occupy in the same year positions differing by $3\frac{1}{3}$ days. Varieties of apples of foreign origin showed no peculiarities in the date of their blossoming."*

* 12*th Report*, pp. 50 and 51.

## CHAPTER VII.

### Investigations on Soil.

Pickering's investigations on soil arose in the main out of his observations on the growth of fruit trees. His equipment for soil work was not very extensive. He made no biological examinations, all his tests were chemical or physical: even here he made few and only simple quantitative measurements. Yet he succeeded in discovering some highly interesting properties of soil which deserve fuller investigation.

#### *Action of Heat and Antiseptics on Soil.*

Early in 1905, while at the Wye Agricultural College, the present writer commenced an investigation into the effects of heat and antiseptics on soil, and showed that fertility was thereby increased. Pickering visited Wye in November, 1906, for the purpose of addressing a conference of fruit growers, and saw the results that were being obtained; he immediately began a series of experiments to observe the growth of trees in heated soils, and found, as the writer had done, an increase in growth.* Pickering, however, made one observation which the writer had missed—that there is a retardation in the setting in of growth in heated soils. This retardation is so small as to be inappreciable in the light chalky loam of the Wye College farm, while it is much more marked on the heavier Oxford clay with which Pickering worked. Subsequent observation has shown that it is general and can be detected in the Wye soil by suitable means.†

The delay in the starting of growth was erratic: it was appreciable in two out of nine experiments, very marked in one, and much less marked, but quite distinct, in the remaining six. The variation in effect suggested some bacteriological factor, but as this threatened to make a long investigation, Pickering decided simply to accumulate data, and he began with a study of the germination of seeds in heated soil.‡ The total number of seeds germinating decreased and the time necessary for germination increased as the soil was heated to successively higher temperatures. The smooth curve which he drew to express his average results is reproduced in fig. 7. At first he seems to have thought

* *Nature* (June 6 and July 4, 1907).

† E. J. Russell and E. R. Petherbridge, *J. Agric. Sci.*, vol. 5, p. 248 (1913).

‡ S. U. Pickering, *J. Agric. Sci.*, vol. 2, p. 411 (1908).

that bacteria might be necessary to germination, but he gave up this view (which had already been put forward and disproved by earlier workers*) when he found that sterilised seeds would germinate in a sterile medium, and that germination took place equally rapidly in sand inoculated with soil bacteria, whether it was subsequently heated or not.

Pickering then sought a chemical explanation of the facts. When soil is

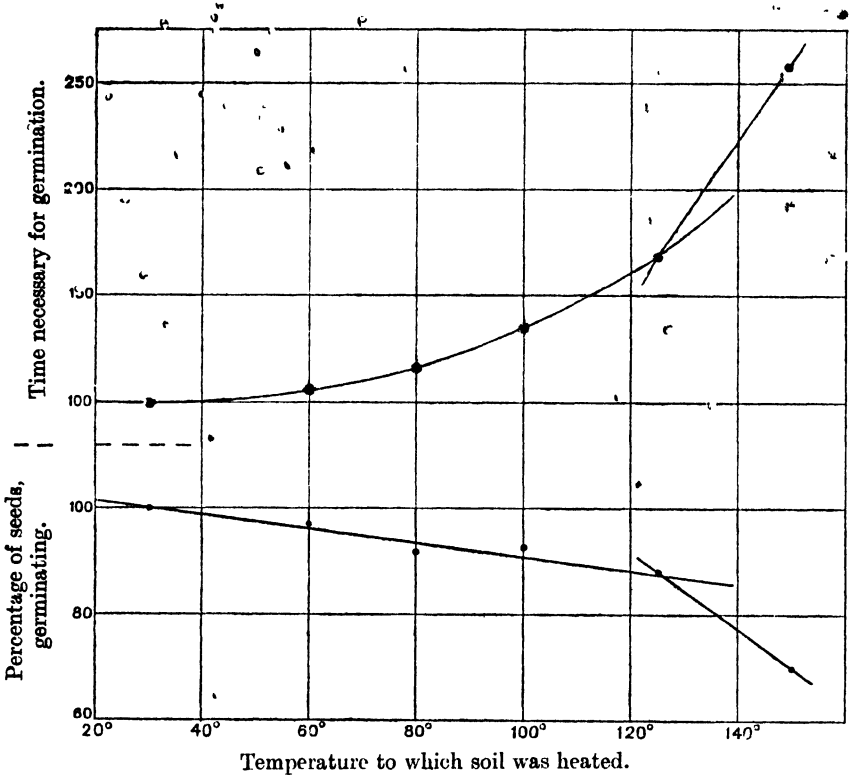


FIG. 7.—Effect of heating the soil on the germination of seeds. 'Jour. Agric. Sci.,' vol. 2, p. 419 (1908).

[*By courtesy of Cambridge University Press.*

heated, the water-soluble organic matter and the water-soluble nitrogen both increase. He thought he found a proportionality between these quantities and the retardation in germination, and he concluded that heating the soil to any temperature, even to 30° C., caused decomposition of the organic matter with formation of some nitrogenous organic compound which causes retardation in germination of the seeds or in the starting into growth of the trees. The higher the temperature to which the soil was heated the greater the amount of this

* The literature is summarised in the above paper by Russell and Petherbridge (p. 256).

toxic substance, and the greater, therefore, the extent of the retardation. In a later paper Pickering somewhat modified this view, as on further examination the direct proportionality was found not to hold; he therefore supposes "either that the inhibiting substance produced by heating different soils is not the same in all cases; or, more probably, that it constitutes only one of the organic products formed when a soil is heated, the proportions between it and the non-inhibiting substances formed varying in each particular case."*

The inhibiting substance, whatever its nature, suffered no appreciable change when the soil was stored for several months at ordinary room temperature and in moderately dry condition, though it fell off in amount if the soil were moist and in access of air. Further, it could be carried in an aqueous extract from a heated to an untreated soil.

The relationship between the quantity of organic matter rendered soluble in the soil and the retardation in germination, or, as Pickering puts it, the incubation time, is shown in fig. 8†, where the data for one of the soils are

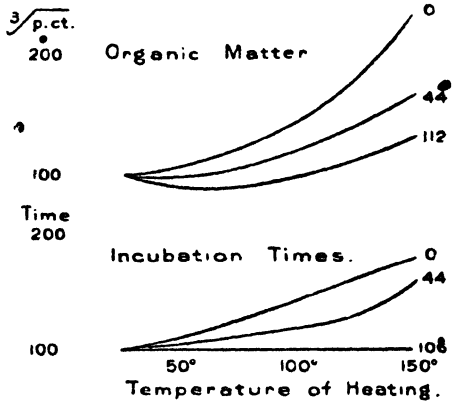


FIG. 8.—Relationship between the amount of organic matter rendered soluble in the soil and the time necessary for the germination of seeds, in soils heated to various temperatures.

[*By courtesy of Messrs. Macmillan.*

plotted: the curve marked "0" gives the results for soils tested immediately after heating, and those marked "44," "106," and "112" give the results for soil stored 44, 106 and 112 days respectively after the heating and before the germination tests were made. The proportionality is less close than it looks, since the upper curve gives the cube roots of the amounts of water-soluble organic matter in the soil, and not the amounts themselves.

* *J. Agric. Sci.*, vol. 3, pp. 32–54 (1908).

† "Science and Fruit Growing," p. 251.

Pickering thought he obtained evidence that germination took place more readily in an inert medium (*e.g.*, wet sand) than in soil, and hence argued that some substance toxic to germination is present even in ordinary unheated soils. He thus summarised his investigations on the changes brought about by heating soils* :—

> "On heating soil the soluble matter available for nutrition is increased, and changes in the bacterial condition are brought about which—the latter especially—conduce to increasing vigour of the plants growing in them; but the heating also results in the formation of some substance or substances which are actively toxic, and which tend to arrest growth. The proportion of toxin formed at low temperatures is small, and is generally insufficient to counteract those conditions favouring increased growth, but this proportion increases at a very rapid rate as the temperature of heating rises above 100°, and its baleful influence in such soils is generally the preponderating factor: hence the results obtained of increased vigour with soils heated up to 100°, and of greatly decreased vigour with those heated to higher temperatures. But the toxic substance is unstable, and gradually disappears by the action of air and moisture so that the results obtained in any individual series will vary considerably with the circumstances obtaining . . . . Whether the substance which is toxic to plant growth is actually the same as that which is toxic towards germination cannot be settled at present, but the heated soil appears to be equally toxic as regards these two processes, and the toxin in both cases is equally susceptible to oxidation: it is legitimate to presume provisionally that it is the same toxin which is active in both cases."

He supposed that this toxin affected different plants to different degrees, and, as some was always in his view present in natural unheated soils, he regarded it as a factor determining the distribution of plants. He further showed† that treatment of the soil with volatile antiseptics, such as toluene, chloroform, etc., caused a retardation in germination of approximately the same extent as that brought about by heating to 65° C.: there was also an increase in the water-soluble nitrogen and water-soluble organic and inorganic matter. He concluded, therefore, that these substances act chemically on the soil, decomposing organic matter in the same way and to the same extent as heat of 65° C.

The work was repeated by Russell and Petherbridge in the Rothamsted

* *J. Agric. Sci.*, vol. 3, p. 283.

† *J. Agric. Sci.*, vol. 3, p. 32 (1908).

investigations on partial sterilisation in soil, and it was substantiated in two main directions. It was, of course, well known that heating to a temperature of 100° C. or more caused decomposition of the soil organic matter, but it had not been clearly recognised that treatment with volatile antiseptics also had the same effect. Russell and Hutchinson had demonstrated the production of ammonia, but they had not shown an increase in water-soluble organic or inorganic constituents. Pickering's work demonstrated that the action of volatile antiseptics was more complex than the writer had supposed, and that some chemical change occurred which had to be taken into account in dealing with the subsequent biological and chemical changes. There is, however, no reason to regard these changes as anything but subsidiary.

The second direction in which work has been confirmed is in regard to the formation of a toxic body when soil is heated to 100° C. A toxic substance is produced, but the process is more complex than Pickering had supposed. His technique had not been very good: he had used only 10 seeds in each germination experiment, and had done no more than duplicate the experiments, so that his results depended on germinations of 20 seeds only. This small number is wholly insufficient: Russell and Petherbridge found it necessary to work with 100 seeds and to repeat each experiment six times, thus using 600 seeds for every test. With this more refined technique it was shown* that the proportion of toxin was not, as Pickering supposed, regular and progressive: it was very slight up to 65° to 70° C., and began to be marked only in soils heated above 80° C. Then it increased rapidly as the temperatures increased. Accelerated germination was often observed in soil heated to 50° C., but this was shown only by certain species of plants and even then only by some of the 600 seeds.

Moreover, there was no proportionality between the analytical data for the soil and the amount of retardation or acceleration in germination; indeed, the effect varied so much with the moisture, temperature and other conditions of the experiment, and with the individuality of the seeds, that it could not be expressed by any single number. Nor was there any evidence that the retardation substance was organic: it might equally have been ammonia. Probably all the soluble constituents of the soil have some effect on germination, and this process is too susceptible to slight variations in the seeds and in external conditions to afford much help in studying the soil.

Lastly, there was no evidence of the presence of toxins in ordinary unheated soils. Germination in soil was sometimes slower and sometimes more rapid than in sand; but no strict comparison was possible, because there was no means of obtaining strictly comparable water conditions.

* *J. Agric. Sci.*, vol. 5, p. 257.

*Presence of Reducing Substances in Soil.*

Almost the last of Pickering's work was to show the presence in soil of substances which decolorise iodine solutions and which therefore he regarded as reducing agents, converting the iodine into hydriodic acid. The reaction proceeded to a greater extent in soils carrying grass than in tilled soils, and he assumed that it was caused by the toxin he associated with plant roots. He gave no proof, but the observation is sufficiently interesting to justify further study.

*Flocculation.*

The heavy soil of the fruit farm must often have made Pickering ponder on the remarkable properties of clay, and the investigations of Hall and Morison* on flocculation which he saw carried out at Rothamsted turned his attention to this particular phenomenon. He describes his investigations on the flocculation of kaolin in a paper read before the Royal Society,† but he gives a fuller account in "Science and Fruit Growing," chapter 30.

The simpler facts of flocculation are readily demonstrated. Clay is rubbed into distilled water, and the muddy liquid is allowed to stand. The larger particles settle more or less rapidly, but the finer ones remain in suspension for a long time, some of them almost indefinitely, forming a permanently turbid liquid. Addition of a trace of any acid or salt causes these fine particles to settle much more rapidly, and examination under the microscope shows that they have collected into groups, forming floccules. The phenomenon is therefore called the flocculation of clay.

A remarkable change accompanies flocculation. The minute particles while in suspension are in a state of Brownian motion, but this at once ceases on the addition of acid or salt. Pickering took this as incontrovertible evidence that the particles had increased in size.

As he could observe no enlargement of the solid, visible particles, he argued that they must have united with something invisible, forming a composite particle exceeding those limits of size for which Brownian motion is possible. He obtained further evidence of an increase in the space occupied by the kaolin after flocculation by measuring its volume when it eventually subsided; and he found that this volume increased as the proportion of acid or salt was increased till, with complete flocculation (shown by the absence of suspended matter in the liquid), the particles of kaolin occupied double or treble their original

* *J. Agric. Sci.*, vol. 2, p. 244 (1907).

† *Roy. Soc. Proc.*, A, vol. 94, p. 315 (1918).

space. Further additions of acid or salt beyond this point produced no further increase in the volume.

He next tried to discover the invisible substance which had united with the kaolin particles. A certain amount of combination took place between the kaolin and the added acid, but only in definite proportions, any excess of acid simply remaining unchanged in the liquid. The total proportion of acid thus combining was, however, only one-fifteenth to one-two-hundredth part of the kaolin—a quantity far too small to account for the observed 100 to 200 per cent. increase in bulk. He therefore recalled his "hydrate hypothesis" of solution, and argued that the acid does not exist in the liquid as such, but in combination with a large proportion of water in the form of hydrates, which contain several molecular proportions of water to each one of acid. The union of these bulky hydrates with the kaolin particles would, he considered, suffice to account for the fact that the composite particles are two or three times larger than the solid, uncombined clay particles.

He finally put forward an ingenious explanation of the formation of the floccules. He regarded each of these composite particles as a solid nucleus enclosed in a liquid envelope of weak acid, the whole forming a sphere floating in the rest of the liquid, which consists of nearly pure water. There must, therefore, be surface tension between the outside of this sphere and the water. When the surface tension is not great, several of the spheres will coalesce to form larger irregular masses, and then solid nuclei will congregate towards the centre as if they were mutually attracted; hence the aggregation of the particles into floccules after the addition of the acid or salt.

Alkalis give substantially the same results as acids or salts, but their combination with the kaolin was not complete unless they were present in excess; a much greater proportion of alkali than of acid was therefore required to effect flocculation. There was a further important result. Alkali insufficient in amount to combine with any appreciable quantity of the kaolin nevertheless exerted considerable attraction for it; hence the kaolin particles remained suspended in the liquid and subsided *less* quickly than in pure water. A small proportion of alkali therefore produces the reverse of flocculation, though not deflocculation in the true sense, since there is no actual diminution in the size of the particles themselves.*

Pickering thus added one more to the various hypotheses that have been set up to account for the peculiar phenomena of flocculation. It has not yet found its place among them, and has so far not been absorbed into the literature.

* "Science and Fruit Growing," pp. 324 and 325.

The work was done before the ionic exchanges between the clay particle and the flocculant had been studied, and it is not clear from the paper whether the combination with the acid involved an absorption of the anion or was simply an exchange of kations. In one respect it anticipated some of the important results since obtained by Gedroiz, Wiegner, and other recent investigators—in its recognition of the importance of the water envelope to the clay particle and of the state of hydration of the flocculating agent, complex hydrates of undissociated molecules in Pickering's view, ions on present-day hypotheses.

In addition to this laboratory work he made certain field observations of considerable interest, which, however, he was unable to follow up.

Samples of soil were taken monthly at the separate depths of 0–6, 6–12, and 12–18 inches from a plot of ground at Ridgmont, and a weighed portion of each was shaken with 10 times its weight of water for 24 hours, and the whole left standing for 4 hours; the upper part of the liquid was then siphoned off and the amount of suspended solid matter was estimated. The amount varied considerably from month to month, the range being from 0·2 to 0·5 per cent. The variations were unconnected with the season, but they showed a direct relationship with the rainfall of the preceding 20 days—not, however, of the preceding 10 or 30 days. The surface soil was much more affected than the lower depths. Pickering published no figures, but gave only the curves reproduced in fig. 9.

The observations are interesting as throwing light on the stickiness in clay induced by rain. It may be supposed that rain washes out the flocculating agent from the clay, thereby deflocculating it, and so increasing the proportion of fine particles as shown in the curves; in drier weather, however, the agent is gradually reformed, or returns to the clay, and flocculation occurs once more.

Pickering also tried to account for the effect of frost, but did not entirely succeed. Although frost improves the physical condition of clay, apparently it does not cause flocculation; its action, indeed, seems to be diametrically opposite in character to that of a flocculating agent, for it tended to reduce, and not to increase, the size of the clay particles. Much of the beneficial action of frost consists in breaking down the large clods by mechanical disruption, due to expansion on the freezing of the water contained in them; but it also affects the particles themselves, depriving them of the chemically combined water which they contained and so causing them to shrink. The particles, therefore, become more dense and agglomerate together, hence they subside more rapidly in water, and the shrinkage observed in different cases varied between 40 and 90 per cent. With clay it amounted to 80 per cent. and

shrinkage to like amount occurred when the clay was deprived of its combined water by long exposure over sulphuric acid.

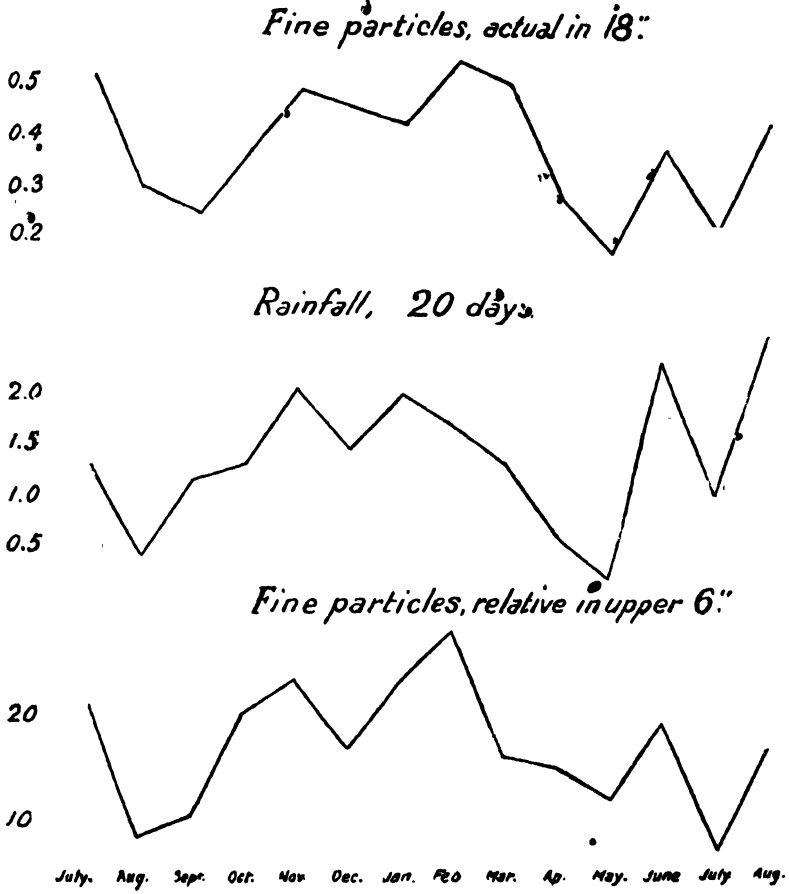


FIG. 9.—Relationship between rainfall of preceding 20 days, and amounts of fine particles in the top 18″ and top 6″ of soil respectively.

[*By courtesy of Messrs. Macmillan.*

Clay which has been dehydrated by freezing or other means is apparently unable to reabsorb the lost water, even when left in contact with water for a long time, yet re-absorption must occur somehow under the conditions in the field.*

These interesting observations are being followed up in the Soil Physics Department at Rothamsted.

* *Ibid.*, pp. 327 and 328.

## CHAPTER VIII.

### The Results of the Work.

In this final chapter it is proposed to draw together the results of the 25 years of experimental work on fruit trees and to indicate the possibilities of further development which it opened up.

Probably the most important result is the demonstration that fruit trees are susceptible to exact scientific study. The Reports afford guidance as to suitable methods, their limitations and the treatment of the data obtained; an investigator embarking on the study of fruit trees now knows some of the difficulties, and can avoid the disappointments that beset the earlier workers.

Pickering opened up the study of the factors that make for fruiting. Vegetative growth has been studied in great detail by plant physiologists and agriculturists, but fruit formation has been much less investigated and is little understood. The Woburn experiments have proved a useful starting-point for fuller investigation.

Looking back on the results which Pickering himself obtained, the following now appear to have been the most important:—

1. The beneficial effect on growth of ramming the soil around the roots of the tree at the time of planting, an observation followed by the discovery that this stimulated the growth of new roots.
2. The reduction in fruit yield following on hard pruning.
3. The apparent ineffectiveness of manures.
4. The harmful effect of grass on fruit trees, afterwards shown to be a general phenomenon.

The beneficial effect of ramming and the uselessness of spreading out the fibrous roots of the tree on planting came as a great surprise to growers, and would probably be regarded as the most unexpected of all the Woburn results. The scientific interest is almost equally great. Pickering clearly established the fact that close contact between the root and the soil stimulated root development, but the cause remains wholly obscure. It may have been simply the result of slight mechanical injury, but there is also the attractive possibility, to which certain Rothamsted observations lend colour, that some soil constituent may act directly on the plant and cause it to put out masses of new roots.

The reduction of fruit yield following on hard pruning is of considerable

practical importance, and no exact information had been available prior to Pickering's experiments. The problem is far from being solved; it is complicated by the fact that the fruits on a hard pruned tree are not comparable with those on one less pruned, being larger and of more market value. Growers, therefore, will often face a loss of yield in the hope of obtaining enhanced prices. Moreover, though Pickering never studied this, the results are influenced by the varieties, the environmental condition, and, as shown by Lorette in France, the method of pruning. The subject is at present in the purely empirical stages, and is not yet susceptible to precise scientific investigation.

The apparent ineffectiveness of manures in trees as distinct from bushes and farm crops was one of the most characteristic features of Woburn, and one on which fruit growers never failed to comment when discussing the experiments. We have already seen that Pickering's results are not altogether decisive; indeed, definite effects can be traced if one confines attention to the trees that yielded normal crops. Whether these effects are general or peculiar to Woburn cannot be determined in the rather uncertain state of the evidence so far available. The experience of fruit growers is, however, that trees which have been brought into condition to give heavy crops respond well to manuring. Whether this practice is always economical is another matter. It seems clear from Pickering's results and from those obtained in America that the effect of fertilisers on fruit trees is less marked than on agricultural crops; otherwise the present state of uncertainty could hardly have arisen. The rate of growth is possibly more affected by manures than the quantity of fruit produced, and it may be that the apparent ineffectiveness of the manures is the resultant of actions of different kinds on these two somewhat antagonistic processes. Further advances can hardly be expected until more knowledge has been obtained as to the physiological basis of fruiting.

Probably the most attractive subject opened up by Pickering arose out of his observations on the effect of grass on fruit trees. So far as many of the present generation of fruit growers is concerned the results were new: they had seen magnificent grassed orchards and did not realise that grass was capable of exercising so depressing an effect on the growth of fruit trees as Pickering demonstrated. It was an investigation peculiarly suited to Pickering's temperament; a less critically minded person would have been satisfied with the water-deficiency hypothesis suggested by earlier observations, and, indeed, accepted by some very competent judges, and so would have missed the best of the work. He has left the problem in a peculiarly interesting position, and if, as certain Rothamsted observations indicate, it is associated with the micro-organic

flora of the soil, great possibilities are opened up. It appears almost certain that some important factor is at work, the consequences of which probably reach beyond anything now suggested. The problem is, however, difficult and elusive, and would require for its solution the co-operation of a plant physiologist, a soil chemist, and a soil bacteriologist.

In addition to these problems that may justly be regarded as of the first importance, there are certain others in the study of which Pickering played a part, though hardly the dominating part which he took in those already discussed.

5. The relation of the fungus *Stereum purpureum* to the silver leaf disease.

The connection had been indicated by Percival but the evidence was not altogether convincing and Pickering made it considerably more definite.

6. The flocculation of clay.

The idea of hydration is, of course, not new to investigators of colloids, but it cannot be said that Pickering's hypothesis has been absorbed into current ideas on flocculation. His language is not easily intelligible to the younger school of workers, who have been brought up on the ionic dissociation hypothesis and find it difficult to think in terms of the hydrates postulated by Pickering and some of the older chemists.

This record of achievement is one of which any scientific worker could feel proud. But it was not all, and, indeed, perhaps not even the most valuable part of what Pickering did. More than most investigators, he stimulated thought and enquiry in the subject to which he devoted the greater part of his life. One of the most progressive fruit growers in the country, Mr. E. A. Bunyard, summed up the attitude of the practical man in words which can hardly be excelled :

" Mr. Pickering has played a part in horticulture similar to that of Mr. Bernard Shaw in ethics and politics. Agree or disagree, we cannot deny that they have aroused us from lethargy, and while the ' knocker up ' cannot expect a warm welcome from the called, he performs an invaluable office, and has his reward in the sight of a busy and curious world which, but for his efforts, might still be deep in conservative slumber."

It was Pickering's crowning achievement that he not only presented his scientific colleagues and successors with a great and attractive array of wholly new problems, but that he made the men in the English countryside

observe and think. Once the leaven starts working it is impossible to forecast the end.

## APPENDIX.

### List of Books, Reports and Papers published by Mr. Pickering on Fruit Growing and Problems arising therefrom.

#### Books.

"Fruit Trees and Their Enemies," with a spraying calendar (with F. V. Theobald). Simpkin Marshall.

"Science and Fruit Growing." Being an account of the results obtained at the Woburn Experimental Fruit Farm since its foundation in 1894 (with the Duke of Bedford). Macmillan, 1919.

#### Reports of the Woburn Experimental Fruit Farm.

All except the 17th and 18th were published jointly with the Duke of Bedford.

1*st Report*, 1897.—Description of the Ground and Methods of Experimentation. Results with Strawberries and Potatoes, and on the Germination of Seeds.

2*nd Report*, 1900.—The Black Currant Mite. Results with Strawberries, Bush Fruits and Apples. Germination of Seeds. Experiments with Potatoes. Meteorological Results.

3*rd Report*, 1903.—The Effect of Grass on Trees.

4*th Report*, 1904.—Manurial Experiments with Strawberries, Bush Fruits and Apples.

5*th Report*, 1905.—Cultural Experiments on Apples, etc.

6*th Report*, 1906.—Mussel Scale and the Winter Washing of Fruit Trees. Investigations on Lead Arsenate, Paraffin Emulsion and other Insecticides.

7*th Report*, 1907.—Pruning.

8*th Report*, 1908.—Insecticides and Fungicides. Bordeaux Mixture, Paraffin Emulsion, etc. Mussel Scale, Psylla, Caterpillars, etc.

9*th Report*, 1908.—Planting, etc.

10*th Report*, 1909.—Insecticides for Woolly Aphis, Psylla, Caterpillars, etc.

11*th Report*, 1909.—Copper Fungicides.

12*th Report*, 1910.—Silver-Leaf Disease.

13*th Report*, 1911.—The Effect of Grass on Trees.

14*th Report*, 1914.—Potato Spraying. Trenching. The Effect of one Crop upon Another. Black Currant Mite. Loss of Weight of Manure in Transit.

15*th Report*, 1916.—Fruiting in Consecutive Seasons. Injury to Roots on Planting. Cutting-Back after Planting, etc.

16*th Report*, 1917.—Manurial Experiments on Fruit Trees, Bushes and other Crops.

17*th Report*, 1920.—The Action of Grass on Fruit Trees. Action of Massed Plants on Each Other, Above-Ground Interference of Plants with Each Other, Behaviour of Outside Rows. Drainage, Toxicity, Flocculation, of Clay and Certain Observations on Soil.

*Note.*—This is the first Report to appear without the name of the Duke of Bedford. In October, 1918, the Duke had relinquished the Station and allowed it to be brought under the supervision of the Lawes Agricultural Trust—the Committee of Management of the Rothamsted Experimental Station.

*18th and Final Report*, 1921. (With Foreword by E. J. Russell, Director of the Rothamsted Experimental Station.)—Fruiting in successive years. Financial Returns from Fruit Plantations. Tables giving Actual Yields, in kilos per tree, from the Individual Plots for the Whole Period from the Commencement in 1894 to the Close in 1921.

The statistical examination of the data was made by Dr. R. A. Fisher, Head of the Statistical Department of the Rothamsted Experimental Station. This Report was published after Mr. Pickering's death, the MS. being seen through the press and the Tables all duly checked by the Staff of the Statistical Department at Rothamsted.

Reports Nos. 1–7 and 18 were issued by Messrs. Eyre and Spottiswoode, and Reports Nos. 8–17 by the Amalgamated Press, London. The stocks of the Reports are now being held by the Duke of Bedford. Pickering's original notebooks and records are, by his direction, all preserved in the Library of the Rothamsted Experimental Station.

CHRONOLOGICAL LIST OF PAPERS COMMUNICATED TO SCIENTIFIC SOCIETIES AND JOURNALS CONNECTED WITH, OR ARISING OUT OF, THE WORK AT THE WOBURN FRUIT FARM.

(1907.) "Note on the Arsenates of Lead and Calcium." *Chem. Soc. Trans.*, vol. 91, p. 307.

(1907.) "The Interaction of Metallic Sulphates and Caustic Alkalis." *Chem. Soc. Trans.*, vol. 91, p. 1981.

(1907.) "The Chemistry of Bordeaux Mixture." *Chem. Soc. Trans.*, vol. 91, p. 1988.

(1907.) "Emulsions." *Chem. Soc. Trans.*, vol. 91, p. 2001.

(1907). "Studies on Germination and Plant-Growth." *Journ. Agric. Sci.*, vol. 2, p. 411.

(1908.) "The Action of Heat and Antiseptics on Soils." *Journ. Agric. Sci.*, vol. 3, p. 32.

(1909.) "The Hydration of Precipitates." *Chem. Soc. Trans.*, vol. 95, p. 123.

(1909.) "The Carbonates of Copper and the Cupricarbonates." *Chem. Soc. Trans.*, vol. 95, p. 1409.

(1910.) "Ueber Emulsionen." *Zeit. für Chemie und Industrie der Kolloide.* Band VII., p. 11.

(1910.) "Studies of the Changes occurring in Heated Soils." *Journ. Agric. Sci.*, vol. 3, p. 258.

(1910.) "Plant-Growth in Heated Soils." *Journ. Agric. Sci.*, vol. 3, p. 277.

(1910.) "The Constitution of Basic Salts." *Chem. Soc. Trans.*, vol. 97, p. 1851.

(1911.) "Experimental Error in Horticultural Work." *Journ. Bd. of Agric.*, Suppl. 7, ol. 18, p. 38.

(1912.) "Copper Fungicides." *Journ. Agric. Sci.*, vol. 4, p. 273.

(1912.) "Copper Salts and their Behaviour with Alkalis." *Trans. Chem. Soc.*, vol. 1, p. 174.

(1914.) "The Effect of Bastard Trenching on the Soil and on Plant Growth" (with E. J. Russell). *Jour. Agric. Sci.*, vol. 8, p. 483.

"The Effect of one Crop on Another" (with the Duke of Bedford). *Journ. Agric. Sci.*, vol. 6, p. 136.

(1916.) "The Fruiting of Trees in Consecutive Seasons." *Journ. Agric. Sci.*, vol. 8, p. 131.

(1917.) "The Detergent Action of Soap." *Chem. Soc. Trans.*, vol. 111, p. 87.

(1917.) "The Effect of one Plant on Another." *Ann. of Botany*, vol. 31, p. 181.

(1918.) "Flocculation." *Roy. Soc. Proc.*, A, vol. 94, p. 315.

(1918.) "The Action of one Crop on Another." *Journ. Roy. Hort. Soc.*, vol. 43, p. 372.

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