

A FORCE FIELD DISSOCIATION THEORY OF SOLUTION APPLIED TO SOME PROPERTIES OF STEEL.

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In Roberts Austen's presidential address before the Iron and Steel Institute in 1900 he states that "In 1806 we find a fundamental statement by Berthollet's countryman and courteous opponent, Proust, which is of singular interest to us. At that early date he describes cast iron as a solution of carbide of iron in iron. He cites it as a case of a compound united to an excess of one of its elements, and clearly anticipates the modern view that carburised irons are solid solutions." More than half a century later Matthiessen in England states that steel and other alloys should be regarded as solid solutions. It was not, however, until some years after Matthiessen's work that the solution theory of steel began to take definite form and to be accepted as a means of interpreting the phenomena resulting from the heat treatment of iron and steel.

The concept that solid solutions like white cast iron or hardened steel have essentially the same mechanism, that is, the same atomic relations between the solutes in solution and the solvent as exist in ordinary aqueous solutions is not fully accepted by most metallurgists at the present time. Some of the reasons for this may be traced to the persistence of several ideas.

The development of inorganic chemistry has depended almost entirely on studies of the properties of liquid aqueous solutions. As a result, the idea that the terms solution and liquid are practically synonymous still persists in the minds of many metallurgists. To them the expression "solid solution" seems to involve a contradiction of terms. The words liquid and solid are used to indicate merely two different physical states. No knowledge of chemical composition is necessary to determine whether a body is a liquid or a solid and we find all stages of differences in viscosity between a perfectly mobile liquid and a typical solid. On the other hand, any solution must be composed of at least two entities, one a solvent and the other a solute or substance dissolved. If we could obtain absolutely pure water we would have a liquid but not a solution. This liquid would become a solution only when some second substance was dissolved in it. In the same way if we had strictly pure iron it would be a solid but not a solution, since it would be composed of but a single chemical entity. As soon, however, as the iron contains any second substance, such as carbon, silicon or other element, it would become a solution just as truly as does the pure water to which a salt has been added.

A second reason why metallurgists and chemists have not been in the habit of regarding metallic solutions in the same way they do aqueous

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solutions is that in experimental work on these latter, the composition is usually expressed in molecular concentration per unit volume, whereas in metallic solutions it is customary to express the composition in weight per cent. For most scientific work the concentration of aqueous solutions is expressed in terms of molar solutions or fractions thereof. A molar solution may be defined as one which contains the molecular weight of the solute in milligrams in one cubic centimetre. The electrical conductance of aqueous solutions is usually expressed in reciprocal ohms times 10^{-6} per centimetre cubed. The electrical resistivity, thermal conductance and magnetic properties of metallic solutions for scientific work are usually expressed in appropriate units per centimetre cubed. If, therefore, we hope to determine the correlation between chemical constitution and physical properties, it would seem only logical to adopt for metallic solutions the same system of expressing the composition as is used for aqueous solutions, giving the composition in terms of volume concentration rather than weight per cent. If the percentage composition of a metallic solution such as white cast iron or steel is known, this may readily be converted into atomic concentration, that is, the number of milligram atoms per cubic centimetre, by means of applying the formula :

$$\frac{10 \times D \times \text{per cent. of element}}{\text{Atomic weight of element}}$$

where "D" is the specific gravity of the alloy, the per cent. and atomic weight being that of the element under consideration. Since the specific gravity gives the weight in grams of one cubic centimetre and the concentration is to be expressed in milligram atoms per cubic centimetre, the 10 comes in because it is first necessary to multiply by 1000 to reduce grams to milligrams and then divide by 100, due to the composition being expressed in weight per cent. If a steel had the following composition: C - 0.945 per cent., Mn - 0.189 per cent., P - 0.013 per cent., S - 0.016 per cent., Si - 0.155 per cent., the atomic concentration of the carbon would be

$$\frac{10 \times 7.85 \times 0.945}{12} = 6.28 \text{ milatoms per c.c.}$$

Similarly the atomic concentration of the other elements would be: Mn - 0.27, P - 0.3, S - 0.4, Si - 1.43 milatoms per c.c.

With comparatively little effort metallurgists, chemists, and physicists could form the habit of thinking in terms of atomic concentrations just as easily as they now do in weight per cent. If this were done many relationships between the chemical constitution and physical properties of metallic solutions would be revealed which will not be easily seen so long as compositions are expressed in weight per cent.

The iron carbon diagram with composition expressed in milligram atoms per centimetre cubed, is shown in Fig. 1. This diagram takes in all of that portion up to and including the liquid eutectic. The temperatures are given as usual on the ordinate and the composition expressed on the abscissa, the values given at the bottom of the diagram being milatoms per centimetre cubed while for comparison the corresponding weight per cents. are indicated at the top. The lettering adopted is that used in the early iron carbon diagrams and still used by most leading metallurgists. Some serious confusion in the discussion of iron carbon equilibrium has arisen from one or two writers thoughtlessly changing the arrangement of letters when discussing the iron carbon diagram,

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instead of adhering to the arrangement so long recognised in this country and abroad.

In addition to the two above mentioned reasons, namely, the confusion arising from the synonymous concept of the terms liquid and solution and the fundamental difference in the system of expressing the composition of metallic and of aqueous solutions, there is a third, probably exerting more influence on the concepts of metallurgists, physicists, and chemists than either of the two mentioned. The third reason is the very generally accepted electrolytic dissociation theory, advanced in 1887 by Arrhenius to account for chemical reaction and reactivity. The electrolytic dissociation theory was suggested as the result of researches on aqueous solutions by electrical methods. For some years prior to 1887 chemists had recognised that of all the molecules of a solute in solution only a portion were reactive, the remainder being inactive. At the time of the announce-

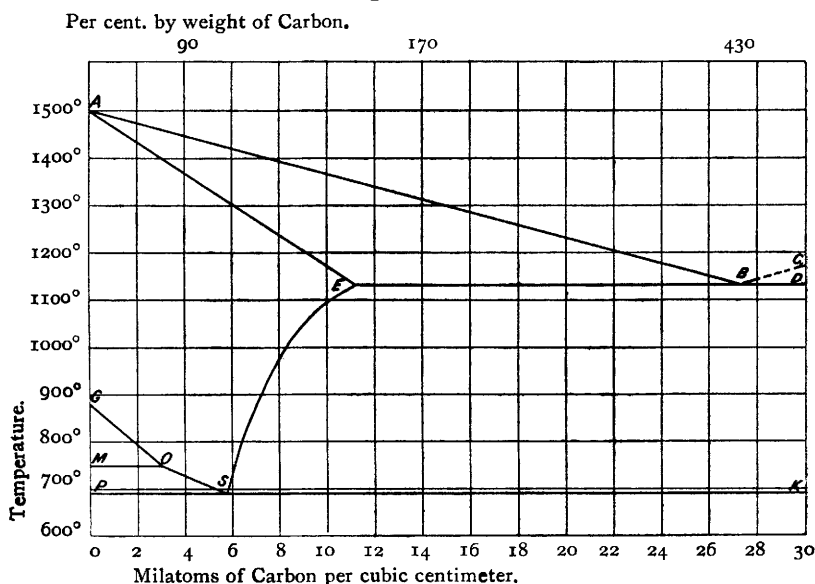


FIG. 1.

ment of the electrolytic dissociation theory, reactive molecules were assumed to be dissociated by action of the solvent into electrically charged particles termed ions. The fundamental assumption was made that chemical reaction takes place only between ions and that these ions owe their reactivity to the presence of the electric charges which they carry.

That theory of solution is most satisfactory which is capable of giving a reasonable explanation for the greatest number of known phenomena and at the same time is not inconsistent with any known facts of observation. While the electrolytic dissociation theory explains very satisfactorily many of the phenomena observed in liquid solutions where the solvent is a dielectric, it does not satisfactorily explain the behaviour of such solutions when subjected to the action of radiant energy in the form of light and is entirely untenable for metallic solutions in which the solvent is not a dielectric, but a conductor of electricity.

In 1915 in an article entitled "A Theory of Chemical Reaction and Reactivity" (*Journ. Amer. Chem. Soc.*, 1915, 979), E. C. C. Baly, as the

result of a series of spectroscopic studies extending over more than ten years, proposed what is now known as the force field theory of solution, to account for chemical reaction and general reactivity of solutions. In the force field theory as described in the above paper the assumption is made that each atom of an element possesses an electro-magnetic force field and when two or more atoms are combined in a molecule the force field of this latter is closed. A second assumption is that when the molecule is dissolved its force field is more or less opened up by action of the solvent, the extent to which the opening takes place being dependent upon the concentration as well as on the composition of both solute and solvent. The force fields of molecules in solution which are not active are assumed to remain closed. The opening of the force fields of active molecules is stated to take place in definite steps, ionic dissociation as usually thought of not being recognized. The experimental evidence given by Baly together with that taken from the results obtained by many astronomers and physicists whose work involves a study of the action of light with both gases and liquids, seems to prove that this reactivity is primarily due to the existence in these solutions of electro-magnetic force fields. The reactivity due to these force fields will depend upon the degree to which they are opened up and the resultant of the reactions will depend upon the form of energy with which the force fields come in contact.

For the past twenty-five years the researches on the constitution of steel which have been carried on in this laboratory have been based on the fundamental concept that there is no essential difference in the atomic relations between the solutes and solvent in iron carbon alloys from those which exist in aqueous solutions. In 1899 in a paper on "The Constitution of Steel" (*J. Iron and Steel Institute*, 1899, II., p. 231), experimental evidence indicating molecular dissociation was given. In 1908 in a second article on "The Constitution of Carbon Steels" (*J. Iron and Steel Institute*, 1908, III., p. 332), the desirability of recognising the complete unity of mechanism of aqueous and metallic solutions, including ionic dissociation in the latter, was pointed out. Almost simultaneously with the publication of Baly's article on "A Theory of Chemical Reaction and Reactivity" the author submitted a paper entitled "Can the Dissociation Theory be Applied to Solid Solutions in Steels" (*J. Amer. Chem. Soc.*, Vol. 37, p. 2039). In this latter article experimental evidence is given to show that it is the products of ionic dissociation of carbides in solution which when a difference in electrical potential is established at two points, react, transforming electronic motion of electricity into atomic or molecular motion of sensible heat while conductance of the electric current takes place through the solvent iron. Thus it was shown that the products of ionic dissociation in a metallic solution are capable of reacting with electrical energy just as truly as are the ions in an aqueous solution, but the resultant of the reactivity in metallic solutions is electrical resistance, while that in aqueous solutions is electrical conductance. The reversal of phenomena, however, is not due to any difference in atomic relations between the dissolved solute and the solvent, but to the reversal in the electrical properties of the solvent. In 1915 when it had been shown that the products of ionic dissociation in both metallic and aqueous solutions are reactive with electrical energy, the author suggested that the term "ionoids" be used to define the products of ionic dissociation in a metallic solution. The term ionoid was suggested because at that time an ion was considered as necessarily carrying an electric charge, to the presence of which, the ion owed its reactivity. Baly's

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publications, which gave such convincing evidence that reactivity in solutions is primarily due to force fields rather than to the presence of electric charges on the reacting particles, clears the way for a theory which would be broad enough to include all solutions whether liquid, solid or gaseous and metallic solutions as well as those in which the solvent is a dielectric. Such a theory might properly be called a force field dissociation theory, since it would embody all the concepts now held concerning ionic dissociation with the exception of the necessary presence on the ion of electric charges to which the ions owe their reactivity. In such a theory reactivity of ions is assumed to be due to open force fields and not to the presence of electric charges, as is assumed in the electrolytic dissociation theory.

Under the force field dissociation theory, chemical reaction is assumed to take place between ions whose open force fields involve primary valences. Molecules or crystals not in solution and consequently whose force fields are assumed to be closed, may possess the property of reacting in definite ways with certain forms of energy. For instance, a liquid or a crystal consisting of a single chemical compound or of an element may react with light, that is, possess characteristic optical properties which are frequently used as a means of identification. Again, strictly pure metals react with electrical energy, that is, possess a definite electrical resistivity, which, however, obeys a different law in regard to the influence of the temperature of measurement than does the resistivity due to the reaction of the open force fields of solutes in solution in the metal. That solutes in solution possess more or less open force fields is strongly suggested by the force field existing around a pole of an ordinary magnet. The hypothesis is proposed that these magnetic force fields represent the cumulative effect resulting from the serial alignment of the poles of the force fields of carbides or other solutes in solution.

The marked difference in the electrical resistance of one milligram atom of a metal when functioning as a solvent or as a solute is strikingly illustrated by the fact that in one cubic centimetre of pure chromium the resistivity at 25° C. produced by each milatom is 0.02 microhms, whereas for the same amount of ionized chromium in solution there results not less than 3.2 microhms, an amount 160 times as great.

The relation between the electrical and thermal resistivity of pure metals has been expressed in Wiedemann and Franz's Law, but whether the same relation holds between electrical and thermal resistivity produced by the reaction of force fields of solutes in metallic solution, remains to be determined. The values reported by the author in 1917 (*J. Iron and Steel Institute*, 1917, No. II, p. 251) would indicate that this is probably not the case.

Although the microhm is the unit used to express electrical resistivity, there is at present no corresponding term for thermal resistance. Many tables are available in which the thermal conductivity of metals is given, the values showing the number of calories flowing per second through one cubic centimetre having a temperature gradient of one degree. In order to have a unit of thermal resistivity which could conveniently be compared with the microhm, the author would suggest a term "calohm" for such a unit. A calohm would be defined as that thermal resistance which would permit one calorie to pass per second through one cubic centimetre with a temperature gradient of one degree. The thermal resistivity of a pure metal expressed in calohms would be the reciprocal of the thermal conductivity. If the same relation between thermal and electrical resistivity is assumed as that on which the Wiedemann and Franz Law is based, one calohm would correspond to 10/6.5 or 1.54 microhms.