ON THE TRANSFORMATIONS OF PURE IRON— INTRODUCTORY PAPER.

Mr. A. E. Oxley, M.A., D.Sc., Lecturer in Physics in the University of Sheffield, then read the following Paper as an Introduction to the General Discussion.

The present communication is composed for the most part of extracts from letters to Sir Robert Hadfield, and deals with the nature of the molecular constitution of pure iron. At Sir Robert's suggestion these extracts are presented to the Faraday Society.

It is now believed by a large school of metallurgists that the A_2 transformation can be satisfactorily explained without assuming allotropic change. The A_3 transformation, on the other hand, is generally regarded as involving allotropy.

The crystalline state is one of extreme molecular association (physical polymerism or the grouping of chemical molecules under the influence of mutual physical forces), and if allotropy is determined solely by the nature and extent of this association, each substance will show an unlimited number of allotropic forms within a finite temperature interval. In some experiments on "The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility,"* I have frequently been led to the conclusion that the molecules of crystalline, and even of liquid, substances are in a distorted state. This distortion is always very slight, and is due to the action of restraining forces exerted by neighbouring molecules on each molecule of the material medium. It is clear, therefore, that the configuration of a molecule in a crystalline medium is slightly different from that of a molecule of the same substance in the liquid. If the mutual influences of the molecules were withdrawn, the molecules of both states would alter their configurations slightly and would become identical. Such a relationship between the molecules is of the nature I have previously called "crystalline grouping," and the distorted condition of the molecule is not to be regarded as indicating allotropy. If, indeed, allotropy were determined in this way, then every degree of association would imply a new allotropic form, the number of which forms would be infinite for each substance throughout a finite interval of temperature and "allotropy" would be a useless term.

To surmount the difficulty presented by the existence of so many allotropes, two different types of allotropy have been recognized: (1) The two-phase (discontinuous) type, (2) the one-phase (continuous) type.†

Benedicks says: "At present the binary state diagrams (temperature-concentration) rest entirely on the phase doctrine as a basis. As is well known, they have for this reason regard only to the equilibrium between phases (heterogeneous equilibrium), no consideration is taken of the internal molecular (homogeneous) equilibrium within each phase, as that is, on the whole, not dealt with in the phase doctrine as developed by Gibbs. We must then take as a fact, at least for the present, and generally speaking, that

* A. E. Oxley, *Phil. Trans. Roy. Soc., A*, vol. 214, p. 109, 1914, and *ibid.*, A, vol. 215, p. 79, 1915.

† *Vide* Benedicks, *Journ. Iron and Steel Inst.*, vol. lxxxix., p. 407, 1914.

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internal molecular transformations cannot be illustrated in our (two-dimensional) state diagrams for two components."

I do not wish to give reasons against the adoption of such conceptions, but having once recognized them it is of the utmost importance to distinguish experimentally between them. This leads us to the large mass of admirable experimental work which has been carried out during recent years, to problems which have been courageously attacked, but involving, it seems, insuperable difficulties.

To show experimentally that a discontinuity in any one property exists is an exceedingly difficult problem, and it does not seem that any method within our power will satisfy an opponent. A reference to the recent work of Honda* on the variation of magnetization with temperature in the neighbourhood of A_3 will illustrate this point.

Leaving aside the transformations of iron for a moment, the fusion-point of a substance is perhaps the nearest approach to a mathematical discontinuity defining the two-phase type of allotropy. But to those who have had the opportunity of examining Lehmann's liquid crystalline state, under the crystallization microscope, it hardly seems that even in this extreme case the fusion-point of ordinary substances can really involve a discontinuity of the kind required by the definition. The liquid crystalline state discloses, as it were, a magnified image of the process which must be going on in all liquids before crystallization, viz. a continuous marshalling of the molecules (perhaps in some cases a labile state is formed which may or may not be doubly refracting) into a flowing space lattice which eventually becomes a rigid crystal. One of these liquid crystal compounds I examined showed no liquid crystalline state on fusion, but did so on re-cooling over a considerable range prior to crystallization in the ordinary sense. Such a substance exhibits two-phase allotropy on heating, one-phase allotropy on cooling, if we examine the rate of growth of the crystalline structure. It is interesting to note that the crystals produced by the one-phase allotropic transformation pass again into the liquid by the two-phase allotropic transformation and that the process can be repeated.

In other words, a property may change rapidly (i.e. in a small temperature interval), but we have no evidence to show that it is discontinuous.

It seems therefore that a sharp distinction cannot be made between these two types of allotropy. The changes observed appear to be better and less vaguely expressed as different degrees of molecular association—the idea of molecular association being continuous.

I have come to the conclusion, from a consideration of the facts, that the mutual influences of the molecules, i.e. the molecular association (physical polymerism) is alone sufficient to account for the phenomena observed. There still remains the possibility that these phenomena may be connected with some intra-molecular change. Such an alteration of the atomic structure of the molecule would be allotropic in the sense of the oxygen to ozone transformation or in the sense of the transformation from one isomer to another. This criterion of allotropy has been adopted and, from the magnetic and thermal points of view, an attempt is made in what follows to show that allotropy in this sense is absent in the transformations which are of interest to the iron and steel metallurgist.

If the molecule of the crystalline structure, on *withdrawal of the restraining forces*, differs in configuration from a free molecule which has originated in some other way (say by an independent chemical or physical

* *Journ. Iron and Steel Inst.*, 1915, and *Science Reports*, Tokio, vol. iv., No. 3, p. 261, 1915.

process), either as regards the integral number of atoms in the molecule or the relative distribution of those atoms, even if their number remains the same, then the substance exhibits allotropy. As examples we may take the oxygen to ozone transformation and the many types of isomers known to organic chemistry. Not only has an allotropic modification characteristic physical properties, but, to some extent, characteristic chemical properties too. The constitutional formulæ of modern chemistry are founded on the assumption that the properties of a substance are determined by the nature, number, and mutual dispositions of the atoms within the molecule.

Now the crystalline forms of allotropic modifications will be characteristic, for the space lattice will be conditioned by the configuration of the molecule which determines the restraining forces.* On the other hand it has been shown† that *molecules of exactly the same configuration* may be packed into quite distinct crystalline aggregates, of different degrees of stability, so that a difference of crystalline symmetry does not necessarily imply allotropy in the sense defined above.

It should be pointed out that this definition is not specially designed to meet magnetic considerations; it is consistent with the recognized chemical view. We must distinguish between the forces holding the molecules in position in the crystalline structure and those holding the atoms together in the molecule,‡ and if the latter forces are large compared with the former (thermo-chemical evidence that this is so will be given later), then the preservation of molecular identity, and hence the rarity of allotropic change, will not be a surprising phenomenon.

The above remarks lead us to a criterion by which the nature of the so-called β to γ transformation may be discussed. Weiss§ has shown that the magnetic properties of β and γ iron can be interpreted in terms of a simple atomic constitution of the iron molecule, and the point of importance for us is that the iron molecule consists of two atoms in the temperature intervals of stability of the β and γ forms, and therefore through the transformation from paramagnetic γ iron to ferro-magnetic β iron there is no change in the integral number of atoms constituting the iron molecule. Weiss's work shows that each state of iron provides a measure of the constant of Curie (C), the parameter of the hyperbolæ representing the variation of specific susceptibility as a function of the absolute temperature. In conclusion he states:—

“Le passage du fer β au fer γ qui correspond à la perte des actions magnétiques mutuelles sans variation du nombre des atomes de la molécule reste à expliquer, mais la concordance des diverses valeurs de C ne peut être due au hasard.”

Hence in so far as the integral number of atoms in the molecule is concerned we cannot regard A_2 as an allotropic change-point.

It is interesting to note that Barlow and Pope|| have pointed out that those elements which crystallize in forms of high symmetry are the ones which show the least tendency to form allotropic modifications. Iron is known to crystallize throughout the β and γ ranges in the cubic system. Further, Retgers¶ has shown that the higher the crystalline symmetry of a particular element the smaller, as a rule, is the number of atoms contained in

* *Phil. Trans. Roy. Soc., A*, vol. 215, p. 79, 1915.

† Barlow and Pope, *Trans. Chem. Soc.*, vol. lxxxix., p. 1741, 1906.

‡ *Ibid.*, loc. cit.

§ *Comptes Rendus*, vol. cxliv., p. 25, January 1907.

|| *Loc. cit.*, p. 1741.

¶ *Zeitschr. Phys. Chem.*, vol. xiv., p. 1, 1894. The rule holds for 85 per cent. of the elements.

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the molecule. These points are consistent, and are in favour of absence of allotropy in iron.

The simple atomic constitution of the iron molecule makes it improbable that changes of physical properties of iron can be due to a rearrangement of the atoms in the molecule. It is conceivable that the two atoms may be slightly displaced relative to one another as the transformation points are passed, but we cannot regard the resulting iron molecule as a distinct type possessing a new set of properties. Moreover, from a magnetic point of view, assuming that magnetism is to be ascribed to polar molecules, however this polarity may originate, the appearance of ferro-magnetism on cooling could not be explained on such a view. Ferro-magnetism demands inter-molecular forces—the forces of crystallization—although no one doubts that inter-molecular forces and intra-molecular forces are inseparable,* and that a small change in the latter may accompany and indeed is essential in a re-grouping of the molecules. If we imagine the inter-molecular restraining forces abstracted, then the molecules of the β and γ forms of iron would be absolutely identical.

If there is no abrupt change of the atomic constitution of the iron molecule, then changes of the properties of pure iron such as occur at A_3 must be ascribed to a change of crystalline grouping of the molecules. This change must be of such a nature that the crystalline symmetry is not affected on passing A_3 ; a change of the closeness of packing of the molecules is all that is required. If the cooling through A_3 is accompanied by a closer grouping of the molecules in the direction (which is characteristic for each crystal) of spontaneous magnetization, there will be no change of crystalline symmetry, while the increased interaction between the molecules will give rise to spontaneous magnetization. The variation of molecular distances in the directions perpendicular to that of spontaneous magnetization for an individual crystal is of small importance from a magnetic point of view, for each molecule is mainly constrained by the molecule in front and the one behind in the direction of its magnetic axis.† Thus this interpretation is not necessarily inconsistent with known magnetostriction data or with determinations of thermal expansion (linear or volume) of a mass of iron crystals.

If there is a change of molecular arrangement at A_3 , then on passing this point there will be a thermal effect determined by the difference between the internal potential energies above and below A_3 . There may be an accompanying molecular distortion, but this will be slight, and (as pointed out on p. 4) cannot be regarded as implying allotropy.

The thermal energy evolved on cooling through A_3 is just the heat of transformation from a more open to a closer packed cubic system, as described above, with probably a small contribution from intra-molecular adjustment *resulting from the change of packing*. As already pointed out, these two parts of the thermal evolution are inseparable, but the existence of the second part does not justify the existence of a new type of iron molecule. Accompanying the re-grouping, the iron molecule takes up a slightly distorted appearance of the iron molecule on the other side of A_3 . Under pressure we should no doubt get a slightly different re-grouping of the molecules, and, as a consequence, a slight variation of the atomic separation in the molecule. This variation of separation will be different for different pressures, and, therefore, like the phenomenon of association mentioned on p. 129, cannot be regarded as implying allotropic change.

It is known that the transformations from ozone to oxygen and from white

* *Phil. Trans. Roy. Soc., A*, vol. 215, p. 100, 1915.

† Ewing, *Magnetic Induction in Iron and Other Metals*, 3rd edition, p. 310.

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phosphorus to red are exothermic. The thermal evolutions accompanying allotropic and isomeric changes are comparable with the heats of formation of chemical compounds, and are *in general* large compared with those involved in the passage from the liquid to the crystalline state or from one crystalline state to another.* The following are some values of the thermal evolution accompanying known allotropic and isomeric changes :—

Allotropic	{ 96 grams ozone = 96 grams oxygen + 59,200 gr.cals.
	{ 31 grams yellow phosphorus = 31 grams red phosphorus + 21,000 gr.cals.
Isomeric	{ 78 grams dipropargyl = 78 grams benzene + 100,000 gr.cals.
	{ 58 grams allyl alcohol = 58 grams acetone + 18,600 gr.cals. = 58 grams propaldehyde + 22,600 gr.cals.

With these may be compared the following values of the latent heats of fusion of some elements † :—

Element.	Latent Heat (gr.cals.).
Bismuth	13
Cadmium... ..	14
Lead	5
Silver	22
Tin	14
Zinc	28
Gallium	19
Phosphorus	5

These latter values are comparable with the thermal evolution during the transformations of pure iron. From the recalescence curves given by Dr. Arnold ‡ for this substance the rise of temperature is largest for the A_3 transformation point, and is approximately 14°C . Hence, taking the specific heat of iron as 0.1, the thermal evolution at A_3 is 1.4 gr.cals. This small thermal evolution favours the view expressed above that the A_3 transition involves a molecular re-grouping, similar to that which occurs in the ordinary process of crystallization, rather than a re-building of the internal structure of the molecule. Therefore from the thermal point of view also, allotropic change, as defined in the present Paper, appears to be absent at A_3 .

The coexistence of thermal expansion and thermal evolution on cooling through A_3 cannot be advanced as an objection to the views developed above, for the same phenomena accompany one another during the transition from water to ice.

The criterion we have adopted does not thrust upon us the difficulty of determining what is happening *at* a given temperature but upon the *sum total of what has happened during an interval of temperature*, which may be large or small, between the two states examined.

In the physical aggregation of molecules we are concerned with residual forces between two or more identical systems. The result is a slight distortion of each system, such as occurs to a small extent in the liquid state and to a larger extent in the crystalline state. In chemical combination we are concerned with a stronger and more direct action between two different systems, resulting probably in a local charging up of each system.

Let us now push our definition of allotropy one step further, and refer it not to the atomic structure of the molecule but to the electric and magnetic structure of the atom. From this point of view the iron atom in iron-

* Pattison Muir, *Elements of Thermal Chemistry*, pp. 250-3.

† *Recueil des Constantes Physiques*, Paris, 1913, pp. 323-4.

‡ *On a Fourth Recalescence in Steel*, B.A. Report, Sheffield, 1910.

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carbonyl ($\text{Fe}(\text{CO})_5$) is quite different from the iron atom in ferrous chloride ($\text{Fe}(\text{Cl})_2$). The latter compound is strongly paramagnetic, the former is diamagnetic; although chlorine and the group CO are each diamagnetic. Do we not here have a kind of atomic allotropy? In this sense the allotropic theory may be consistent with the carbide theory which attributes the properties of carbon steels to definite compounds of iron with carbon (such as cementite, Fe_3C).

I am much indebted to Sir Robert Hadfield, first for suggesting the application of the results of my earlier work to the transformation-points of iron, and second for the encouragement he has given me throughout the whole of our correspondence.

THE ALLOTROPY OF IRON.

Mr. F. C. Thompson, M.Met., B.Sc. (University of Sheffield), sent the following communication on "The Allotropy of Iron" as a contribution to the Discussion.

Since the appearance of the exceedingly important work by Burgess and Crowe* on the heating and cooling curves of very pure iron, the thermal changes accompanying the allotropic ones in that metal may be regarded as finally settled. The curves published are, with the exception of the single peak at Ar_2 , in complete agreement with the results of Arnold, but in view of the importance of the definite establishment of the existence of the thermal point Ac_2 , an independent curve is here reproduced (Fig. 1). The specimen on which the curve was taken was an exceedingly pure sample of American ingot iron made several years ago. The analysis, according to Mr. W. Bagnall, B.Met., who very kindly placed the material at the author's disposal, is:—

Carbon per Cent.	Silicon per Cent.	Manganese per Cent.	Sulphur per Cent.	Phosphorus per Cent.	Copper per Cent.	Fe per Cent. by Difference.
less than 0.01	trace	trace	trace	trace	0.02	99.97

A micrographic examination revealed merely the allotriomorphic crystals of iron without even traces of carbide, sulphide, or slag. The heating curve here reproduced was the third successive one taken *in vacuo*. The evolution of gas during heating had almost ceased, and the third and fourth curves were identical. The experiment was conducted with the new potentiometric apparatus recently installed by Professor J. O. Arnold, D.Met., F.R.S., and readings were taken telescopically about every 2°C . The existence of the point Ac_2 is obvious at 765°C ., Ac_3 being at 920°C .

The definite proof of the existence of the thermal point Ac_2 robs of much of its weight the argument of Benedicks† against the allotropy of β iron. The evolution of heat at this point‡ in what is almost chemically pure iron can be due to nothing but an atomic or molecular rearrangement. As a result of their work the investigators first mentioned § say: " . . . Nevertheless all the

* Burgess and Crowe, *Proc. Am. Phys. Soc.*, 11, 5, p. 404, November, 1913.

† Benedicks, *Journ. Iron and Steel Inst.*, 11, 1912, p. 242.

‡ The weight of the piece used was about 20 grams, which robs the curve of the beautiful sharpness of those taken by Burgess and Crowe using 0.7 grams only.

§ Burgess and Crowe, *loc. cit.*

physical properties of iron which have been studied, with the single notable exception of crystallographic structure, have shown, in the hands of one or more skilful experimenters, a distinct discontinuity for the lower critical range A_2 as well as for the upper A_3 range. For several of the phenomena, such as electrical resistance, thermo-electricity, specific heat, and magnetism, it would appear that the discontinuity is at least as great for A_2 as for A_3 , while the thermal effect has, of course, been long recognized as being much the more pronounced at A_3 ."

FIG. 1.—Heating Curve.

Ingot Iron, 99.97 per cent. Fe.

It was also found impossible to eliminate or attenuate A_2 by thermal treatment, a result incompatible with any theory of β iron as under-cooled γ iron, and, in addition, occluded gases, to which at various times so many effects have been attributed, exert no essential action on either point.

The points A_2 and A_3 , although by far the most important, are by no means the only ones at which discontinuity in a physical property or properties has been observed. With regard to the thermal point which has been supposed to exist in the neighbourhood of 600°C ., the author has been unable to observe it in spite of repeated endeavours with pyrometric appliances of the highest degree of sensitiveness, a result in accord

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with those of several other workers. At or about 830°C. , however, a marked discontinuity in the magnetic properties of iron has been detected by both Curie and Weiss and Foex.* Benedicks† also at the same temperature has observed a bending off in the dilatation curves of iron, so that still further complication of the properties of iron at high temperatures is possible. At temperatures approaching a white heat, another, and more definite, point, first suspected many years ago, seems now to be definitely established as a result of the work of Ruer and Klesper,‡ and δ iron must take its place along with α , β , and γ . This point, first detected by Ball§ in the neighbourhood of $1,300^{\circ}\text{C.}$, was ascribed by Osmond|| to oxidation of the samples, but Curie's discovery of a change of magnetic properties of pure iron in the same temperature region indicated that the "Ball" point was a true allotropic change. The pyrometric uncertainties of the earlier workers caused the point to be ascribed to a temperature about 100°C. too low, and the most exact work of Ruer and Klesper, confirmed by several other individual observers, shows that in pure iron the change from γ to δ occurs at $1,400^{\circ}\text{C.}$ This change, like that from α to β , is essentially reversible on heating and cooling. The influence of carbon in raising the temperature at which this transformation occurs is unexpected, and in mild steels certain difficulties of interpretation are still existent, but the occurrence of the fourth δ modification of pure iron seems now to be definitely proved.

The experimental material discussed above will now probably be accepted by most metallographers, but the interpretation of the facts from the point of view of the theory of allotropy is a different matter.

The extremely interesting and valuable paper of Dr. Oxley reopens the discussion of the validity of the assumption that the thermal and other changes are evidences of the existence of the allotropic modifications of iron. β iron has already borne the weight of many attacks, but the new battle-line extends to γ iron as well. To a certain extent the question of whether iron at 800°C. and iron at $1,000^{\circ}\text{C.}$ are allotropes must remain one of definition, but in the present case there is more than this, and, whether the α , β , γ , and δ forms of iron are allotropic or not, Dr. Oxley has shown beyond doubt that the nature of the allotropy is essentially distinct from that involved in the transformation from oxygen to ozone. The new definition of allotropy is on a very different plane from, for instance, Nernst's definition as a *sudden* change in internal energy, and is apparently much more narrow, so much so as to cut out almost every example of allotropy in metals, and also such a typically allotropic change as the transition from rhombic to monoclinic sulphur. It eliminates as allotropic the changes in tin which have up to the present been regarded as classical examples of such transformations in metals. A total recrystallization with a different system, e.g. rhombic to tetragonal, involving a *sudden* change of volume amounting to 30 per cent., together with alterations of electromotive force, electrical resistance, specific heat, and thermo-electric power, do not, according to Dr. Oxley, denote allotropy, since the heat change accompanying them is small. Such a standpoint will result merely in a multiplication of terms, since some other name must be found for changes of this kind.

Adopting, however, for the time being, the definition which Dr. Oxley

* Weiss and Foex, *Arch. Sci. Phys. Nat.*, **4**, 1911, 31, pp. 4, 89.

† Benedicks, *Fourn. Iron and Steel Inst.*, **1**, 1914, p. 430.

‡ Ruer and Klesper, *Ferrum*, June, 1914, **9**, p. 257.

§ Ball, *Fourn. Iron and Steel Inst.*, **1**, 1890, p. 85.

|| Osmond, *ibid.*, p. 102.

proposes, the only definite evidence of which the author is aware regarding the intra-molecular structure of the different forms of iron is the work of Weiss summarized in the *Transactions* of this Society for 1912.* As a result of his work on the "magneton" Weiss arrived at the following conclusion :—

"The experiments made on β iron have shown that its molecule is Fe_3 , that of γ iron Fe_2 , and that of δ iron is probably Fe . In nickel and cobalt the molecule above the Curie point is composed of a single atom. The magnetic forms have probably three atoms per molecule."

This is the view of Weiss in 1912, arrived at from the magneton theory five years later than that which is quoted by Dr. Oxley, that the transformation from paramagnetic γ iron to ferromagnetic δ iron is unaccompanied by any atomic change.

The researches of Honda† have failed to confirm the existence of the magneton, but for the present, and until further results are available, the work of Weiss regarding the constitution of the various modifications of iron is the only direct evidence available. Additional interest attaches to these results in that the evidence in favour of a fourth variety of iron, stable only at exceedingly high temperatures, is strongly confirmed. In a private discussion with Dr. Oxley the latter has suggested a way, however, in which the two antagonistic views of Weiss may be reconciled.

The American investigators whose work has already been quoted have endeavoured to exclude β iron from the position of a definite allotrope, since crystallographically it is regarded as strictly isomorphous with α iron.‡ This was the conclusion arrived at by Osmond and Cartaud§ as a result of their experiments on the reduction of iron salts at temperatures within the different critical ranges. The same investigators, however, were able later|| to amplify these results, and were able to interpret their newer work on the figures produced in iron by plastic deformation, on twinning, etc., as follows :—

"One is led to think that the mesh of α iron is a simple cube, and that of γ iron a cube with centred faces; then that of β iron would be a centred cube. The only positive conclusion that we can draw from these researches is that *the three (α , β , and γ) allotropic varieties of iron, although they all crystallize in the cubic system, present well-marked specific characters, and cannot have the same internal structure.*"

These crystallographic results point merely to a different mode of packing of the iron molecules, which, beyond suffering slight distortion as a result, might be essentially unaltered. The magnetic work of Weiss has rendered it highly probable, however, that the differences extend beyond the mere molecular packing, each molecule having a definitely different atomicity. Combining these two results, the question of the allotropy of iron seems to have been placed beyond question.

If the paper of Dr. Oxley had been confined to no more than the novel and extremely valuable thermal argument concerning allotropy, it would have been of the highest service in arriving at definite conclusions. His new line of thought is of immense help in affording an insight into the whole question. The results, taken as a whole, are decidedly antagonistic to the allotropic standpoint, and at any rate the immense advance has been made that the allotropy of iron and that of oxygen differ in essentials.

It may be doubted, however, whether the evidence is so overwhelmingly

* Vol. viii., p. 153.

† Honda and Takagi, *Four. Iron and Steel Inst.*, I, 1915.

‡ Burgess and Crowe, loc. cit.

§ Osmond and Cartaud, *The Crystallization of Iron*.

|| Ibid., *Four. Iron and Steel Inst.*, III, 1906, p. 486.

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against the allotropy of iron as Dr. Oxley himself thinks. In the first place, a definition of allotropy which will, in practice, depend on whether the accompanying heat change is large or small is somewhat unsatisfactory. To the author, a definition such as the one due to Nernst, based on *sudden* changes of physical or chemical properties, appears far more workable. If Nernst's view be adopted that an allotropic change is one resulting in a *sudden* change of internal energy, the allotropy of iron is established. Again, the application of Dr. Oxley's thermal test to the allotropic changes in iron, and equally in other metals, is complicated by the fact that the heat effect observed is the algebraical sum of several changes of which the allotropic change is only one. At Ar_3 , when γ iron changes to β , a "decrystallization" of the γ iron and a recrystallization of the amorphous material which results to form β iron crystals also occur, both changes from which thermal evolutions or absorptions may be expected. To state exactly the quantity of heat evolved, due solely to the change of allotropic form, is therefore a matter of difficulty. The most serious objection to the thermal solution appears to be the fact that practically every case of well-defined metallic allotropy is excluded, the fate also of other examples in non-metallic elements which have been regarded as typical. Among the metals no example of allotropy has been examined more carefully, nor apparently received stronger confirmation, than the change from grey to white tin. The remarkably important physical changes which result from this transformation are too well known to need repetition,* but the heat change per gram at 0°C . is only 4.5 gm.-cals.† The thermal argument of Dr. Oxley would make this change, therefore, inter-molecular rather than intra-molecular, and hence not allotropic. Similarly, the heat change per gram in the change from α cadmium to γ ‡ cadmium is only 6.6 gm.-cals., whence the allotropic nature of this change would also be denied. *The final proof that this definition of allotropy is too narrow is obtained from the fact that, since the heat change per gram is but 3.2 gm.-cals.,§ the transition from rhombic to monoclinic sulphur is not an allotropic one.*

Two further points may deserve brief reference. The relationship which the temperature at which allotropic changes take place bears to the pressure and to the presence of dissolved substances is well known, and it is of interest to discover to what extent the changes in iron usually referred to as allotropic follow similar laws.

If T is the absolute temperature of the transformation, r the heat change in gm.-cals. per gram, and σ and τ the specific volumes of the allotropes at temperature T , then the change of the temperature of the transition with pressure

$$\frac{dT}{dp} = 24.2 \frac{T(\sigma - \tau)}{1,000 r}.$$

For the β to γ change in iron, $T = 916^\circ\text{C}$. ($1,189^\circ\text{A}$.) and r is 1.4 gm.-cals.

According to Benedicks|| the linear change due to the transformation is 0.082 per cent., corresponding to a volume change of 0.25 per cent., whence :—

$$\begin{aligned} (\sigma - \tau) &= .0025 \times 0.13 = .000325 \\ \therefore \frac{dT}{dp} &= 0.0067^\circ\text{C. per atmosphere pressure.} \end{aligned}$$

$$= 1.02^\circ\text{C. per ton per sq. in.}$$

* Cohen, *Trans. Far. Soc.*, VII, 1911, p. 122. † Ibid.,¹ May, 1915, x., p. 231.

‡ Ibid., May, 1915, x., p. 233.

§ Nernst, *Theoretical Chemistry*, 1911, p. 642.

|| Benedicks, *Four. Iron and Steel Inst.*, I, 1914, p. 429.

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So far as the author is aware there are no experimental determinations available for the checking of this value. Roberts-Austen commenced some work* which led to no definite result with regard to Ar_3 and does not appear to have been continued. It may be said with confidence, however, that the result is of exactly the right order of magnitude, a statement which is strongly confirmed by the cooling curves obtained from a 0.9 per cent. carbon steel under no pressure and under one of 30 tons per sq. in. The pressure has caused the depression of the point $Ar_{3,2,1}$ by about 40° C., and since the absence of any appreciable volume change at Ar_2 means that the pressure is without influence on the temperature at which this change occurs, the exact correspondence of the observed fall with that calculated for Ar_3 is the more interesting.

Tammann† has made the same calculation, using earlier and less accurate data. The results obtained were not considered to be in accord with the experimental data.

Attention may now be turned to the effect of dissolved substances, the depression of temperature caused by which is proportional to the number of molecules (in the case of metals, atoms) of the solute added. The author is at present engaged in work intended to investigate the constitution of carbon and special steels from this depression of the allotropic points, but for the present the following table will indicate that the A_3 change-point is governed by laws exactly the same as those holding for others which are undoubtedly allotropic. The figures for the nickel and chrome steels are those of McWilliam and Barnes,‡ and that for tungsten is due to Swinden.§

TABLE I.

Percentage of Dissolved Element.	Temperature of Ar_3 .	Depression Ar_3 .	Atomic Weight.	Atomic Depression.
	° C.	° C.		° C.
Pure iron	897	—	—	—
0.22 per cent. carbon ...	830	67	12	3,660
1.98 per cent. chromium ...	785	112	52	2,940
3.05 per cent. nickel ...	728	169	58.7	3,250
3.24 per cent. tungsten ...	845	52	184	2,950
			Mean	3,270

These results, considering the divergent sources of the temperatures of Ar_3 , are sufficiently concordant to show that *the temperature of the A_3 change, like every allotropic change, is depressed by an amount proportional to the number of atoms of the dissolved substance.*

CONCLUSIONS.

1. Sudden changes in the directions of one or more curves showing the relationships of the physical properties of iron to temperature indicate with certainty the existence of α , β , γ , and δ iron, with change-points at 768° C.,

* Roberts-Austen, *Jour. Inst. Mech. Engs.*, April, 1893.

† Tammann, *Zeit. f. Anorg. Chem.*, p. 126.

‡ McWilliam and Barnes, *Jour. Iron and Steel Inst.*, I, 1911, p. 280 and I, 1910, p. 255.

§ Swinden, *ibid.*, 1907.

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900°C. and 1,400°C., while another slight change has been detected magnetically and dilatometrically at about 830°C.

2. The A_3 point in iron, taken as typical of all the changes, is shown to obey the same laws as hold for other acknowledged allotropic transformations.

3. Magnetic evidence is available that the molecule of β iron is Fe_3 , of γ iron Fe_2 , and of δ iron Fe .

4. A distinct mode of packing of the α , the β , and the γ molecules is indicated crystallographically.

5. Thermally it may be shown that the changes occurring in iron are of the same nature as those which occur in other cases of allotropy in metals, e.g. tin and cadmium, and also as in the case of the change from rhombic to monoclinic sulphur.

The author is therefore strongly of the opinion that the transformations in iron are essentially allotropic. At the same time he dissociates himself entirely from the view that to any of the allotropic forms *per se* is the hardness of hardened steel due. Some of the modifications will dissolve carbon as Fe_3C and some to all intents will not, but in this fact alone does the allotropy of iron bear on the constitution of steel. Whether iron is allotropic or not, it is to the solution of Fe_3C in it that the characteristic properties of hardened steels must be ascribed. The views of Arnold²⁸ expressed in 1895 are essentially accepted to-day by the majority of metallographers, and the "hard β iron" to which, according to the "allotropic school" of metallurgists, the strength of hardened steels was due, is dead.