was determined by means of the solubility curve. A mixture of 2,4-dimethylpyridine and water was distilled, and the distillate which boiled constantly at 96.5° consisted of two layers. When the distillate was cooled below 23.2°, it became homogeneous. Reference to the misci-bility data showed that it contained 66% of water.

Summary.

The densities of aqueous solutions of pyridine, 2-methylpyridine and 3-methylpyridine have been determined. The compositions of the con-stant-boiling mixtures have also been ascertained, and found to be 42%, 48% and 61% of water respectively. Solubility data for 2,4-dimethyl-pyridine have also been given.

MANCHESTER, ENGLAND.

A THEORY OF ALLOTROPY.

By MAURICE COPISAROW.

The term *allotropy* was first introduced by Berzelius,[1] as denoting the appearance of an element in several states distinguished from one another by different properties, a definition lacking in precision, owing to the numerous possible interpretations of the "different properties."

Allotropy is taken as a term covering the different physical states of matter, and also isomerism, polymerism and polymorphism,[2] and in this sense might appear, perhaps, to be an unnecessary term without exact meaning in chemical nomenclature.

This inclusion of different phenomena, along with Ostwald's and Nernst's definition of allotropy on the basis of energy changes, and Benedick's, Honda's and Le Chatelier's conception based upon the discontinuity of forms, phases and properties, is due to the consideration of *effects* of, in-stead of *causes* underlying phenomena.

While a close study of the various properties of matter consequent to a certain phenomenon may help us in comprehending the phenomenon itself and its relationship to other natural manifestations, it is wrong to define a phenomenon by its effects, especially when these effects are anything but specific or characteristic. A far truer and more productive definition would be based upon the study of the *causes* of a phenomenon, the un-masking of which should naturally throw much light upon the phenomenon itself and its probable effects.

The possible causes of allotropy may be either (a) a variation in the intramolecular structure of elements, or (b) a change in the intermo-lecular association or aggregation of elements.

[1] Berzelius, *Jahresber.* **20**, [II] 13 (1841).

[2] Lehmann, *Z. Kryst. Min.*, **1**, 97 (1877); Lowry, *Trans. Faraday.*, **11**, 150 (1916).

Considering that (1) molecular aggregation subject to the laws of crystallography accounts for polymorphism,[3] and that (2) allotropic modifications present in most cases considerable chemical and physical differences, it would appear that allotropy is due to intramolecular differences.[4] We can regard allotropy not only as a function of valence, but also define it as the capacity of an element to exist in forms differing in the mode of their intramolecular linkage.

The conception of valence adopted by the author is that represented by the "primary valence" of Abegg and Werner.

This conception of allotropy is in full accord with (a) the hypothesis of dynamic allotropy,[5] as on this basis only a simple space lattice, revealed by the reflection of X-rays from the internal planes of crystals, can be deduced; and (b) the *view* of different ions existing in solution in presence of two allotropes of an element.[6]

In this sense allotropy, although a function of valence, does not imply isomerism or polymerism, as allotropes need not necessarily contain the same or a multiple number of atoms in their respective molecules. This conception of allotropy can be clearly understood on the basis of the electronic theory. According to this theory the valence bonds are considered as having a definite direction. The relative direction of these bonds in the molecule may be influenced by the conditions under which such a molecule is formed. Variation in the direction would give rise to molecular structures differing in the distribution of electric charges among the constituent atoms. These would be allotropes, and that configuration in which the charges were most symmetrically arranged or neutralized would be the stable form under these conditions.

Recognizing allotropy as a function of valence and knowing the valence of an element (the maximum one in case of elements of variable valence), we should be able to indicate not only the possible constitutional formulas of allotropes, but also the maximum number of allotropes possible for each individual element. Studying the possible constitutional formulas for molecules of elements on the basis of their valences we find that the problem resolves itself into the definition of the number of possible conditions or modes of freedom of an atom of the element in question.

I. An atom of the monoatomic *inert* gases can exist in *one* condition only.

[3] Wyroubow, *Bull. sos. min.*, **26**, 335 (1906).
[4] Blanshard, *Chem. News*, **70**, 295 (1894).
   Köppel, *Naturw. Rund.*, **19**, 249, 261 (1904).
   Guthrie, *J. Roy. Soc. N. S. Wales*, **14**, 318 (1911).
   Oxley, *Trans. Faraday Soc.*, **11**, 129 (1916).
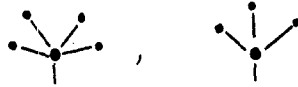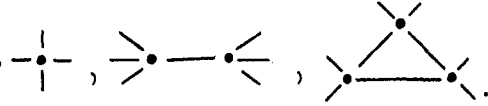[5] Smits, *Verslag. Akad. Wetenschappen Amsterdam*, **19101–920.**
[6] Holt, *J. Soc. Chem. Ind.*, **34**, 693 (1915).

II. An atom of a *monovalent* element can exist in *two* conditions only: (*a*) fixed valence, •——•; (*b*) free valence, •—— . Halogens at high temperature and probably nascent hydrogen are cases of monovalent elements containing a free valence.

III. An atom of a *divalent* element may exist in *two* conditions only (*a*) fixed valence, ; (*b*) free valence, —•——•—— or valences, —•——

IV. An atom of a *trivalent* element may exist in *two* forms only: (*a*) a saturated state with no free valences, , (*b*) an unsaturated condition with free valences.

V. An atom of a tetra-, penta- or other polyvalent element may exist in *three* forms or conditions only: (*a*) a saturated condition, in which the atom is rigidly fixed, ; (*b*) an unsaturated condition, in which the atom is rigidly fixed by having three or more of its valences fixed,

; (*c*) an unsaturated condition, in which the atom is not rigidly fixed,

It appears that while a polyvalent atom linked to one or two other atoms has the power of free rotation (the valences being regarded as axes, representing polar forces, the axis of rotation may not be common to any valence, but represented by the resolved effect of all valences concerned), an atom linked to 3 or more atoms has no such power of rotation, and can be regarded as rigidly fixed. As atoms of each condition can form by their combination with one another one and only one distinct molecular form, and as a combination of atoms, individually in different states, is most improbable, we are justified in concluding the maximum number of allotropic modifications of an element under the most favorable conditions of temperature and pressure (forms not neccessarily occurring in *all* physical states) to be as follows: (1) the inert gases may exist in *one* form only; (2) the mono-, di-, and trivalent elements may exist in *two* forms only; and (3) the tetra-, penta- and other polyvalent elements may exist in not more than *three* distinct intramolecular forms.

While the valence of an element determines the number of possible allotropes, comparative examination of the chemical and physical properties of any element in all its forms should enable us to define with fair precision the intramolecular structure of each allotrope.

A scrutiny of the possible molecular forms of elements shows that theoretically it is possible for an element to have in certain cases more than one molecular form corresponding to each mode of linkage indicated above; that is, there may occur more than one form of an element with a rigid or non-rigid configuration. But regarding allotropes as the most chemically and physically distinct forms of an element it is obvious that several molecular forms, each containing a different number of atoms, but all having the power of free rotation, will differ among themselves to a less extent than when compared with a molecular structure of the same element, in which all atoms are rigidly fixed. Thus it follows that valence and the saturation or fixation of the atoms, and not the actual number of atoms, play the predominant part in the determination of allotropes. In this light allotropy becomes the capacity of an element to exist in forms differing in the mode of their intramolecular linkage. Molecular forms differing in the number of atoms or distribution of linkages, but all belonging to one and the same type of mode of linkage indicated above can be termed *allotropoids*. These molecular forms serve as a transition or link between polymorphism and allotropy proper. Each modification of an element, which is an allotropoid in relation to forms belonging to the same mode of linkage, is an allotrope when viewed in connection with modifications belonging to a different type of linkage. Allotropoids differ among themselves less in physical, and still less in chemical properties than allotropes of the same element.

The problem of discriminating between allotropy and polymorphism or intra- and inter-molecular structures,—comparatively easily solvable in the case of a few advanced characteristic instances, becomes therefore complicated and the available methods uncertain, not only owing to the inert character of some elements, which compels us to draw conclusions from their physical properties only, but also owing to the fact that in some cases we may deal with substances which are simultaneously either (1) allotropes and polymorphic forms, or (2) allotropoids and polymorphic forms. Thus the physical data may indicate the combined effect of intra- and inter-molecular rearrangements in the element; and as the components, the combination of which gives us the total effect, need not necessarily be magnitudes in the same direction, the physical data lose much of their comparative value.

The knowledge of the maximum possible number of allotropes, serving as a guiding limitation, augmented by the chemical and physical properties of the modifications, should be sufficient in most cases in identifying the

allotropes of an element. In cases where owing to the inertness of an element we have to depend upon the physical factor only, as many physical properties as possible are to be taken into consideration, since no single feature or property is sufficiently characteristic to serve as a decisive indication of allotropy. The functional connection of physical constants with the periodic system of atomic weights and volumes of elements make it very necessary, if any generalizations are to be made, to have the experimental conditions for the determination of physical constants specific for every element with special relation to the absolute melting and transition points of every modification of an element.[7]

Differences in crystalline symmetry are indefinite as a criterion or definition of allotropy, owing to the possibility of substances belonging either to different crystalline systems or different classes of the same system. The observation that the higher the crystalline symmetry of an element the smaller is the number of atoms constituting its molecule,[8] and consequently the smaller is its tendency to allotropy[9] is of an empirical character, and can hardly serve as a guiding principle in distinguishing allotropic from polymorphic forms, this being especially so as crystalline structures may depend at least as much upon molecular aggregation as on the intramolecular configuration of the atoms.

The sudden changes in the discontinuity of properties can be accepted as an indication of allotropy but with reserve, not only owing to the difficulty of establishing such discontinuity,[10] but also owing to the fact that such changes accompany both allotropy and polymorphism, and if there is any difference, it is in the degree, not the kind of change. The thermal changes so characteristic of the most pronounced allotropic transformations of the non-metallic elements, though often very useful as an indication, are not completely to be relied upon, as all thermal measurements for metals give decidedly lower values than for non-metals, and considerable changes of volume, hardness, porosity, electromotive forces, electrical resistance, specific heat, and the thermo-electric power are not necessarily accompanied by great heat changes. Considerable heat changes may be taken as a positive indication of allotropic rearrangement, but small heat changes are hardly safe as a negative proof, the more so as the heat evolution actually recorded may be the sum of two or more values of reactions, some exothermic and others endothermic.

As mentioned above, the allotropes of metals are more difficult to isolate and distinguish, than those of the non-metals. But even in cases

[7] Copisarow, *J. Inst. Metals*, **20**, 98 (1918).

[8] Retgers, *Z. physik. Chem.*, **14**, 1 (1894).

[9] Barlow and Pope, *J. Chem. Soc.*, **81**, 1741 (1906).

[10] Honda, *J. Iron Steel Inst.*, **91**, 199 (1915); *Science Repts. Tohoku Imp. Univ.*, [4] **3**, 261 (1915).

when no separate allotropic modifications have been isolated, (a) the dependence of such physical properties as density, specific heat, expansion, electrical conductivity, and the melting, solidification, and transition-points upon the thermal history of the specimen, and (b) the variation of the chemical behavior with the past history of the metal, are best explained on the basis of the allotropy hypothesis.

The constitutional formulas of allotropes developed on the basis of valence and the chemical and physical properties of each modification, although not actually solving the interesting problem of molecular complexity, offer us substantial aid in this respect, insofar as they often indicate the minimum molecular complexity satisfying the requirements of the formulas.

The consideration of the allotropy of elements, applying to elements mainly in their solid state, throws incidentally much light upon the general constitution of the solid state of matter.

The modern X-ray spectrometric investigations, though failing to indicate the display of forces between atoms, are showing the positions of atoms in space, thus affording a possible method of study of allotropes. Now as characteristic cases of allotropy we may discuss the allotropy of phosphorus, carbon, iron and nickel.

Allotropy of Phosphorus.

The number of forms of phosphorus recorded from time to time in the literature is considerable. In several instances, however, a difference in color, mode of fracture, size of particles or slight deviation in the specific gravity (regardless of impurities) was taken as a sufficient basis for the announcement of a new form of phosphorus.

In addition to the white (ordinary, colorless or yellow) and red phosphorus, the following are described as distinct modifications: (1) *black* phosphorus (Thénard[11]); (2) *red* phosphorus, soluble in alkalies (Schenck[12]); (3) *scarlet* (ruby-red) phosphorus (Troost and Hautefeuille[13]); (4) *dense-red* phosphorus (Bridgman[14]); (5) *violet* (metallic or crystalline) phosphorus (Hittorf[15]); (6) *black* phosphorus (Bridgman[14]). Thénard's black phosphorus was proved by Blondlot, Ritter and Gernez[16] to be ordinary red phosphorus, contaminated with mercury and arsenic. Schenck's soluble red phosphorus appears to be ordinary red phosphorus in a state

[11] Thénard, *Compt. rend.*, **95**, 409 (1882).
[12] Schenck, *Ber.*, **36**, 979, 4202 (1903).
[13] Troost and Hautefeuille, *Compt. rend.*, **78**, 748 (1874).
[14] Bridgman, THIS JOURNAL, **36**, 1344 (1914).
[15] Hittorf, *Pogg. Ann.*, **126**, 193 (1865).
[16] Blondlot, *Compt. rend.*, **70**, 856 (1870); **78**, 1130 (1874). Ritter, *ibid.*, **78**, 192 (1874). Gernez, *ibid.*, **151**, 12 (1910).

of fine division.[17]   Troost and Hautefeuille's intensely colored form of phosphorus, as well as Bridgman's dense-red phosphorus, differing from red and Hittorf's violet modifications in no other property than color and a very slight deviation in specific gravity, must be regarded as belonging to one of the latter forms.   Notwithstanding the considerable attention paid by investigators to ordinary red and Hittorf's violet phosphorus the question of their distinct character or individuality still remains unsettled.[18]   But even assuming that red and violet phosphorus exist as two separate forms, we must admit that the very slight difference in physical properties, and the absence of any chemical differences make the contrast between red and violet phosphorus in no way as pronounced as that with either white or Bridgman's black modification.   The character of the possible co-existence of red and violet phosphorus will be discussed at a later stage.   Black phosphorus[19] must be regarded as a distinct modification of phosphorus, as it is characterized by its high density, conductivity of heat and electricity, low specific heat and vapor pressure, and general stability.   Thus we find that phosphorus occurs in three chemically and physically distinct forms: (1) white, colorless or yellow; (2) red, and Hittorf's violet or metallic; and (3) black phosphorus.

Now on the basis of the theory of allotropy phosphorus, being pentavalent, may exist in *not more* than three chemically and physically distinct forms: (I) a *non-rigid* molecular form, in which *some* valences are

free,   (formula) ,   (formula) ,   (formula) ; (II) a *rigid* molecular
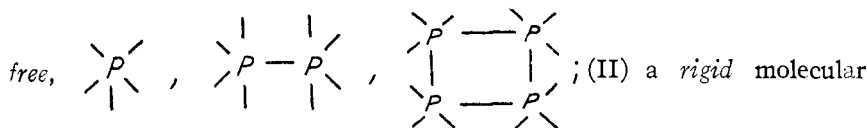
form, *some* valences of which are *free* (Fig. 1, tetrahedron); (III) a *rigid* molecular form, *all* valences of which are *fixed* (Fig. 2, icosahedron).

It is clear from the three constitutional formulas that a molecule represented by non-rigid configuration (Class I) will be characterized by comparative reactivity, small specific gravity, high vapor pressure, low melting point, etc.

A molecule represented by a rigid configuration (Class III) will exhibit properties exactly opposite to those just indicated, while the molecular structure, Class II, will be intermediate in all its properties.   Comparing

[17] Pedler, *J. Chem. Soc.*, **57**, 599 (1890).

[18] Wegscheider and Kaufler, *Monatsh.*, **22**, 700 (1901).
        Linck and Möller, *Ber.*, **41**, 1404 (1908).
        Jolibois, *Compt. rend.*, **151**, 382 (1910).
        Stock, Schrader and Stamm, *Ber.*, **45**, 1514 (1912).

[19] Bridgman, THIS JOURNAL, **38**, 609 (1916).
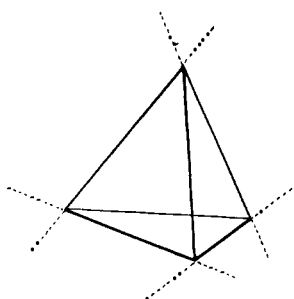   Smits, Meyer and Black, *Verslag Akad. Wetenschappen Amsterdam*, **18**, 992 (1916).
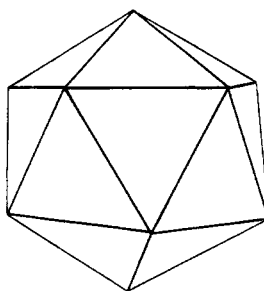
Fig. 1.

Fig. 2.

the physical and chemical properties of white, red (violet) and black phosphorus with those which we may exect to accompany certain molec-

Form of Phosphorus.	Vapor Press. (400–447°) Mm. of Hg.	Sp. Gravity.
White	570.	1.83
Black	58.5	2.691
Red. i. ordinary	164.0	
ii. Troost and Hautefeuille	133.0	2.05
iii. Bridgman	73.2	to
iv. violet	93.0	2.34

ular configurations, we find no difficulty in assigning to each distinct form of phosphorus its constitution formula, viz., white, Class I; red, Class II; and black, Class III.

The following considerations show not only the existence of a striking agreement between the theory of allotropy and the deductions based upon it, and the experimental facts, but also the remarkable way in which this theory elucidates and consolidates isolated and uninterpreted facts.

1. Class I may be taken as a just representation of the constitution of both white phosphorus and phosphorus vapor since the molecular complexity of white phosphorus,[20] as well as that of phosphorus vapor[21] is represented by P_4 and the transition of white phosphorus to vapor is reversible.[21]

2. A regular tetrahedron (P_4), is a correct representation of the molecular constitution of red phosphorus, as (a) the vapors of white, red and black phosphorus are identical; (b) the transition from red phosphorus

[20] Schenck, Ber., **35**, 351 (1902).
Stock, Gibson and Stamm, ibid., **45**, 3527 (1912).
[21] Mitscherlich, Ann., **12**, 137 (1834).
Deville and Troost, Compt. rend., **56**, 891 (1863).
Paterno and Nasini, Ber., **21**, 2153 (1888).
Hertz, Z. physik. Chem., **6**, 358 (1890).
Beckmann, ibid., **5**, 76 (1890).
Chapman, J. Chem. Soc., **75**, 735 (1899).

to vapor is irreversible; and (c) the transformation of white to red phosphorus is a monomolecular reaction.[22]

The transformation of white to red phosphorus is represented by the passage from a *plane* configuration to a *three-dimensional* structure.
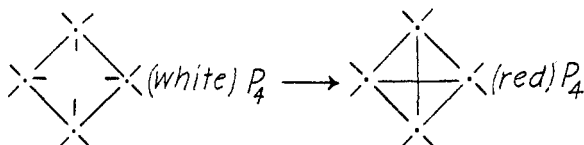

3. A close examination of the constitution formulas deduced above for white, red and black phosphorus offers us a clear explanation of the fact observed by Bridgman,[19] *i. e.*, the transformation of white phosphorus to black, and the failure of red (or violet) to undergo such a change.

No polymerization unaccompanied by a complete disruption of the molecule can transform a molecular structure represented by a tetrahedron (red phosphorus) into one represented by a regular icosahedron (black phosphorus). On the other hand the transformation of white phosphorus to black is constitutionally a simple polymerization closely resembling the acetylene ⟶ benzene transformation, *viz.*, $3 P_4 = P_{12}$.

Following up this polymerization we see that there is a probability of an intermediate stage or form between white and black phosphorus.

The *plane* configuration of white phosphorus probably passes at 200° and 11000–12000 kg./cm². pressure, through an asymmetric, apparently unstable, *two-plane* form, before polymerizing to black phosphorus.
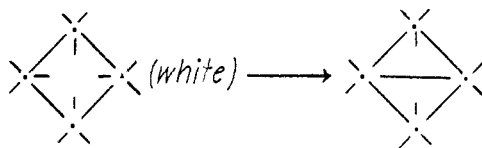
This consideration is in remarkable agreement with Bridgman's observation of a preliminary reaction, a "preparation-period" in the transformation of white to black phosphorus.

The question of violet phosphorus, as previously indicated, is still unsettled; but even assuming that violet phosphorus is a distinct form, such an assumption would in no way undermine the validity of the theory of allotropy.

As indicated in the theory of allotropy in case of polyvalent elements more than one molecular form, belonging to the same type of configuration, is possible, *i. e.*, molecular forms differing in the number of atoms, without any radical difference in the mode of linkage. Thus a molecular con-

[22] Schenck, *Ber.*, **36**, 4202 (1903).

figuration, P_8, represented by a cube (see Fig. 3) would offer a satisfactory conception of the constitution of violet phosphorus, as such representation similar to Fig. 1 assigned to red phosphorus would be a *rigid* form, containing *free* valences. A molecular form of such constitution, a direct product of polymerization of white phosphorus by the condensation of two molecules, would be quite tangible, as the conditions of transformation of white to violet are more drastic than those of white to red phosphorus.

Therefore, should the separate existence of red and violet phosphorus be established, they will have to be regarded as *allotropoids* in relation to each other, and as *allotropes* in relation to *white* and *black* phosphorus. P_1 and P_2, the high temperature dissociation products of phosphorus vapor,[23] belonging qualitatively to the molecular structure represented by by Class I are hence *allotropoids* in relation to the vapor P_4 and white phosphorus, and *allotropes* in relation to red (violet) and black phosphorus.
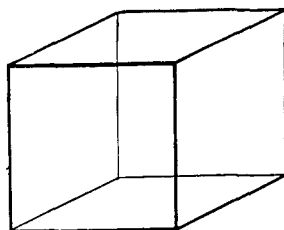

Fig. 3.

Allotropy of Carbon.

In the light of the chemistry of carbon compounds a carbon atom can be regarded as always potentially tetravalent. The polyatomicity of a carbon molecule is proved by (1) the existence of several distinct forms of carbon; (2) the high volatilization point of carbon; (3) the products of moist oxidation; (4) the combustion of carbon;[24] (5) the X-ray spectrometric study of the modifications of carbon.[25] Attempts have been made to study the complexity of carbon molecules and to establish the constitutional molecular formulas of one or more forms of carbon by Kekulé,[26] Vaubel,[27] Barlow and Pope,[28] Dewar,[29] Aschan,[30] Dimroth and Kerkovius,[31] Bragg,[32] Meyer,[33] and Debye and Scherrer.[25]

Reviewing these investigations we find that a method of study so general as to be applicable to all forms of carbon has not yet been proposed.

[23] Preuner and Brockmöller, *Z. physik. Chem.*, **18**, 129 (1913).
Stock and Stamm, *Ber.*, **46**, 3497 (1913).

[24] Rhead and Wheeler, *J. Chem. Soc.*, **97**, 2181 (1910); **99**, 1140 (1911); **103**, 461 (1913).

[25] Debye and Scherrer, *Physik. Z.*, **17**, 277 (1916); **18**, 291 (1917).
Olie and Byl, *Verslag Akad. Wetenschappen Amsterdam*, **19**, 920 (1917).

[26] Kekulé, *Z. angew. Chem.*, **12**, 950 (1899).

[27] Vaubel, *ibid.*, **13**, 60 (1900).

[28] Barlow and Pope, *J. Chem. Soc.*, **89**, 1742 (1906).

[29] Dewar, *Chem. News*, **97**, 16 (1908).

[30] Aschan, *Chem. Ztg.*, **33**, 561 (1909).

[31] Dimroth and Kerkovius, *Ann.*, **399**, 120 (1913).

[32] Bragg, *Proc. Roy. Soc.*, **89A**, 280 (1913).

[33] Meyer, *Monatsh.*, **35**, 163 (1914).

While the method of moist oxidation can be applied more or less successfully to amorphous carbon and to some extent to graphite, the X-ray method is confined to diamond with a somewhat strained extension to graphite.

Now if we consider the problem from the point of view of valence, *i. e.*, molecular structure, we secure at once a general method of investigation. In the light of the theory of allotropy, carbon having a valence greater than three may exist in three distinct molecular forms: (I) a *non-rigid*
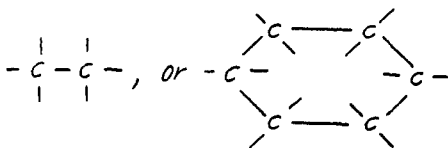
molecular configuration, some valences of which are *free* (see also Fig. 4); (II) a *rigid* molecular configuration, some valences of which are *free* (see Fig. 5); and (III) a *rigid* molecular configuration, all valences of which are fixed (see Fig. 6).
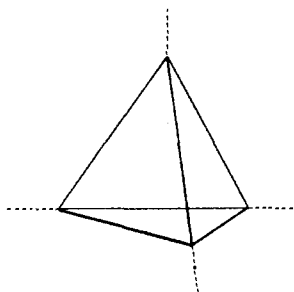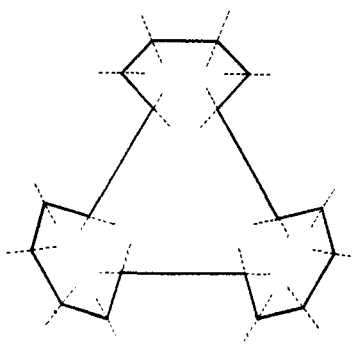

Fig. 4.   Fig. 5.

The several new modifications of carbon (graphitoid, graphitite, etc.) suggested by Brodie, Berthelot, Luzi and others have been proved to be either compounds, solutions or mixtures of carbon with some other elements.[34]

[34] Porcher, *Chem. News*, **44**, 203 (1881).

Bartoli and Papasogli, *Gazz. chim. ital.*, **12**, 113 (1882); **13**, 37 (1883); **15**, 445 (1885).

Moissan, *Compt. rend.*, **116**, 609 (1883); **119**, 976 (1894); **120**, 17 (1895); **121**, 540 (1895); *Ann. chim. phys.*, [VII] **8**, 289, 306, 466 (1896).

Wiesner, *Monatsh.*, **13**, 371 (1892).

Weinschenk, *Z. Kryst. Min.*, **28**, 291 (1897).

Hyde, *J. Soc. Chem. Ind.*, **23**, 300 (1904).

Trener, *Jahresber. Geol. Reichs. Wien.*, **1906**, 405; *Z. Kryst. Min.*, **46**, 124 (1909).

Charpy, *Compt. rend.*, **145**, 1173 (1907); **148**, 920 (1909).

Le Chatelier and Wologdine, *ibid.*, **146**, 49 (1908).

Debye and Scherrer's[25] experiments merely indicate the presence of graphite in amorphous carbon, and the absence of other crystalline forms. These experiments afford, however, no ground for the unification of graphite with amorphous carbon.

No matter how finely divided graphite may be (Acheson's or "colloidal" graphite), its behavior towards moist oxidants, its products of oxidation, mode of combustion and physical properties—all greatly differ from those of amorphous carbon.

Meyer[33] and Meyer and Steiner,[35] recording the dependence of the yield of mellitic acid from charcoal upon the latter's source and temperature

Fig. 6.

of carbonization, express some doubt as to the entity of the carbon "molecule" and the close connection of its constitution with the product of oxidation. Now the yield of mellitic acid *does* vary with the sources of the charcoal employed, and the temperature, pressure and duration of carbonization; but the formation of the mellitic acid cannot be attributed to the presence of complex hydrocarbons, possibly retained by the charcoal carbonized at a comparatively low temperature, since a quantitative determination of the percentage of hydrogen, oxygen and nitrogen, invariably accompanying this kind of charcoal, gives not more than 1% of these elements, while the yield of mellitic acid reaches as high a value as 40%. The dark residue "mellogen,"[36] remaining after the first oxidation, gives on exhaustive oxidation again mellitic acid and also some oxalic acid. To attribute the varying yields of mellitic acid to the existence of several modifications of amorphous carbon, as some investigators are inclined to do, is quite unwarranted, as such an explanation of the somewhat varying quality and properties of charcoal would necessitate the assumption of a whole series of modifications of amorphous carbon, corresponding to every source of charcoal and practically to every change of 20° to 50° in the temperature of carbonization. The causes of the dissimilar behavior of various samples of charcoal are probably much simpler. Such causes may be (a) a high temperature of carbonization, which reducing the porosity of the resulting amorphous carbon or charcoal, increases in consequence its resistance to oxidation; (b) a high temperature of carbonization, which facilitates the conversion of amorphous carbon into graphite, so that we may deal with charcoal containing a high percentage of finely divided graphite;[37] (c) a high percentage of mineral matter,
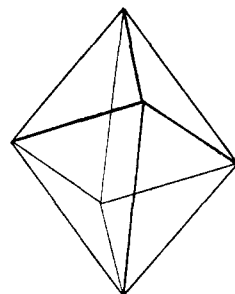
[35] Meyer and Steiner, *Monatsh.*, **35**, 475 (1914).
[36] Bartoli and Papasogli, Reference 34.
    Dickson and Easterfield, *Proc. Chem. Soc.*, **1898**, 163.
[37] Arsem, *Trans. Am. Electrochem. Soc.*, **20**, 105 (1911).

contaminating charcoal, may affect its properties in more than one way.

Thus we find that there are three distinct forms of carbon, corresponding to the three, theoretically possible, fundamentally different configurations. The following considerations may help to assign to each modification its constitutional formula. The calorimetric measurements of the heat of complete combustion of carbon per gram-atom give[38] for amorphous carbon, 97.650 Cals.; for graphite, 94.810 Cals.; and for diamond, 94.310 Cals. These figures indicate the sum total of the energy liberated during the formation and degradation of the possible complexes[24] plus that of the oxidation of the carbon monoxide to carbon dioxide.

It must be noted that the calorimetric measurements of the heats of combustion of the modifications of carbon differ considerably with every experimenter.[39] Taking equal weights of amorphous carbon, graphite and diamond, and subjecting them to complete combustion, we find that the amount of heat evolved is different for each form of carbon, although the number of atoms taken and the number of molecules of carbon dioxide formed is identical in all cases.

Looking for the cause of this dissimilarity of thermic values we are driven to attribute it to the different stabilities of the molecules in the three cases, which must depend upon the mode of linkage of the units constituting the molecule, as well as the complexity of the molecule itself.

Returning to our classification of theoretically possible configurations we expect that the least stability will be exhibited by molecules whose units have the power of·free rotation or, in other words, which have more than one free valence; the maximum stability will be found in the molecule, all constituent units of which are in a state of rigidity and all valences fixed; the intermediate case being a molecule which has some valences free, but a rigid structure.

Now considering the fact that the greater the stability the smaller will be the evolution of heat on complete combustion (compare the case of phosphorus), and correlating this with the calorimetric measurements quoted above, we find that amorphous carbon is represented by Class I, where *none of the atoms* is rigid; graphite by Class II, where the atoms are rigid, but *some* valences free; and diamond by Class III, in which all atoms are rigid and *all* valences fixed. These deductions find strong support in the character of the products of the moist oxidation of carbon. The molecule of amorphous carbon with none of its units rigidly fixed, as might be expected, is the least resisting to oxidants and yields mellitic

[38] Berthelot and Petit, *Ann. chim.*, [VI] **18**, 89, 98 (1889).
[39] Favre and Silberman, *ibid.*, [III] **35**, 357 (1852).
   Mixter, *Am. J. Sci.*, [IV] **19**, 440 (1905).
   Roth and Wallasch, *Ber.*, **46**, 896 (1913).

acid. Graphite with its partly fixed units gives rise to graphitic oxide or acid, an acid more complex than mellitic. The rigidly fixed units of diamond are practically unaffected under the same conditions of oxidation.[35,40]

Similar to the heats of combustion we may expect the values of any other physical property to show a regular gradation from amorphous carbon to the diamond, the value for graphite lying between the values for the two other forms, such gradation serving as confirming evidence in support of the theory under discussion. Below are collected the values for a number of physical constants, which have been determined for all three forms of carbon. The numbers are taken from Landolt-Börnstein, "Tabellen," 4th Edition, 1912.

TABLE I.

Properties of Carbon.

	Density.	Coefficient of cubical expansion.	Thermal conductivity.	Specific heat.[42]	Electrical conductivity.
Diamond	3.51	0.00000375	$0.33(0°)$[41]	$0.1128(10.7°)$	$\begin{cases} 0.211 \times 10^{-14} \text{ to} \\ 0.309 \times 10^{-13}(15°) \end{cases}$
Graphite	2.10–2.32	0.0000104	0.0117	$0.1604^a(10.8°)$	$0.0802 \times 10^4(15°)$
Amorphous carbon					
Gas coke	1.885	0.0000162			
Coconut charcoal	1.67–1.86				
Lamp black, sugar charcoal and wood charcoal	1.70–1.80		0.000405	$0.1653(0–24°)$	$0.25(12°)$

^{a} Ceylon graphite.

An inspection of this table shows that, with the single exception of the electrical conductivity, all the physical properties are in the order we should expect. In the case of the electrical conductivity graphite occupies an anomalous position, in that its conductivity is very much greater than that of either the diamond or amorphous carbon. The explanation may be found in the fact that in diamond *all* electrons, being immobilized in linkages, leave *none* free to conduct a current, while in graphite the single free valence, serving as a directive, polar force, facilitates the electric current. Amorphous carbon with its several free valences—counteracting forces—occupies an intermediate position.

The elucidation of the molecular structure of the carbon allotropes throws much light upon the mechanism of the combustion of carbon, a problem which has received a good deal of attention.

[40] Meyer, *Ber.*, **4**, 801 (1871); *Ann.*, **180**, 175 (1875).

Schulze, *Ber.*, **4**, 802, 806 (1871).

Standenmaier, *ibid.*, **31**, 1481 (1898); **32**, 1394, 2824 (1899).

Dickson and Easterfield, Reference 36.

[41] Eucken, *Physik. Z.*, **12**, 1005 (1911).

[42] Weber, *Pogg. Ann.*, **154**, 367, 553 (1875).

Under the stress of experimental evidence the *reduction theory* of Lang[43] has been replaced by that of *gradual* oxidation by Baker[44] and Dixon,[45] which in its turn is being replaced by the *theory of complexes*, proposed by Rhead and Wheeler.[24]

The conception of a non-rigid configuration containing free valences, for amorphous carbon, affords a complete explanation of (1) the comparatively easy combustibility of this form of carbon; and (2) the simultaneous evolution of carbon monoxide and dioxide, products of disruption of the complexes, logically constituting the first stage of oxidation. The conception of a rigid configuration for diamond and graphite explains the considerable resistance to combustion exhibited by these allotropes, and suggests that no intermediate complexes, assumed in the case of amorphous carbon, are likely in the course of combustion of diamond.

Allotropy of Iron and Nickel.

The lack of distinctive chemical properties makes the recognition of separate forms of iron practically dependent upon the variation of physical properties, as indicated by transition points. The study of the graphs, representing the changes of temperature, volume,[46] tenacity, electrical conductivity[47] and the solubility of carbon and hydrogen[48] indicates there transition points, *viz.*, at 769°, 906° and 1401°, the solidification point[49] of iron lying at 1528°.

The precision of the determinations of the transition points is greatly influenced by the impurities (carbon, hydrogen, nickel, etc.) persistently

[43] Lang, *Z. physik. Chem.*, **2**, 62 (1888).

[44] Baker, *Phil. Trans.*, [*A*] **179**, 571 (1888).

[45] Dixon, *J. Chem. Soc.*, **69**, 774 (1896); **75**, 630 (1899). See also Johnson and McIntosh, *Trans. Roy. Soc. Canada*, [III] **7**, 161 (1913); Müller, *Z. angew. Chem.*, **33**, 36 (1920).

[46] Gore, *Proc. Roy. Soc.*, **17**, 260 (1869).
   Barrett, *Phil. Mag.*, [4] **46**, 472 (1873).
   Osmond, *J. Iron Steel Inst.*, **49**, 180 (1896).
   Pionchon, *Compt. rend.*, **102**, 1145 (1886).
   Osmond, *ibid.*, **103**, 743 (1886).
   Heyn, *Stahl u. Eisen*, **20**, 625 (1900).
   Rooseboom, *Z. physik. Chem.*, **34**, 437(1900).
   Tammann, *Z. anorg. Chem.*, **37**, 448 (1903).
   Charpy and Grenet, *Compt. rend.*, **139**, 567 (1904).
   Burgess and Crowe, *J. Washington Acad. Sci.*, **3**, 329 (1913).
   Broniewiski, *Compt. rend.*, **156**, 669 (1913).
   Ruer and Klesper, *Ferrum*, **11**, 257 (1914).

[47] Le Chatelier, *Z. physik. Chem.*, **8**, 183 (1891).
   Fournel, *Compt. rend.*, **143**, 46 (1906).

[48] Benedicks, *Z. physik. Chem.*, **40**, 545 (1902).
   Sieverts, *ibid.*, **77**, 591 (1911).
   Jurisch, *Stahl u. Eisen*, **34**, 252 (1914).

[49] Ruer and Goerrens, *Ferrum*, **13**, 1 (1915).

accompanying iron. The presence of these impurities results in the depression of the transition points, which converge gradually to one point at $700°$.[50] The persistence of impurities in iron can be seen from the fact that electric measurements of even the purest iron show as much as 0.27% of carbon[48] (0.08% according to Fournel[47]).

The experimental data on the comparative hardness of the modifications of iron are conflicting, owing to the disturbing factors of the different solubilities and varying percentages of dissolved carbon,[51] etc. While the $\beta \rightleftharpoons \gamma$ and the $\gamma \rightleftharpoons \delta$ transitions, as indicated by the specific heat, thermal measurements,[52] electrical resistance, change of crystal structure,[53] dilation,[54] electromotive forces[55] and magnetism,[56] are definite and sudden, the $\alpha \rightleftharpoons \beta$ transition is gradual, extending over a range of $40°$ to $100°$, and is accompanied by a change of magnetic properties.[57] The study of the specific heat indicates that the $\alpha \rightleftharpoons \beta$ transformation is completed by a continuous series of mixed crystals.[58] These fundamental differences revealed in the course of a comparative study of the transition points of iron make it manifest that the $\alpha \rightleftharpoons \beta$ critical point, or rather range, cannot be regarded as a true allotropic change.[52,59] The $\alpha \rightleftharpoons \beta$ transformation point may be regarded as merely the termination of the $\alpha \rightleftharpoons \gamma$ change. The β form is simply a solid solution of γ in α, the proportion of γ iron increasing with temperature.[60] Thus $\alpha \rightleftharpoons \beta$ is the point at which γ ceases to be metastable and becomes unstable. This point is enhanced by impurities becoming in quenched steel as definite as the $\beta \rightleftharpoons \gamma$ point,[58] and vanishes gradually with the decrease of the percentage of solid and gaseous matter dissolved in the iron.[61]

[50] Osmond, Compt. rend., 103, 1135 (1886).
 Rooseboom, Reference 46.
[51] Benedicks, Reference 48.
 Skrabal, Z. Elektrochem., 10, 749 (1904).
 Rosenhain and Humphrey, Proc. Roy. Soc., 83A, 200 (1910).
[52] Honda, Science Repts. Tohoku Imp. Univ., [1] 2, 69 (1913).
 Carpenter, J. Iron Steel Inst., 87, 315 (1913).
[53] Burgess and Kellberg, J. Washington Acad. Sci., 4, 436 (1914).
[54] Rosenhain and Humphrey, J. Iron Steel Inst., 87, 219 (1913).
 Benedicks, ibid., 89 440 (1914).
 Driesen, Ferrum, 13, 27 (1915).
[55] Benedicks, Compt. rend., 162, 297 (1916).
[56] Ishiwara, J. Iron Steel Inst., 97, 551 (1918).
[57] Osmond, Ann. Mines, 17, 110 (1900).
 Osmond and Cartand, ibid., 18, 113 (1900).
 Boudouard, J. Iron Steel Inst., 63, 299 (1903).
[58] Oberhoffer, Stahl u. Eisen, 27, 1764 (1907).
 Carpenter and Stead, J. Iron Steel Inst., 88, 119 (1913).
[59] Honda, Science Repts. Tohoku Imp. Univ., 6, 217 (1917).
[60] Benedicks, J. Iron Steel Inst., 86, 242 (1912).
[61] Carpenter, ibid., 87, 326 (1913).

The loss of magnetism at the $\alpha \rightleftharpoons \beta$ point is therefore due not merely to the increased velocity of vibration of the molecules, but to the formation of γ in α iron, the former not only reducing the "effective section" of the conducting substance, but also breaking the current lines, when beyond a certain limit, thus resulting in a rapid fall of intensity in the magnetic forces.[62] Another view is that the $\alpha \rightleftharpoons \beta$ transformation, accompanied by loss of magnetism, is a polymorphic change, magnetism being due either to a polar arrangement of molecules,[63] or to a specific property of the α form of iron.[64]
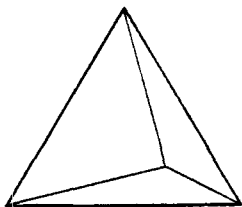

Fig. 7.

Thus we find that the α, γ and δ iron are the forms recognized as having a separate existence.[65]

Now in the light of the theory of allotropy, a trivalent element (as iron always is potentially) may exist in two distinct molecular forms: (I) a saturated molecular configuration, having no free valences (see Fig. 7), and (II) an unsaturated molecular form, having free valences;
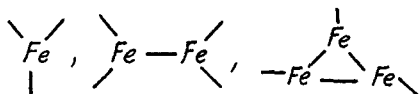
Considering that practically all experimental evidence tends to show that the $\alpha \rightleftharpoons \beta$ point is merely a retardation of the $\alpha \rightleftharpoons \gamma$ transition point, thus disposing of the β form, and also the fact that the $\gamma \rightleftharpoons \delta$ point, although sharply defined, is of a considerably smaller magnitude than the $\alpha \rightleftharpoons \gamma$ change, we may take the two theoretically possible forms to correspond to the α and γ forms of iron.

Considering that (a) generally molecular complexity decreases with the rise of temperature, and that (b) according to the magneton theory[66] molecular complexity decreases from α to γ, we may take it that the α form is represented by the saturated molecular configuration (tetrahedron), and γ by an unsaturated molecular form. The δ modification formed at high temperature and differing from γ to a less degree than α, can be re-

[62] Benedicks, *J. Iron Steel Inst.*, **87**, 333 (1913); also **89**, 440 (1914).
  Honda, *ibid.*, **99**, 457 (1919).
  Oknov, *Ferrum*, **11**, 1 (1913).
  Driesen, *ibid.*, **13**, 27 (1915).
  Lashchenko, *J. Russ. Phys. Chem. Soc.*, **46**, 311 (1914).
[63] Le Chatelier, *Compt. rend.*, **136**, 664 (1903).
  Hilpert, *Z. Elektrochem.*, **16**, 390 (1910).
[64] Weiss, *Rev. metal.*, **6**, 680 (1908).
  Sauveur, *J. Inst. Metals*, **88**, 171 (1913).
[65] Honda, *J. Iron Steel Inst.*, **91**, 199 (1915).
[66] Weiss, *Compt. rend.*, **152**, 688 (1911).

garded[67] as an *allotropoid; i. e.,* γ and δ both belong to the same type or class of molecular configuration (unsaturated), but each differs from the other in complexity, γ-iron being represented by a tri-atomic and δ iron by a di-atomic molecule.

The vapor of iron is probably mono-atomic, similar to mercury, phosphorus and the halogens at high temperature. The vapor of iron would thus together with γ and δ iron form three allotropoids, belonging to the same type of molecular configuration. The molecular complexity of the modifications of iron may thus be represented in the following tabular form.

Forms of iron.	Transition temperatures. °C.	Minimum molecular complexity, or number of atoms in the molecule.
α	906	4
γ	1401	3
δ	1528	2
Vapor		1

The conception of the various forms of iron as being due not to molecular differences, but to different groupings of atoms[68] explains nothing, and represents a misinterpretation of the recent X-ray spectrometric work.

Allotropy of Nickel.

The transformation of nickel has received considerably less attention than that of iron. Nevertheless sufficient data are available to show that the main transition point lies at 345–346°, being accompanied by a change in the rate of loss of permeability, coefficient of expansion, specific heat, magnetic and thermo-electric properties and electrical conductivity.

The fact that the several determinations of the transition point of nickel vary within 20° to 25°, is probably due not only to the different methods of determination, but also in a large degree to the different states of purity of the nickel under investigation.

A second transition point, decidedly less pronounced, accompanied by a change in crystalline form, has been observed[69] at 700°. These transition-points resemble the $\beta \rightleftharpoons \gamma$ and $\gamma \rightleftharpoons \delta$ changes in iron, and we can with sufficient justification draw the same conclusion as to the molecular complexity of the forms of nickel, as in the case of iron.

[67] Desch, *Trans. Faraday Soc.,* **11,** 136 (1916).

[68] Oxley, *ibid.,* **11,** 129 (1916).

[69] Tomlinson, *Phil. Mag.,* [5] **25,** 372 (1888).

Harrison, *ibid.,* [6] **7,** 626 (1904).

Schlott, *Ann. Physik.,* [4] **26,** 201 (1908).

Schukoff, *J. Russ. Phys. Chem. Soc.,* **40,** 1784 (1908).

Werner, *Z. anorg. Chem.,* **83,** 275 (1913).

Cohen, *Z. Elektrochem.,* **15,** 686 (1909).

Lashchenko, Reference 62.

Jänecke, *Z. angew. Chem.,* **31,** 229 (1918).

In conclusion the author wishes to thank Messrs. W. Lamb and G. Greenwood for revising the literature on phosphorus and iron respectively.

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AROMATIC MERCURI-ORGANIC DERIVATIVES. THE HOFMANN REARRANGEMENT AND THE NATURE OF VALENCES OF MERCURY IN MERCURI-ORGANIC DERIVATIVES.

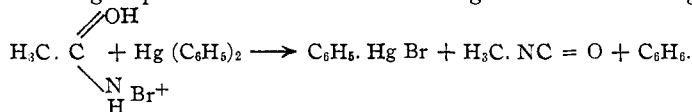### BY MORRIS S. KHARASCH.[1]

The effect of the halogens on mercury diphenyl has been studied by Otto[2] who found that bromine (one molecule) in water solution or in anhydrous media, gave rise to phenyl mercury bromide, and phenyl bromide. When, however, an excess of bromine was used, the resulting products were mercuric bromide and phenyl bromide. The behavior of mercury diphenyl with bromine is representative of the behavior with any other halogen. With the halogen acids the result was similar but, of course, instead of the phenyl halide, benzene was the other product. It was, therefore, of interest to find out just what the effect of positive halogen[3] alone on mercury diphenyl would be.

It was with this idea in mind that the effect of N-bromo-acetamide in sodium-dried benzene upon mercury diphenyl, dissolved in the same solvent, was tried. After the solution was warmed for about 10 minutes on the water-bath, a solid separated which was identified as phenyl mercury bromide.[4]

The reaction when studied in greater detail, and also, with other N-bromo-amides revealed the fact that mercury diphenyl played the same part in this reaction as sodium hydroxide in aqueous solution and sodium ethylate in absolute alcohol,[5] and that it also led to a rearrangement in which the group attached to the carbon migrated to the nitrogen.

$$H_3C . C \overset{\displaystyle /\!/OH}{\underset{\displaystyle \overset{N}{H} Br^+}{\diagdown}} + Hg (C_6H_5)_2 \longrightarrow C_6H_5 . Hg Br + H_3C . NC = O + C_6H_6.$$

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[1] National Research Fellow in Organic Chemistry.

[2] Otto, J. prakt. Chem., [2] 1, 182 (1870).

[3] Seliwanow, Ber., 25, 3617 (1892); Lengfeld and Stieglitz, Am. Chem. J., 15, 215, 504 (1893); W. A. Noyes, THIS JOURNAL, 23, 450 (1901); J. Stieglitz, ibid., 23, 796 (1901), etc.

[4] The same reaction takes place also in bright sunlight in the course of a few minutes, without any heating whatsoever.

[5] Lengfeld and Stieglitz, Am. Chem. J., 15, 215, 504 (1893).