Summary.

Spongy silver, prepared by igniting pure silver tartrate, was treated at the ordinary temperature with strong nitric acid (sp. gr. 1.42) from which lower oxides of nitrogen had been removed by boiling with carbamide. At first some action took place with the formation of silver nitrate and nitrous acid, but after a time the solution of silver stopped, and on allowing the mixture to stand with occasional shaking for about two weeks, the remaining silver was converted into long needle-shaped crystals easily visible to the naked eye; slender needles which are first formed, appear floating on the surface of the acid liquid. This is considered to be a new variety of crystalline silver, belonging to the cubical system.

The author desires to express his indebtedness to his professor, Dr. E. R. Watson, who took an active interest in course of this work.

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CAN THE DISSOCIATION THEORY BE APPLIED TO SOLID SOLUTIONS IN STEELS?

BY EDWARD D. CAMPBELL.

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The conception that many metals and alloys might be regarded as solidified solutions, either of miscible liquids or of compounds in solution, was clearly pointed out more than fifty years ago by A. Matthiessen.[1] Under this conception pure or nearly pure metals and alloys would be regarded as liquids or mixtures of liquids, differing from ordinary ones only in viscosity, but still being solutions in which the atomic relations existing between solutes and solvent do not differ fundamentally from the same relations in ordinary solutions. Matthiessen made numerous measurements on the conductivity of metals and alloys but drew no general conclusions as to the relation between chemical constitution and electrical properties.

Some twenty years later, Barus and Strouhal[2] carried on a long series of very careful experiments to show the relation existing between the hardness of tool steel and its electrical properties. The changes in specific resistance in tool steel induced by sudden quenching and reheating to various temperatures for different lengths of time were carefully investigated, but apparently no definite connection between change in specific resistance and chemical constitution was pointed out.

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[1] Report of the British Association for the Advancement of Science, 1863, p. 37.

[2] U. S. Geological Survey, *Bull.* 14, 1885.

Barus endeavored to show that the hardness of steel is a function of the specific resistance. If by the hardness of steel is, in reality, meant viscosity, that is, the resistance to flow under high pressure as applied in a Brinell ball testing machine, then the hardness is not a function of the specific resistance, since the latter in a piece of hardened steel may be reduced by moderate tempering more than 40% without any measurable reduction in the hardness.

The hardness of steel is becoming generally recognized to be due to a certain portion of the iron existing in a state of strain, the extent of which internal tension or interstrain is dependent upon the chemical constitution at the instant of quenching and the rate of cooling through the critical range. Iron lends itself perhaps better than any other metal to a study in solid solution, since iron exists in the two well-known allotropic forms, the stable alpha form, soft, magnetic and of low solvent power and the gamma form, probably somewhat harder than the alpha, nonmagnetic, and possessing at least ten times the solvent power of iron in the alpha condition. Pure iron when converted into the gamma form by heating above the Ac_3 critical point, is transformed on cooling through the critical range into the alpha form with such velocity that, no matter how quickly cooled, there is but little evidence of the presence of gamma iron in the cold specimen. The rate of transformation of the gamma into the alpha form, when passing through the critical range is very markedly influenced by the presence of solutes, particularly carbides in solid solution, and it is largely through control of the concentration of solutes at the instant of quenching that the extent of transformation of the gamma into the alpha form, hence the extent of internal or interstrain, and thus the hardness, is controlled.

If a piece of steel of moderate carbon content be very quickly cooled from a temperature sufficiently above the critical range to insure complete solid solution of the carbides, the quenched metal will consist of an unstable solid solution of carbides in gamma iron, together with some alpha iron in the state of strain. If, on the other hand, the same steel were cooled slowly through the critical range, the gamma iron would be completely transformed to the alpha form and the carbides, in consequence of their slight solubility in alpha iron, would be almost completely precipitated.

The object of the experimental work described in this paper, which was carried on by Mr. Robert Atkinson, was to bring out the relation which exists between the concentration of the carbides in solid solution in steel and the specific resistance.

In the well-known colorimetric method for the estimation of carbon in steel, the brown color of the dinitro derivatives produced by the interaction of nitric acid on the iron and the unsaturated hydrocarbons derived from the carbides, is used as a basis for determining the percentage of carbon in the steel. It has been well known for many years that if even reasonably accurate results are to be obtained, the unknown steel and the standard steel, if a steel standard is used, must both have approximately the same composition and be subjected to approximately the same heat treatment. If the color of the dinitro derivatives obtained by dissolving a sample of steel in nitric acid is compared with that of a mixed solution of ferric, cupric and cobaltous chlorides, made up as a permanent color standard, the absolute value of each scale division of a colorimeter in terms of carbon percentage cannot be expressed as a constant, since the molecular weight of the carbides, hence that of the hydrocarbons from which the dinitro derivatives are formed, will vary with the carbon content and heat-treatment of the steel.

In an article, "The Effect of Heat Treatment on the Colorimetric Test for Carbon in a 0.32 Carbon Steel,"[1] details are given showing the method of analysis used in the present work to estimate colorimetrically, the quantity of dinitro compounds derived from carbides soluble in cold nitric acid and those insoluble in cold but soluble on heating for thirty minutes in boiling water. The depth of color was estimated by comparison with a standard solution of ferric, cupric and cobaltous chlorides, contained in a modified colorimeter,[2] the strength of the chloride solution being such that one scale division of the colorimeter was equivalent to a little less than 0.01% carbon when a sample of 0.250 g. of the steel was used.

The steel used in these experiments, which for convenience has been termed H 35, was furnished through the courtesy of the Halcomb Steel Company and has the following composition: Carbon, 0.35; manganese, 0.08; phosphorus, 0.009; sulfur, 0.024; silicon, 0.18. Bars of this steel about 15 cm. long and a little over 6 mm. square were suspended in an electrically heated furnace, so arranged that oxidation during heating was completely avoided. The temperature of the bars was measured by means of a standard platinum rhodium thermocouple placed close to them. They were allowed to remain in the furnace one hour to attain the same temperature as that indicated by the thermocouple, 892°, after which they were quickly removed and quenched in a large excess of water. The temperature of the water at the beginning was +4° and at the conclusion of the work about +14°. The time required to transfer a specimen from the furnace to the quenching bath, taken with a stop watch, averaged four-fifths of a second. From the time the specimen entered the water until it was black was from four-fifths of a second to one second, while between five and six seconds were required to bring it to the tempera-

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[1] *J. Iron and Steel Inst.*, **2**, 367–84 (1913).

[2] THIS JOURNAL, **33**, 1112 (1911).

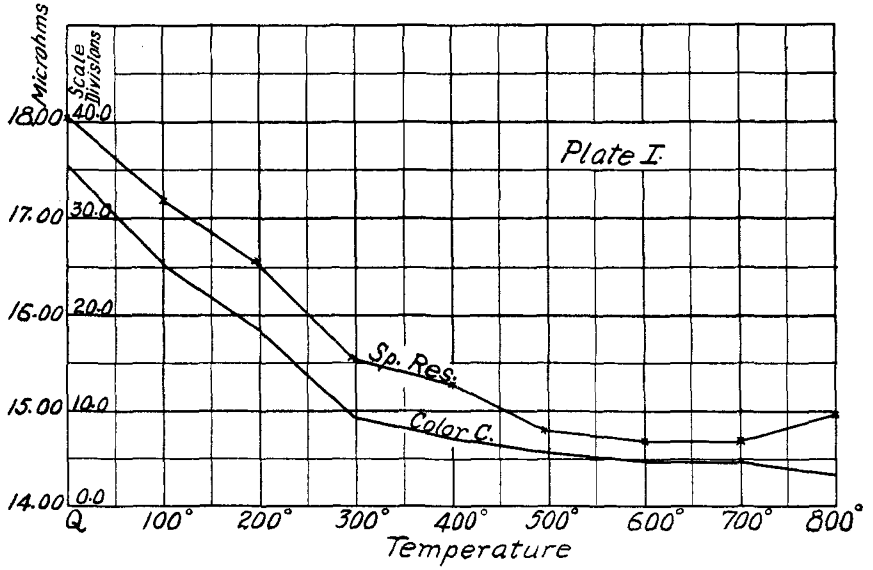
ture of the bath. No oxidation took place during the time the bars were in the furnace, and the film of oxide which formed on the surface during the time the bars were being transferred from the furnace to the quenching bath was so slight as to be only a discoloration. After quenching, the bars were polished and the specific resistance determined. Sufficient drillings were taken from one bar to make the necessary colorimetric determinations. The specific resistance was determined by measuring the fall in potential between knife edges 10 cm. apart on bars of accurately measured cross-section, while a known current was flowing through them. The knife edges were bolted to a small glass plate, thus insuring constancy of distance apart, and the bars during measurements were immersed in a bath of refined, paraffin oil, so that their temperature could be determined and all readings reduced to a standard of 20°. The fall in potential was compared with that of a standard resistance bar calibrated by means of a standard potentiometer and certified standard cell. Duplicate determinations could be easily kept within 0.05 microhms and it is thought that the absolute values of resistance are correct within less than 0.2 of a microhm. After measuring the specific resistance and taking sufficient drillings for making colorimetric determinations, the quenched bars were placed in a steam drying oven at from 100–105° for two days, after which they were removed, the specific resistance measured and drillings taken for colorimetric work. In the subsequent heat treatments the bars from the previous treatment were packed in a steel tube to avoid oxidation, together with a tube for the insertion of a thermocouple and the whole placed in an electric furnace, which was then gradually raised to the temperatures shown in the table of specific resistances. When the desired temperature, as indicated by the thermocouple, was reached, it was held as nearly as possible for from one to two hours, after which the furnace was allowed to cool over night. After each heat treatment the specific resistance was again measured and drillings taken for colorimetric comparisons.

As it is impossible to express in absolute percentages the amount of carbon represented in the dinitro derivatives, the color due to these is expressed in scale divisions of the colorimeter. The results of the measurements are given in the following table, in which Column I shows the temperature to which the bars were reheated after quenching from 892°; Column II, the specific resistance in microhms per cm^3. at 20°; Column III, the amount of dinitro compounds derived from carbides soluble in cold nitric acid, expressed in scale divisions of the colorimeter; and Column IV, the amount of dinitro compounds derived from carbides insoluble in cold nitric acid, but soluble at the temperature of boiling water.

TABLE I.—SHOWING INFLUENCE OF HEAT TREATMENT ON SPECIFIC RESISTANCE AND COLOR TESTS.

Column I.	Column II.	Column III.	Column IV.
20°	18.07	35.2	12.8
100°	17.15	25.0	....
195°	16.57	18.5	....
295°	15.55	9.3	....
400°	15.30	6.7	....
492°	14.79	5.8	....
600°	14.67	4.6	....
700°	14.69	4.5	....
800°	14.95	3.0	39.0

The results given in Columns I, II and III of Table I are shown graphically in the accompanying Plate I, in which the abscissae represent the temperatures of reheating, while the ordinates show the specific resistance in microhms and the color of the dinitro derivatives due to carbides soluble in cold nitric acid, in scale divisions.



A study of the figures in Table I or, more easily, a glance at the curves in Plate I, reveals clearly the close relationship existing between the concentration of the carbides in solid solution and the specific resistance.

However, it will be noted that in the sample reheated to 800° there is an increase in specific resistance accompanied by a decrease in the dinitro derivatives. Metal cooled very slowly from 800° would have the carbides distinctly segregated into relatively large masses, and although the precipitation would be most nearly complete the separated cementite would consist of carbides saturated with iron in solid solution; hence the increase in specific resistance.

The question may properly be asked, to what may this relationship probably be due? If a metal such as iron be regarded as a solvent, differing, it is true, in viscosity from ordinary liquids, but in which the atomic relations existing between solutes in true solid solution and the solvent are essentially the same as the relations existing in ordinary solution, we may find the reasonable explanation for the correlation between the concentration of the carbides in solid solution and the specific resistance of steel.

While in most research work in physical chemistry attention is focused on the solutes, and the influence of concentration, temperature, etc., on these, in most work in metallurgy attention is, perhaps unconsciously, focused on the properties of the solvent; and the influence of temperature and concentration of solutes on the properties of this latter is what is most carefully studied. It is seldom that ordinary chemistry is regarded as a study of the influence of solutes on the properties of water, and yet this is the habitual view-point taken in the study of the influence of impurities on the properties of metals. If iron is regarded from the same view-point as ordinary solutions, we may calculate the molar concentration of solutes in solid solution in a manner exactly similar to that employed in such calculations in ordinary solutions. If the assumption is made that one liter of steel weighs 7800 g., the molecular concentration of solutes in solid solution in iron would be represented by the following formulae given in the table below, in which the symbol of the element stands for the number of "points" (0.01%) of that element, and N, the number of atoms of the element in each molecule of the solute.

TABLE II.—SHOWING FORMULAE AND MOLECULAR CONCENTRATIONS OF STEEL, H 35.

Element.	Formula.	Molecular concentration.
C	$\frac{C}{15.4\,N}$	$\frac{2.27}{N}$
P	$\frac{P}{39.8\,N}$	$\frac{0.02}{N}$
S	$\frac{S}{41.1\,N}$	$\frac{0.06}{N}$
Si	$\frac{Si}{36.3\,N}$	$\frac{0.49}{N}$

Manganese is not included in the above table since in steel it functions as a metal, entering partly into combination with carbon and sulfur and partly into the constitution of the solvent, iron, the law of mass action determining its distribution. The same law applies to the distribution of Ni, Cr, and some other elements frequently found in steel.

In an article on "The Constitution of Steel,"[1] it was shown that N of the above table in the case of carbides, is a function of the carbon content and heat treatment of the steel. In the case of a slowly cooled, low carbon steel, N is more than four (4), while in high carbon steel it averages less than this figure. In a metal suddenly cooled from above the critical point, the value of N is distinctly lower than when the same metal is in the annealed condition.

In the dissociation theory as applied to aqueous solutions, when solutes dissolve, a certain proportion of the molecules are assumed to be separated into parts, termed ions. When a solute is dissolved in water it dissociates to a large extent and the chemical or internal energy is decreased, with the appearance of equivalent quantities of electrical energy in the form of equivalent positive and negative charges on the respective ions. It is because the solvent in the case of an aqueous solution is a dielectric that the ions are able to acquire and retain their charges, and thus conduct the electric current by transporting these charges between the electrodes. It is assumed that the ions only are electrically active, since the electrolytic conductance is used as a measure of the ionic concentration. On account of the high electrical resistance of the solvent in the case of aqueous solutions, an almost negligible proportion of the total current carried is carried by the solvent. If ions resulting from the dissociation of molecules in aqueous solution are capable of acquiring energy in the form of electric charges, but in these solutions retain and transport this electrical energy only because of the dielectric property of the solvent, one might properly ask, What should we expect if solutes were dissolved and dissociated in a solvent which was in itself a conductor possessed of very low specific resistance? In such a case there seems to be no inherent reason why the mechanism of solution and dissociation of the molecules of the solute into constituent parts bearing precisely the same atomic relations to the solvent, should differ essentially from that which holds when a solute is dissolved in a dielectric solvent. In case the solvent were a metal it would be obviously impossible for the products of ionic dissociation to retain electric charges; hence it would be clearly out of the question to call these products ions, so that we have suggested the term "ionoids" to indicate the products of ionic dissociation in solutions in which the solvent is a metal. The "ionoids" in metallic solutions, like the ions in aqueous solutions, constitute that portion of the solute which has undergone dissociation and which is electrolytically active. The result of this electrolytic activity of "ionoids," however, will manifest itself in a manner directly the reverse of that manifested in the behavior of ions, not because of any fundamental difference in the atomic relations existing between the "ionoids" or ions and the solvent, but because of the reverse

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[1] *J. Iron and Steel Inst.*, 2, 223 (1899).

of the electrical properties of the solvents. In a metallic solution practically the whole of the conductance is through the solvent and undissociated solutes, while the "ionoids" which are electrolytically active tend, like ions, to acquire energy in the form of electric charges, but on account of the nature of the solvent retention of this energy is impossible and it is, in consequence, transformed and dissipated in the form of heat. Thus the electrical energy transformed into heat by the "ionoids" may be expressed in terms of specific resistance and consequently the ionic concentration in solid solution in metals may be determined by deducting from the total specific resistance that due to the solvent and undissociated solutes. Under the above conceptions the dissociation theory of solution would be just as applicable to solid solutions in metals as to aqueous solutions, although the phenomena, when the two solutions were subjected to a difference of potential at two points, would manifest themselves in opposite directions. The differences, however, in electrical behavior of the two solutions are due not to any fundamental difference in the atomic relations existing between solutes and solvent, but to the differences in the electrical properties of the solvents.

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THE ATOMIC WEIGHT OF MOLYBDENUM.

BY JOHN H. MÜLLER.

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The purpose of the present investigation was to redetermine the atomic weight of molybdenum by the oxidation of pure metal. It will be recalled that as early as 1859 Dumas[1] oxidized the sulfide, reducing the resulting oxide in hydrogen to metal. The mean of six determinations was 95.942.

In 1868 Debray used the method of Dumas.[2] The trioxide, in this case, was purified by sublimation from platinum. The mean of three determinations was found to be 95.524. Later Rammelsberg,[3] from a single experiment, obtained a result very close to that of Dumas.

In 1895 Seubert and Pollard[4] determined the indirect ratio 2.AgCl :- MoO_3, subsequently reducing the trioxide to metal in hydrogen, with the result, Mo = 96.006.

Vandenberghe[5] reduced the dibromide to metal and oxidized the latter to trioxide by means of nitric acid. The mean of five determinations by this procedure was 96.088.

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[1] *Ann. Chem. Pharm.*, **105**, 84, and **113**, 23.

[2] *Compt. rend.*, **66**, 734.

[3] *Berlin. Monatsb.*, **1877**, p. 574.

[4] *Z. anorg. Chem.*, **8**, 434 (1895).

[5] "Acad. Roy. Belge Mem. couronnes T.," 56.