Scientific Studies of Non-ferrous Alloys.*

By C. T. HEYCOCK, M.A., F.R.S.

THE production of metals and their alloys undoubtedly constitutes the oldest of those chemical arts which ultimately expanded into the modern science of chemistry, with all its overwhelming mass of experimental detail and its intricate interweaving of theoretical interpretation of the observed facts. Tubal-cain lived during the lifetime of our common ancestor, and was "an instructor of every artificer in brass and iron"; and although it may be doubted whether the philologists have yet satisfactorily determined whether Tubal-cain was really acquainted with the manufacture of such a complex metallic alloy as brass, it is certain that chemical science had its beginnings in the reduction of metals from their ores and in the preparation of useful alloys from those metals. In fact, metallic alloys, or mixtures of metals, have been used by mankind for the manufacture of implements of war and of agriculture, of coinage, statuary, cooking vessels, and the like from the very earliest times.

In the course of past ages an immense amount of practical information has been accumulated concerning methods of reducing metals, or mixtures of metals, from their ores, and by subsequent treatment, usually by heating and cooling, of adapting the resulting metallic product to the purpose for which it was required. Until quite recent times, however, the whole of this knowledge was entirely empirical in character, because it had no foundation in general theoretical principles; it was collected in haphazard fashion in accordance with that method of trial and error which led our forerunners surely, but with excessive expenditure of time and effort, to valuable results.

To-day I purpose dealing chiefly with the non-ferrous alloys, not because any essential difference in type exists between the ferrous and non-ferrous alloys, but merely because the whole field presented by the chemistry of the metals and their alloys is too vast to be covered in any reasonable length of time.

The earliest recorded scientific investigations on alloys were made in 1722 by Reaumur, who employed the microscope to examine the fractured surfaces of white and grey cast-iron and steel. In 1808 Widmanstätten cut sections from meteorites, which he polished and etched. The founder, however, of modern metallography is undoubtedly H. C. Sorby, of Sheffield. Sorby's early petrographic work on the examination of thin sections of rock under the microscope led him to a study of meteorites and of iron and steel, and in a paper read before the British Association in 1864 he describes briefly (I quote his own words) how sections "of iron and steel may be prepared for the microscope so as to exhibit their structure to a perfection that leaves little to be desired. They show various mixtures of iron, and two or three well-defined compounds of iron and carbon, graphite, and slag; these constituents, being present in different proportions and arranged in various manners, give rise to a large number of varieties of iron and steel, differing by well-marked and very striking peculiarities of structure." The methods described by Sorby for polishing and etching alloys and his method of vertical illumination (afterwards improved by Beck) are employed to-day by all who work at this branch of metallography.

From 1854-68 Mattheisen published in the Reports of the British Association and in the Proceedings and

Transactions of the Royal Society a large number of papers on the electrical conductivity, tenacity, and specific gravity of pure metals and alloys. He concluded that alloys are either mixtures of definite chemical compounds with an excess of one or other metal, or solutions of the definite alloy in the excess of one of the metals employed, forming in their solid condition what he called a solidified solution. This idea of a solidified solution has developed into a most fruitful theory upon which much of our modern notions of alloys depends. Although, at the time, the experiments on the electrical conductivity did not lead to very definite conclusions, the method has since been used with great success in testing for the presence of minute quantities of impurities in the copper used for conductors. In the *Philosophical Magazine* for 1875 F. Guthrie, in a remarkable paper quite unconnected with alloys, gave an account of his experiments on salt solutions and attached water. He was led to undertake this work by a consideration of a paper by Dr. J. Rea, the Arctic explorer, on the comparative saltiness of freshly formed and of older ice-floes. Guthrie showed that the freezing point of solutions was continuously diminished as the percentage of common salt increased, and that this lowering increased up to 23.6 per cent. of salt, when the solution solidified as a whole at about 22° C. He further showed, and this is of great importance, that the substance which first separated from solutions more dilute than 23.6 per cent. was pure ice. To the substance which froze as a whole, giving crystals of the same composition as the mother-liquor, he gave the name "cryohydrate."

In the *Philosophical Magazine* for 1876 Guthrie gave an account of his experiments, using solvents other than water, and states that the substances which separate at the lowest temperature are neither atomic nor molecular; this lowest melting-point mixture of two bodies he names the eutectic mixture. In the same paper he details the methods of obtaining various eutectic alloys of bismuth, lead, tin, and cadmium.

We have in these papers of Guthrie's the first important clue to what occurs on cooling a fused mixture of metals. The researches of Sorby and Guthrie, undertaken as they were for the sake of investigating natural phenomena, are a remarkable example of how purely scientific experiment can lead to most important practical results. It is not too much to claim for these investigators the honour of being the originators of all our modern ideas of metallurgy. Although much valuable information had been accumulated, no rapid advance could be made until some general theory of solution had been developed. In 1878 Raoult first began his work on the depression of the freezing point of solvents due to the addition of dissolved substances, and he continued at frequent intervals to publish the results of his experiments up to the time of his death in 1901.

In a paper in the *Zeit. Physikal. Chem.* for 1888 on "Osmotic Pressure in the Analogy between Solutions and Gases," van't Hoff showed that the experiments of Pfeffer on osmotic pressure could be explained on the theory that dissolved substances were, at any rate for dilute solutions, in a condition similar to that of a gas; that they obeyed the laws of Boyle, Charles, and Avogadro; and that on this assumption the depression of the freezing point of a solvent could be calculated by means of a simple formula. He also showed that the exceptions which occurred to Raoult's

*From the opening address of the President of Section B (Chemistry) delivered at the Cardiff meeting of the British Association on August 24.

laws, when applied to aqueous solutions of electrolytes, could be explained by the assumption, first made by Arrhenius, that these latter in solution are partly dissociated into their ions. The result of all this work was to establish a general theory applicable to all solutions which has been widespread in its applications. From this time the study of alloys began to make rapid progress.

The experiments of Laurie, Tannman, and Neville and myself in 1888 and 1889 helped to establish the similarity between the behaviour of metallic solutions or alloys and that of aqueous and other solutions of organic compounds in organic solvents. That our experiments were correct seemed probable from the agreement between the observed depression of the freezing point and the value calculated from van't Hoff's formula for the case of those few metals the latent heats of fusion of which had been determined with any approach to accuracy.

Our experiments, afterwards extended to other solvents, led to the conclusion that in the case of most metals dissolved in tin the molecular weight is identical with the atomic weight; in other words, that the metals in solution are monatomic. This conclusion, however, involves certain assumptions. Sir William Ramsay's experiments on the lowering of the vapour pressure of certain amalgams point to a similar conclusion.

So far our work had been carried out with mercury thermometers, standardised against a platinum resistance pyrometer, but it was evident that, if it was to be continued, we must have some method of extending our experiments to alloys which freeze at high temperatures. The thermo-couple was not at this stage a trustworthy instrument; fortunately, however, Callendar and Griffiths had brought to great perfection the electrical resistance pyrometer (Phil. Trans., A, 1887 and 1891). Dr. E. H. Griffiths kindly came to our aid, and with his help we installed a complete electrical resistance set. As at this time the freezing points of pure substances above 300° were not known with any degree of accuracy, we began by making these measurements:—

Table of Freezing Points.

	Carnelly's Tables	Holborn and Wien, 1892	Callendar and Griffiths, 1892	Neville and Heycock, 1895	Burgess and Le Chatelier, 1902. High Temperature Measurements
Tin ...	—	—	231.7	231.9	231.9
Zinc ...	433	—	417.6	419.0	419.4
Lead ...	—	—	—	327.6	327.4
Antimony...	432	—	—	629.5	630.7 & 629.2
Magnesium	—	—	—	632.6 ¹	650
Aluminium	700	—	—	654.5 ²	658
Silver ...	954	968	972	960.7	960.9
Gold ...	1045	1072	1037	1061.7	1062.4
Copper ...	1054	1082	—	1080.5	1083
Sulphur B.P.	448	—	444.53	—	444.7

¹ Contaminated with silicon.

² Known to be impure.

With the exception of silver and gold, these metals were the purest obtainable in commerce.

During the period that the above work on non-ferrous alloys was being done, great progress was being made in the study of iron and steel by Osmond and Le Chatelier. In 1890 the Institution of Mechanical Engineers formed an Alloys Research Committee. This committee invited Prof. (afterwards Sir William) Roberts-Austen to undertake research work for it. The results of his investigations are contained in a series of five valuable reports extending

from 1891 to 1899, published in the Journal of the Institution. The fifth is of especial importance, because, besides a description of the thermal effects produced by carbon, which he carefully plotted and photographed, he described the microscopical appearance of the various constituents of iron. The materials of this report, together with the work of Osmond and others on steel and iron, provided much of the material on which Prof. Bakhuis Roozeboom founded the iron-carbon equilibrium diagram. Reference should also be made to the very valuable paper by Stansfield on the present position of the solution theory of carbonised iron (Journ. Iron and Steel Inst., vol. xi., 1900, p. 317). It may be said of this fifth report, and of the two papers just referred to, that they form the most important contribution to the study of iron and steel that has ever been published. Although the diagram for the equilibrium of iron and carbon does not represent the whole of the facts, it affords the most important clue to these alloys, and undoubtedly forms the basis of most of the modern practice of steel manufacture. Many workers, both at home and abroad, were now actively engaged in metallurgical work—Stead, Osmond, Le Chatelier, Arnold, Hadfield, Carpenter, Ewing, Rosenhain, and others too numerous to mention.

In 1897 Neville and I determined the complete freezing-point curve of the copper-tin alloys, confirming and extending the work of Roberts-Austen, Stansfield, and Le Chatelier; but the real meaning of the curve remained as much of a mystery as ever. Early in 1900 Sir G. Stokes suggested to us that we should make a microscopic examination of a few bronzes as an aid to the interpretation of the singularities of the freezing-point curve. An account of this work, which occupied us for more than two years, was published as the Bakerian lecture of the Royal Society in February, 1903. Whilst preparing a number of copper-tin alloys of known composition we were struck by the fact that the crystalline pattern which developed on the free surface of the slowly cooled alloys was entirely unlike the structure developed by polishing and etching sections cut from the interior; it therefore appeared probable that changes were going on within the alloys as they cooled. In the hope that, as Sorby had shown in the case of steel, we could stereotype or fix the change by sudden cooling, we melted small ingots of the copper-tin alloys and slowly cooled them to selected temperatures and then suddenly chilled them in water. The results of this treatment were communicated to the Royal Society and published in the Proceedings of February, 1901.

To apply this method to a selected alloy we first determined its cooling curve by means of an automatic recorder, the curve usually showing several halts or steps in it. The temperature of the highest of these steps corresponded with a point on the liquidus, i.e. when solid first separated out from the molten mass. To ascertain what occurred at the later halts, ingots of the melted alloy were slowly cooled to within a few degrees above and below the halt and then chilled.

The method of chilling also enabled us to fix, with some degree of accuracy, the position of points on the solidus. If an alloy, chilled when it is partly solid and partly liquid, is polished and etched, it will be seen to consist of large primary combs embedded in a matrix consisting of mother-liquor, in which are disseminated numerous small combs, which we called "chilled primary." By repeating the process at successively lower and lower temperatures we obtained a point at which the chilled primary no longer formed, i.e. the upper limit of the solidus.

Although we made but few determinations of the physical properties of the alloys, it is needless to say how much they vary with the temperature and with the rapidity with which they are heated or cooled.

From a consideration of the singularities in the liquidus curve, coupled with the microscopic examination of slowly cooled and chilled alloys, we were able to divide the copper-tin alloys into certain groups having special qualities.

So far I have directed attention to some of the difficulties encountered in the examination of binary alloys. When we come to ternary alloys the difficulties of carrying out an investigation are enormously increased, whilst with quaternary alloys they seem almost insurmountable; in the case of steels containing always six, and usually more, constituents we can hope at present to get information only by purely empirical methods. Large numbers of the elements and their compounds, which originally were laboriously prepared and investigated in the laboratory and remained dormant as chemical curiosities for many years, have, in the fullness of time, taken their places as important, and indeed essential, articles of commerce. I may remark that even during my own lifetime I have seen a vast number of substances transferred from the category of rare laboratory products to that which comprises materials of the utmost importance to the modern metallurgical industries. A few decades ago aluminium, chromium, cerium, thorium, tungsten, manganese, magnesium, molybdenum, nickel, calcium and calcium carbide, carborundum, and acetylene were unknown outside the chemical laboratory of the purely scientific investigator; to-day, these elements, their compounds and alloys, are amongst the most valuable of our industrial metallic products. They are essential in the manufacture of high-speed steels, of armour-plate, of filaments for the electric bulb lamp, of incandescent gas mantles, and of countless other products of modern scientific industry. All these metallic elements and compounds were discovered, and their industrial uses foreshadowed, during the course of the purely academic research work carried out in our universities and colleges; all have become the materials upon which great and lucrative industries have been built up. Although the scientific worker has certainly not exhibited any cupidity in the past, and has been content to rejoice in his own contributions to knowledge and to see great manufacturing enterprises founded upon his work, it is clear that the obligation devolves upon those who have reaped in the world's markets the fruit of scientific discovery to provide from their harvest the financial aid without which scientific research cannot be continued.

The truth of this statement is well understood by those of our great industrial leaders who are engaged in translating the results of scientific research into technical practice. As evidence of this I may quote the magnificent donation of 210,000*l.* by the British oil companies towards the endowment of the school of chemistry in the University of Cambridge; the noble bequest of the late Dr. Messel, one of the most enlightened of our technical chemists, for defraying the cost of scientific research; the gifts of the late Dr. Ludwig Mond towards the upkeep and expansion of the Royal Institution, one of the strongholds of British chemical research; and the financial support given by the Goldsmiths' and others of the great City of London Livery Companies (initiated largely by the late Sir Frederick Abel, Sir Frederick Bramwell, and Mr. George Matthey) to the foundation of the Imperial College of Science and Technology. The men

who initiated these gifts have been themselves intimately associated with developments in both science and industry; they have understood that the field must be prepared before the crop can be reaped. Fortunately, our great chemical industries are, for the most part, controlled and administered by men fully conversant with the mode in which technical progress and prosperity follow upon scientific achievement; and it is my pleasant duty to record that within the last few weeks the directors of one of our greatest chemical manufacturing concerns have, with the consent of their shareholders, devoted 100,000*l.* to research. Doubtless other chemical industries will in due course realise what they have to gain by an adequate appreciation of pure science. If the effort now being made to establish a comprehensive scheme for the resuscitation of chemical industry within our Empire is to succeed, financial support on a very liberal scale must be forthcoming from the industry itself for the advancement of purely scientific research. This question has been treated recently in so able a fashion by Lord Moulton that nothing now remains but to await the results of his appeal for funds in aid of the advancement of pure science.

In order to prevent disappointment and a possible reaction in the future in those who endow pure research, it is necessary to give a word of warning. It must be remembered that the history of science abounds in illustrations of discoveries, regarded at the time as trivial, which have in after-years become epoch-making. In illustration I would cite Faraday's discovery of electro-magnetic induction. He found that when a bar-magnet was thrust into the core of a bobbin of insulated copper wire, the terminals of which were connected with a galvanometer, a momentary current was produced; while on withdrawing the magnet a momentary reverse current occurred—a purely scientific experiment destined in later years to develop into the dynamo and with it the whole electrical industry. Another illustration may be given: Guyton de Morveau, Northmore, Davy, Faraday, and Cagniard Latour between 1800 and 1850 were engaged in liquefying many of the gases. Hydrogen, oxygen, nitrogen, marsh gas, carbon monoxide, and nitric oxide, however, resisted all efforts until the work of Joule and Andrews gave the clue to the causes of failure. Some thirty years later, by careful application of the theoretical considerations, all the gases were liquefied. The liquefaction of oxygen and nitrogen now forms the basis of a very large and important industry.

Such cases can be multiplied indefinitely in all branches of science.

Perhaps the most pressing need of the present day lies in the cultivation of a better understanding between our great masters of productive industry, the shareholders to whom they are in the first degree responsible, and our scientific workers; if, by reason of any turbidity of vision, our large manufacturing corporations fail to discern that, in their own interest, the financial support of purely scientific research should be one of their first cares, technical advance will slacken, and other nations adopting a more far-sighted policy will forge ahead in science and technology. It should, I venture to think, be the bounden duty of everyone who has at heart the aims and objects of the British Association to preach the doctrine that in closer sympathy between all classes of productive labour, manual and intellectual, lies our only hope for the future. I cannot do better than conclude by quoting the words of Pope, one of our most characteristically British poets:

By mutual confidence and mutual aid
Great deeds are done and great discoveries made.